DIRECTORATE OF DISTANCE AND CONTINUING EDUCATION
MANONMANIAM SUNDARANAR UNIVERSITY
TIRUNELVELI - 627102

OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023 - 2024 ONWARDS)

B.Sc. CHEMISTRY
COURSE MATERIAL
INORGANIC CHEMISTRY - I

COURSE CODE : JMCH52

Prepared by
Dr. NAGARAJAN S
Assistant Professor
Department of Chemistry
Manonmaniam Sundaranar University
Tirunelveli - 627012

SYLLABUS

UNIT - 1 : COORDINATION CHEMISTRY - I

IUPAC Nomenclature of coordination compounds, Isomerism in coordination compounds. Werner's coordination theory - effective atomic number - interpretation of geometry and magnetic properties by Pauling's theory - geometry of co-ordination compounds with co-ordination number 4 &6.

Chelates - types of ligands forming chelates - stability of chelates, applications of chelates in qualitative and quantitative analysis - application of DMG and oxine in gravimetric analysis - estimation of hardness of water using EDTA, metal ion indicators.

Role of metal chelates in living systems - haemoglobin and chlorophyll

UNIT - 2 : COORDINATION CHEMISTRY - II

Crystal field theory - Crystal field splitting of energy levels in octahedral and tetrahedral complexes, Crystal field stabilization energy (CFSE), spectrochemical series - calculation of CFSE in octahedral and tetrahedral complexes - factors influencing the magnitude of crystal field splitting, crystal field effect on ionic radii, lattice energies, heats of ligation with water as a ligand (heat of hydration), interpretation of magnetic properties, spectra of $[Ti(H_2O)_6]^{3+}$ - Jahn - Teller effect. Stability of complexes in aqueous solution, stability constants - factors affecting the stability of a complex ion, thermodynamic and kinetic stability (elementary idea). Comparison of VBT and CFT.

UNIT - 3 : ORGANOMETALLIC COMPOUNDS

Metal Carbonyls

Mono and polynuclear carbonyls, General methods of preparation of carbonyls - general properties of binary carbonyls - bonding in carbonyls - structure and bonding in carbonyls of Ni, Fe, Cr, Co, Mn, Ru and Os. EAN rule as applied to metal carbonyls.

Ferrocene - Methods of preparation, physical and chemical properties.

UNIT - 4 : INNER TRANSITION ELEMENTS *(Lanthanides and Actinides)*

General characteristics of f-block elements - Comparative account of lanthanoids and actinoids - Occurrence, Oxidation states, Magnetic properties, Colour and spectra - Lanthanoids and Actinoids, Separation by ion - exchange and solvent extraction methods - Lanthanoids contraction - Chemistry of thorium and Uranium - Occurrence, Ores, Extraction, properties and uses - Preparation, Properties and uses of ceric ammonium sulphate, thorium dioxide and uranyl acetate.

UNIT - 5 : INORGANIC POLYMERS

General properties – classification of inorganic polymers based on element in the backbone (Si, S, B and P) - preparation and properties of silicones (polydimethylsiloxane and polymethylhydrosiloxane) phosphorous based polymer (polyphosphazines and polyphosphonitrilic chloride), sulphur based polymer (polysulfide and polymeric sulphur nitride), boron based polymers (borazine polymers) – industrial applications of inorganic polymers.

RECOMMENDED TEXTS

1. Puri B R, Sharma L R, Kalia K C (2011), Principles of Inorganic Chemistry, 31th Edition, Milestone Publishers & Distributors, Delhi.
2. Satya Prakash, Tuli G. D., Basu S. K., Madan R. D. (2009), Advanced Inorganic Chemistry, 18th Edition, S. Chand & Co., New Delhi.
3. Lee J D, (1991), Concise Inorganic Chemistry, 4th Edition, ELBS William Heinemann, London.
4. W V Malik, G D Tuli, R D Madan, (2000), Selected Topics in Inorganic Chemistry, S. Chand and Company Ltd.
5. A. K. De, Text book of Inorganic Chemistry, Wiley East Ltd, seventh edition, 1992.

UNIT - 1

COORDINATION CHEMISTRY - I

"Coordination Compounds are the backbone of modern inorganic and bio–inorganic chemistry and chemical industry"

One of the general characteristics of the transition metals is their tendency to form a large number of complex compounds in which the metal atoms are bound to a number of anions or neutral molecules by sharing of electrons. In modern terminology such compounds are called *coordination compounds*. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of these compounds as vital components of biological systems.

SOME IMPORTANT TERMS RELATED TO COORDINATION COMPLEXES

1) Coordination entity

Coordination entity is an ion or a neutral molecule, composed of a central atom, usually a metal and the array of other atoms or groups of atoms (ligands) that are attached to it. In the formula, the coordination entity is enclosed in square brackets. For example, in potassium ferrocyanide, $K_4[Fe(CN)_6]$, the coordination entity is $[Fe(CN)_6]^{4-}$. In nickel tetracarbonyl, the coordination entity is $[Ni(CO)_4]$.

2) Central atom /ion

The central atom/ion is the one that occupies the central position in a coordination entity and binds other atoms or groups of atoms (ligands) to itself, through a coordinate covalent bond. For example, in $K_4[Fe(CN)_6]$, the central metal ion is Fe^{2+}. In the coordination entity $[Fe(CN)_6]^{4-}$, the Fe^{2+} accepts an electron pair from each ligand, CN^- and thereby forming six coordinate covalent bonds with them. Since the central metal ion has an ability to accept electron pairs, it is referred to as a Lewis acid.

3) Ligands

The ligands are the atoms or groups of atoms bound to the central atom/ion. The atom in a ligand that is bound directly to the central metal atom is known as a donor atom. For example, in $K_4[Fe(CN)_6]$, the ligand is CN^- ion, but the donor atom is carbon and in $[Co(NH_3)_6]Cl_3$ the ligand is NH_3 molecule and the donor atom is nitrogen.

4) *Coordination sphere*

The complex ion of the coordination compound containing the central metal atom/ion and the ligands attached to it, is collectively called coordination sphere and are usually enclosed in square brackets with the net charge. The other ionisable ions, written outside the bracket are called counter ions. For example, the coordination compound $K_4[Fe(CN)_6]$ contains the complex ion $[Fe(CN)_6]^{4-}$ and is referred to as the coordination sphere. The other associated ion K^+ is called the counter ion.

5) *Coordination number*

The number of ligand donor atoms bonded to a central metal ion in a complex is called the coordination number of the metal. In other words, the coordination number is equal to the number of σ-bonds between ligands and the central atom.

For example

i. In $K_4[Fe(CN)_6]$, the coordination number of Fe^{2+} is 6.

ii. In $[Ni(en)_3]Cl_2$, the coordination number of Ni^{2+} is also 6. Here the ligand 'en' represents ethane-1,2-diamine (NH_2-CH_2-CH_2-NH_2) and it contains two donor atoms (Nitrogen). Each ligand forms two coordination bonds with nickel. So,there are six coordination bonds between them.

6) *Oxidation state of the central metal ion*

The oxidation state of a central atom in a coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. In naming a complex, it is represented by a Roman numeral. For example, in the coordination entity $[Fe(CN)_6]^{4-}$, the oxidation state of iron is represented as (II). The net charge on the complex ion is equal to the sum of the oxidation state of the central metal and the charge on the ligands attached to it. Using this relation the oxidation number can be calculated as follows

Net charge = (oxidation state of the central metal) + [(No. of ligands) X (charge on the ligand)]

For example

i. In $[Fe(CN)_6]^{4-}$, let the oxidation number of iron is x.

The net charge: -4 = x + 6 (-1) => x = +2

ii. In $[Co(NH_3)_5Cl]^{2+}$, let the oxidation number of cobalt is x.

The net charge: +2 = x + 5 (0) + 1 (-1) => x = +3

IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

Formulas of mononuclear coordination entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom.

The following rules are applied while writing the formulas:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In the case of an abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

Note: *The 2004 IUPAC draft recommends that ligands will be sorted alphabetically, irrespective of charge.*

Naming of mononuclear coordination compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers.

The following rules are used when naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing the formula).

(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3 , carbonyl for CO and nitrosyl for NO. While writing the formula of coordination entity, these are enclosed in brackets ( ).

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named the same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion $[Co(SCN)_4]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, e.g., ferrate for Fe.

(vii) The neutral complex molecule is named similarly to that of the complex cation.

Note: *The 2004 IUPAC draft recommends that anionic ligands will end with–ido so that chloro would become chlorido, etc.*

Examples

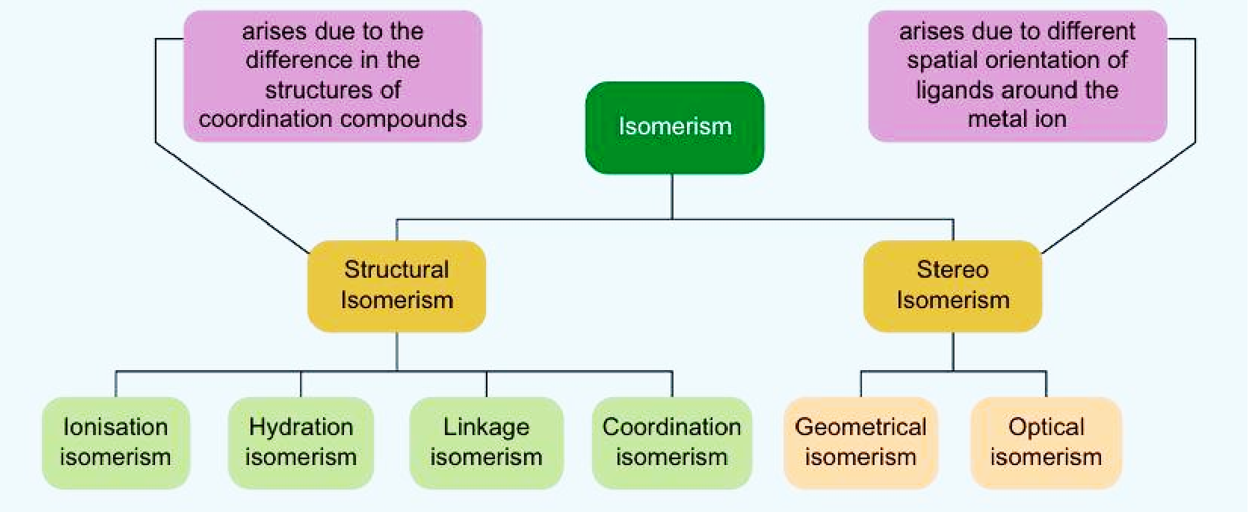
1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ - Triamminetriaquachromium(III) chloride
2. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ - Tris(ethane-1,2–diamine)cobalt(III) sulphate
3. $[Ag(NH_3)_2][Ag(CN)_2]$ - Diamminesilver(I)dicyanidoargentate(I)

Notice how the name of the metal differs in cation and anion even though they contain the same metal ions.

4. $[PdI_2(ONO)_2(H_2O)_2]$ - Diaquadiiodidodinitrito-Opalladium(IV)

ISOMERISM IN COORDINATION COMPOUNDS

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.



1) STRUCTURAL ISOMERISM

The coordination compounds with the same formula, but have different connections among their constituent atoms are called structural isomers or constitutional isomers.

(i) Ionisation isomerism

This type of isomerism arises when an ionisable counter ion (simple ion) itself can act as a ligand. The exchange of such counter ions with one or more ligands in the coordination entity will result in ionisation isomers. These isomers will give different ions in solution. For example, consider the coordination compound $[Pt(en)_2Cl_2]Br_2$. In this compound, both Br^- and Cl^- have the ability to act as a ligand and the exchange of these two ions result in a different isomer $[Pt(en)_2Br_2]Cl_2$. In solution the first compound gives Br^- ions while the later gives Cl^- ions and hence these compounds are called ionisation isomers.

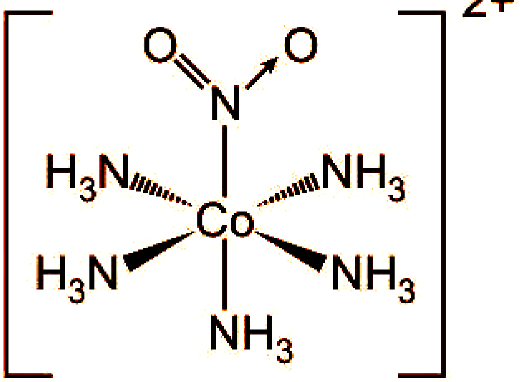
Some more examples for the isomers are $[Cr(NH_3)_4ClBr]NO_2$ and $[Cr(NH_3)_4ClNO_2]Br_2$; $[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4ClBr]Br$.

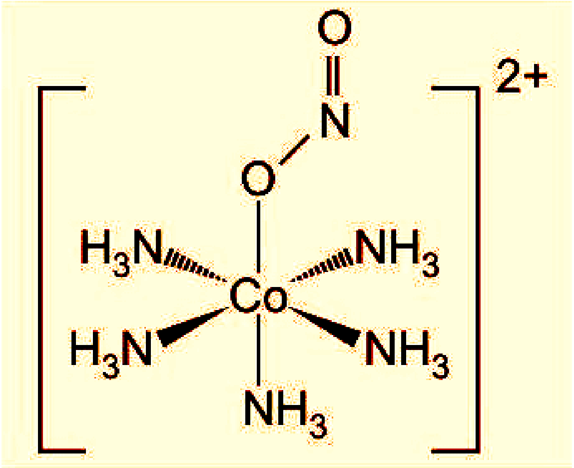
(ii) Solvate isomerism

This form of isomerism is known as 'hydrate isomerism' in cases where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

(iii) Linkage isomerism

Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS-, which may bind through the nitrogen to give M-NCS or through sulphur to give M-SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($–NO_2$).





(iv) Coordination isomerism

This type of isomerism arises in the coordination compounds having both the cation and anion as complex ions. The interchange of one or more ligands between the cationic and the anionic coordination entities result in different isomers. For example, in the coordination compound, $[Co(NH_3)_6][Cr(CN)_6]$ the ligands ammonia and cyanide were bound respectively to cobalt and chromium while in its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$ they are reversed.

Some more examples for coordination isomers

1. $[Cr(NH_3)_5CN][Co(NH_3)(CN)_5]$ and $[Co(NH_3)_5CN][Cr(NH_3)(CN)_5]$
2. $[Pt(NH_3)_4][Pd(Cl)_4]$ and $[Pd(NH_3)_4][Pt(Cl)_4]$.

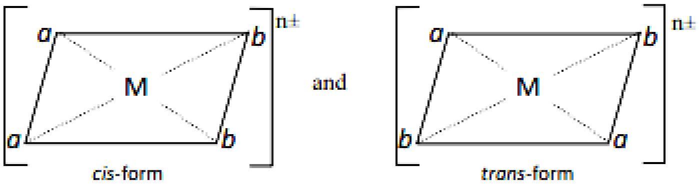
2) STEREOISOMERISM

Similar to organic compounds, coordination compounds also exhibit stereoisomerism. The stereoisomers of a coordination compound have the same chemical formula and connectivity between the central metal atom and the ligands. But they differ in the spatial arrangement of ligands in three dimensional space. They can be further classified as geometrical isomers and optical isomers.

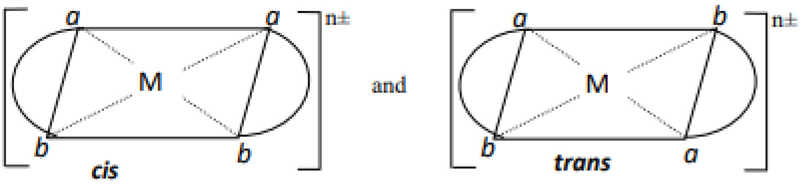
(i) Geometrical isomerism

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6.

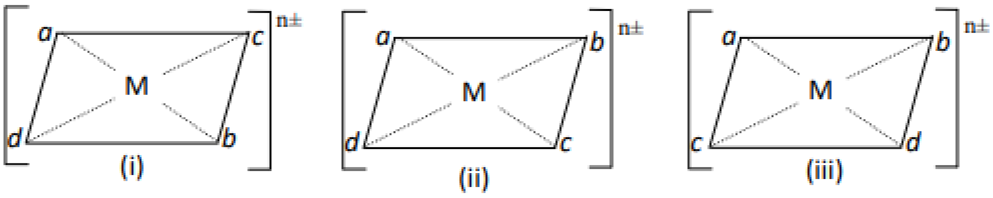
In *square planar* complexes of the form $[MA_2B_2]^{n\pm}$ and $[MA_2BC]^{n\pm}$ (where A, B and C are mono dentate ligands and M is the central metal ion/atom), Similar groups (A or B) present either on same side or on the opposite side of the central metal atom (M) give rise to two different geometrical isomers, and they are called, cis and trans isomers respectively.



The square planar complex of the type $[M(xy)_2]^{n\pm}$ where xy is a bidentate ligand with two different coordinating atoms also shows cis-trans isomerism.

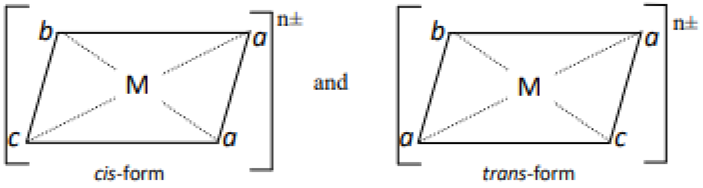


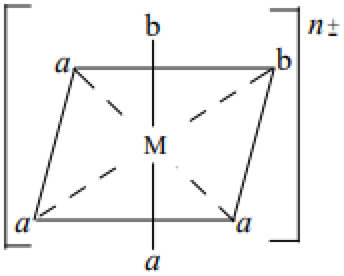
A square planar complex of the form $[MABCD]^{n\pm}$ also shows geometrical isomerism. In this case, by considering any one of the ligands (A, B, C or D) as a reference, the rest of the ligands can be arranged in three different ways leading to three geometrical isomers.



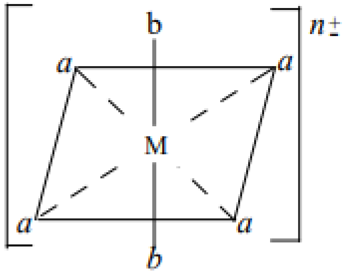
Such isomerism is not possible for complexes having *tetrahedral* geometry.

Octahedral complexes of the type $[MA_2B_4]^{n\pm}$, $[M(xx)_2B_2]^{n\pm}$ show cis-trans isomerism. Here A and B are monodentate ligands and xx is bidentate ligand with two same kinds of donor atoms.





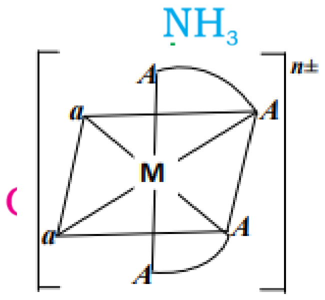
cis-form (1,2-isomer)



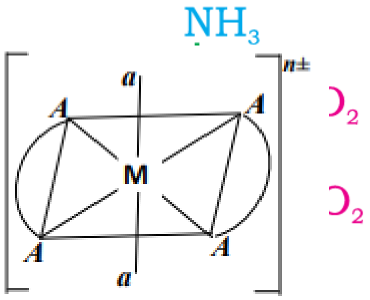
trans-form (1,6-isomer)

As the number of different ligands increases, the number of possible isomers also increases. For the octahedral complex of the type [M(ABCDEF)]$^{n\pm}$, where A, B, C, D, E and F are monodentate ligands, fifteen different orientations are possible corresponding to 15 geometrical isomers.

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma_3b_3] like [$Co(NH_3)_3(NO_2)_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer.



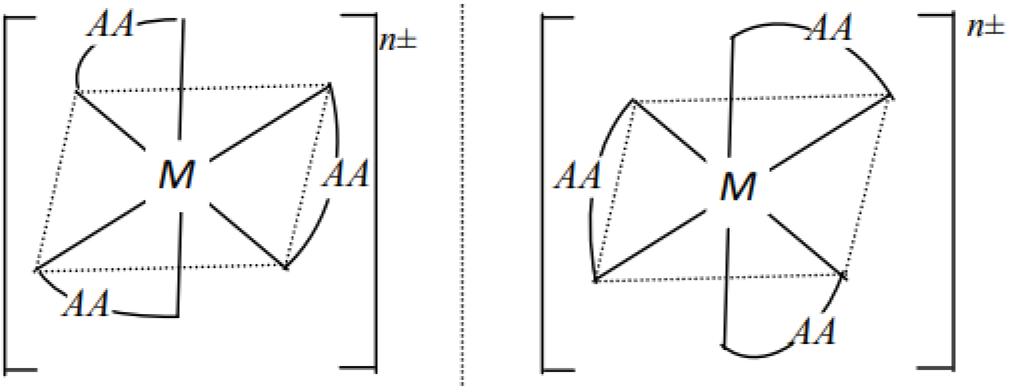
fac–

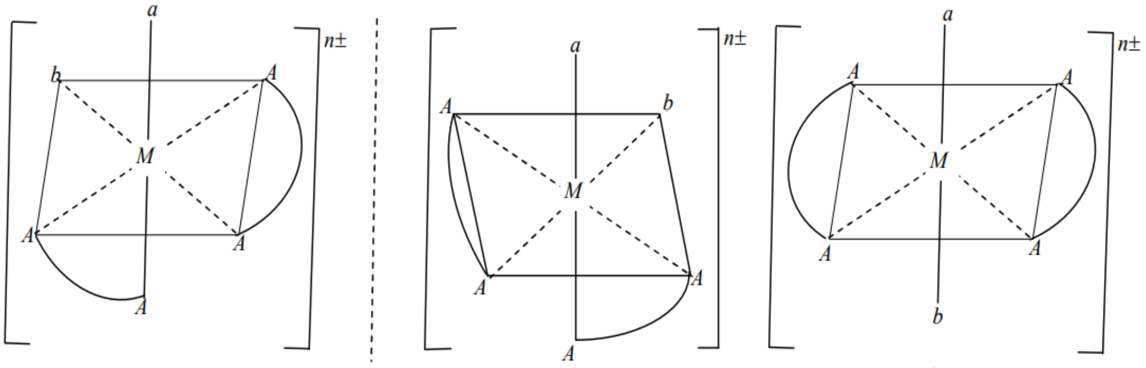


mer–

(ii) Optical isomerism

Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers. The molecules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, l to the left). Optical isomerism is common in octahedral complexes involving bidentate ligands.The octahedral complexes of type $[M(xx)_3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism.

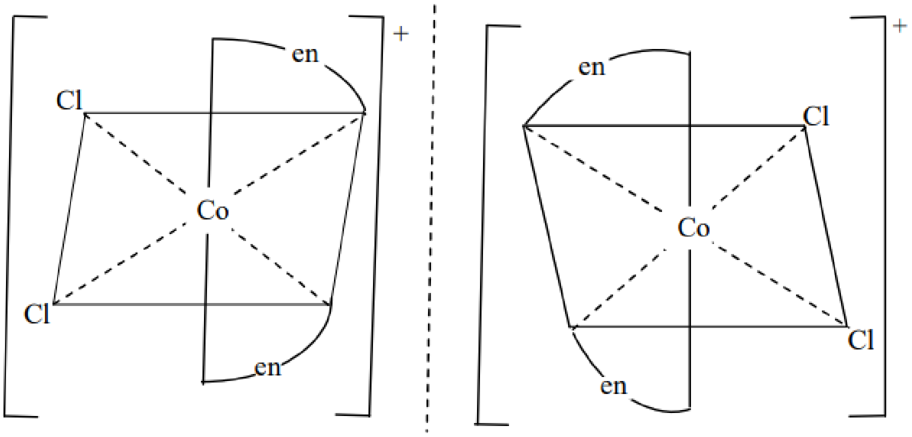




d-form

l-form

Meso-form



THEORIES OF COORDINATION COMPOUNDS

WERNER'S THEORY OF COORDINATION COMPOUNDS

Swiss chemist Alfred Werner was the first one to propose a theory of coordination compounds to explain the observed behaviour of them. The main postulates are:

1. In coordination compounds metals show two types of linkages (valences) - primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination polyhedra. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.

He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^{+}$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

EFFECTIVE ATOMIC NUMBER RULE (EAN RULE)

The EAN rule is also known as the 18-electron rule or noble gas rule. According to this rule, the total number of electrons around the central metal ion including those gained through coordination by the ligands is known as the effective atomic number (EAN) of the central metal ion. In many cases, this number is equal to the atomic number of the next higher inert gas. Such coordination compounds or said to obey the EAN rule.

EAN for a central metal ion is obtained as follows:

EAN = Atomic number of the central metal ± the number of electrons gained or lost in ion formation + the number of electrons gained through coordination

Some examples for the calculation of EAN are as follows:

Complex	**Central metal M**	**Atomic number of M**	**Oxidation state of M**	**Electrons gained through coordination**	**EAN**	**Atomic number of next higher inert gas**
$[Ni(CO)_4]$	Ni	28	0	8	28+0+08 = **36**	36
$[V(CO)_6]$	V	23	0	12	23+0+12 = **35**	36
$[Zn(NH_3)_4]^{2+}$	Zn	30	2+	8	30-2+08 = **36**	36
$[Fe(CN)_6]^{3-}$	Fe	26	3+	12	26-3+12 = **35**	36
$[Fe(CN)_6]^{4-}$	Fe	26	2+	12	26-2+12 = **36**	36
$[Mn(CO)_4]^{2-}$	Mn	25	2+	8	25-2+08 = **31**	36
$[Fe(CO)_5]$	Fe	26	0	10	26+0+10 = **36**	36

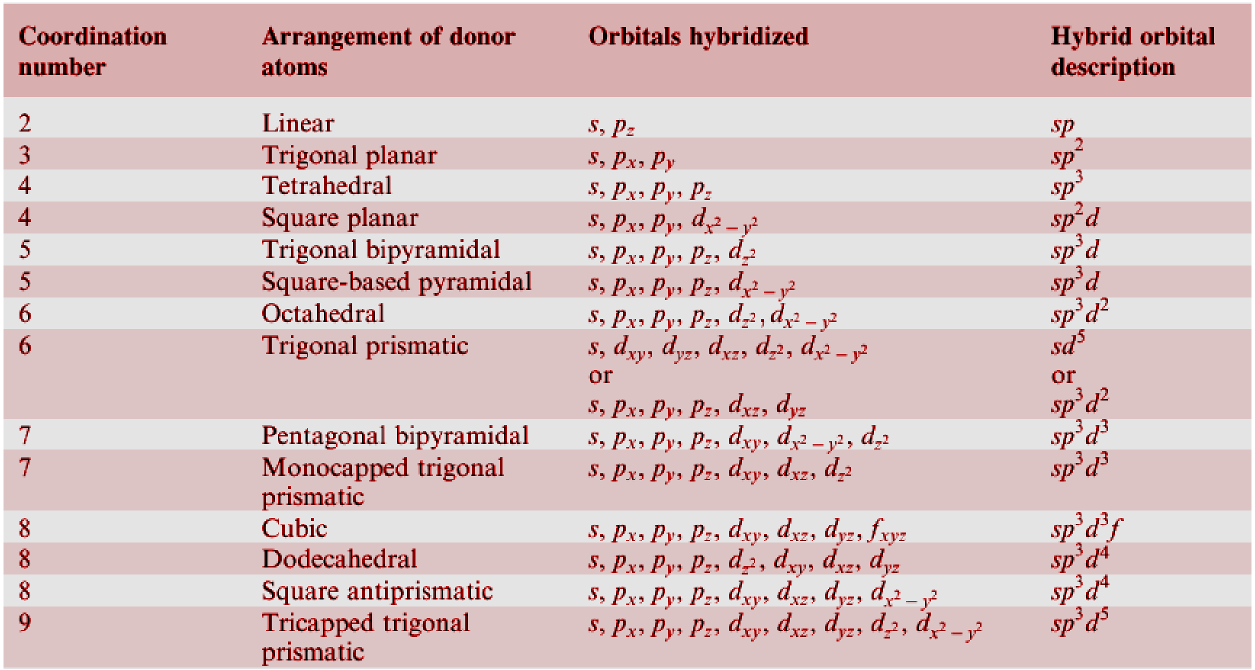
VALENCE BOND THEORY (VBT)

Following Werner's theory, Linus Pauling proposed the Valence Bond Theory (VBT) which assumes that the bond formed between the central metal atom and the ligand is purely covalent. According to this theory, the bond formed between the central metal atom and the ligand is due to the overlap of filled ligand orbitals containing a lone pair of electrons with the vacant hybrid orbitals of the central metal atom.

The main assumptions of VBT are as follows:

1. The ligand → metal bond in a coordination complex is covalent in nature. It is formed by sharing of electrons (provided by the ligands) between the central metal atom and the ligand.
2. Each ligand should have at least one filled orbital containing a lone pair of electrons.
3. In order to accommodate the electron pairs donated by the ligands, the central metal ion present in a complex provides the required number (coordination number) of vacant orbitals.
4. These vacant orbitals of the central metal atom undergo hybridisation, the process of mixing of atomic orbitals of comparable energy to form an equal number of new orbitals called hybridised orbitals with the same energy.

   It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of the wave equation for the atomic orbitals involved.
5. The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.
6. The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.
7. In the octahedral complexes, if the (n-1) d orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the nd orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principal quantum number of the outermost shell.
8. The complexes containing a central metal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes will be diamagnetic.
9. Ligands such as CO, CN^-, en, and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.
10. Greater the overlapping between the ligand orbitals and the hybridised metal orbital, greater is the bond strength.

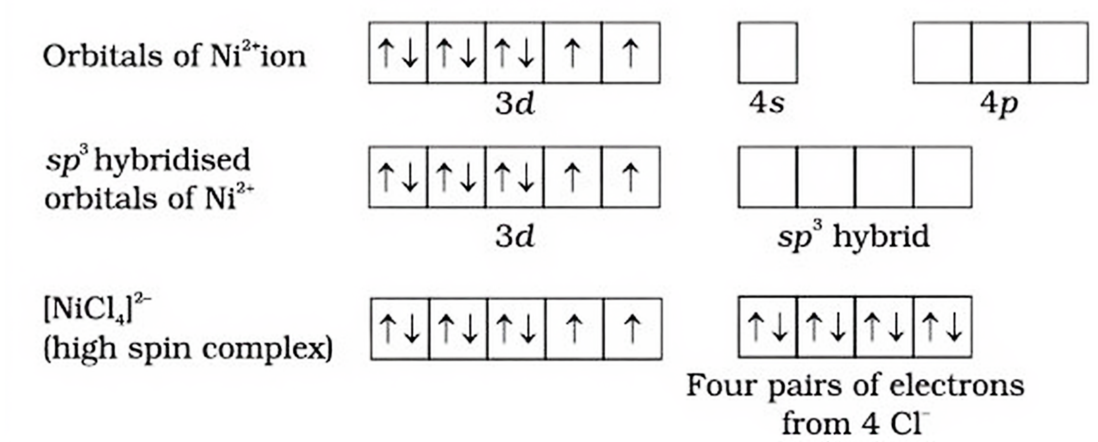


Coordination number	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description
2	Linear	s, p_z	sp
3	Trigonal planar	s, p_x, p_y	sp^2
4	Tetrahedral	s, p_x, p_y, p_z	sp^3
4	Square planar	$s, p_x, p_y, d_{x^2-y^2}$	sp^2d
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp^3d
5	Square-based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	sp^3d
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	sp^3d^2
6	Trigonal prismatic	$s, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$ or $s, p_x, p_y, p_z, d_{xz}, d_{yz}$	sd^5 or sp^3d^2
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	sp^3d^3
7	Monocapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	sp^3d^3
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, f_{xyz}$	sp^3d^3f
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{xz}, d_{yz}$	sp^3d^4
8	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$	sp^3d^4
9	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{yz}, d_{z^2}, d_{x^2-y^2}$	sp^3d^5

Geometry of coordination compounds with coordination number 4 and 6

In tetrahedral complexes

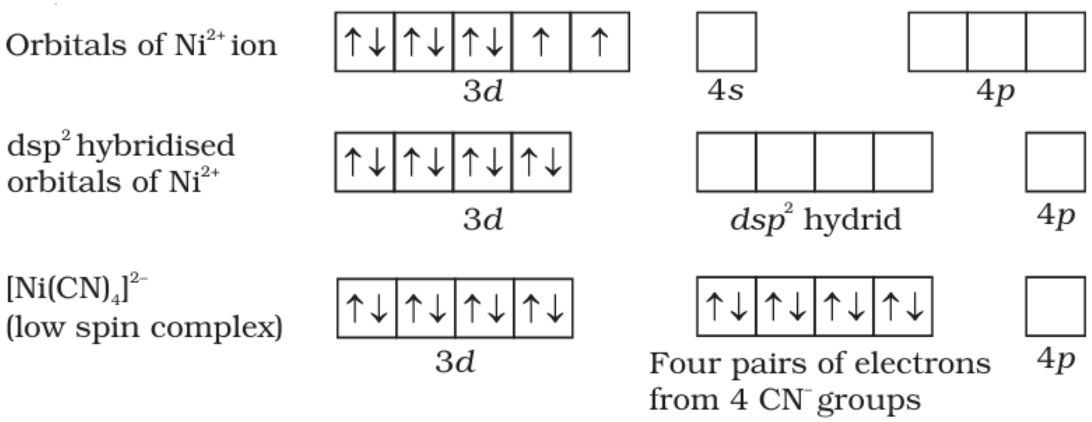
In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent sp^3 orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$.



Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in the diagram above. Each Cl^- ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.

In square planar complexes

In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram:

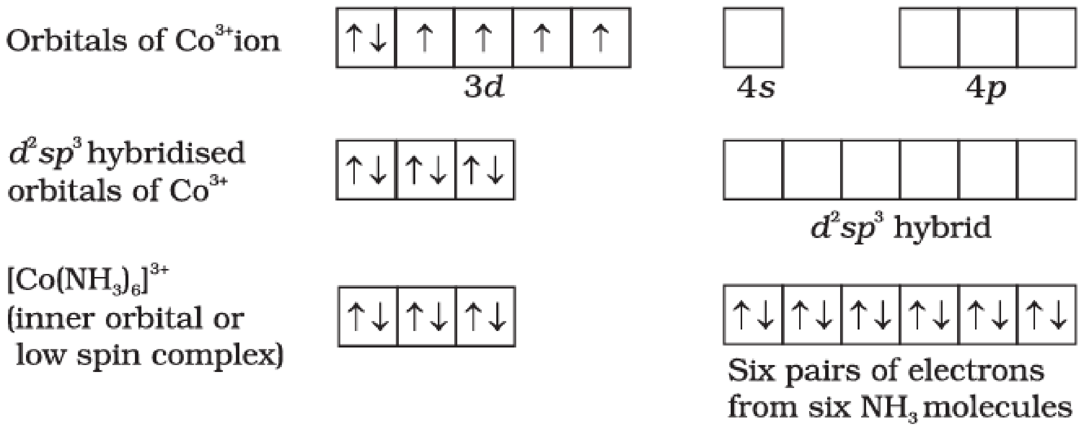


Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electrons.

In octahedral complexes

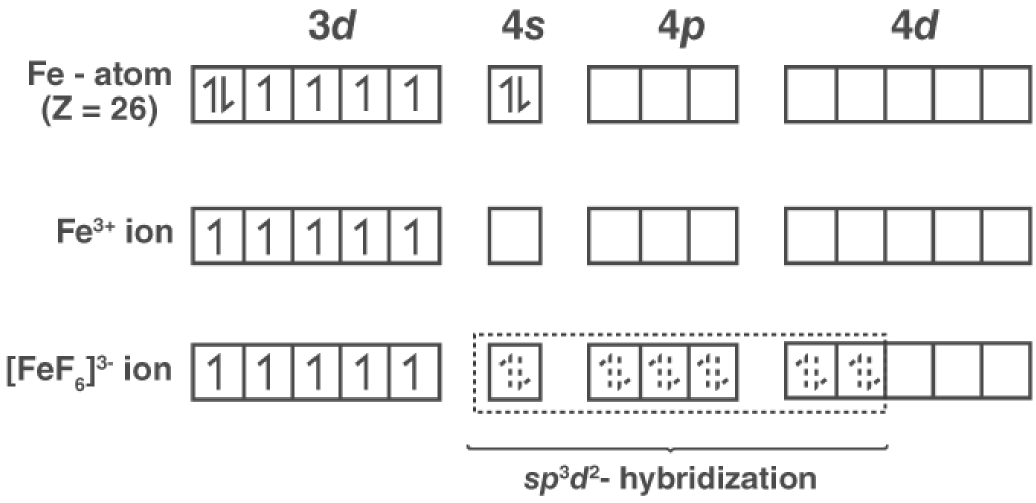
(i) Inner orbital octahedral complexes

Consider the diamagnetic octahedral complex $[Co(NH_3)_6]^{3+}$. The cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in the diagram. Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electrons. In the formation of this complex, since the inner d orbital (3d) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an **inner orbital** or **low spin** or **spin paired** complex.



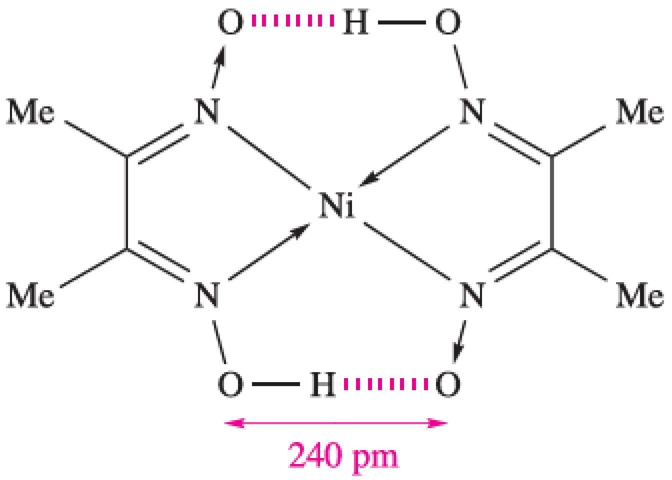
(ii) Outer orbital octahedral complex

The paramagnetic octahedral complex, $[FeF_6]^{3-}$ uses an outer orbital (4d) in hybridisation (sp^3d^2). It is thus called **outer orbital** or **high spin** or **spin free** complex.



CHELATES

A ligand having more than one point of attachment to the central metal ion in a complex is called a polydentate ligand. Some examples of such ligands include ethylenediamine (en), dimethylglyoxime (DMG), acetylacetonate (acac), etc. These polydentate ligands coordinate through their points of attachment to the same central metal ion to form complexes with ring structures. Such ring-structured metal complexes with metal forming a part of the ring system are called the *chelates* (Greek word *chela* = crab's claw). Examples include $[Ni(DMG)_2]$, $[Ca(EDTA)]^{2-}$ and $[Cu(acac)_2]$.



Structure of $[Ni(DMG)_2]$ chelate

The polydentate ligands that form the chelates are called the chelating agents. The process of chelate formation is called chelation. Due to chelation, the stability of the complex is enhanced. The extra stability conferred on a complex due to chelation is called the chelate effect.

Conditions for chelation

1. The chelating agents must possess atleast two donor groups per molecule, i.e. the ligands should be polydentate.
2. The donor groups must be situated in the molecule in such a way that they permit the formation of a ring with the metal atom without any strain. The donor atoms should be sterically capable of coordinating to the same metal to form a chelate.

Stability of chelates

In thermodynamic point of view, the stability of chelates can be related to the entropy change of the reaction. Consider the following example of chelation of nickel with ethyelenediamine.

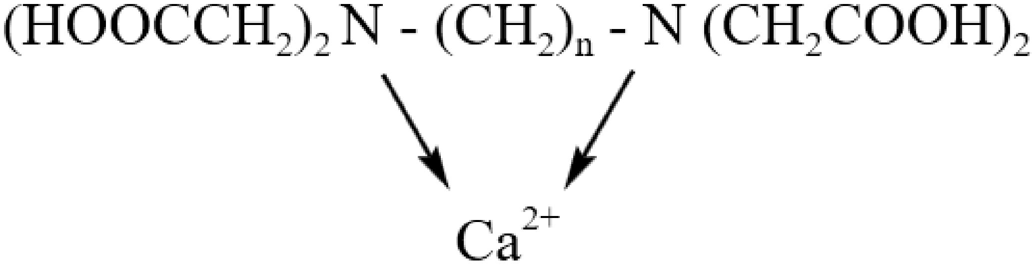
$$[Ni(H_2O)_6]^{2+} + 3\ en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$$

1 + 3 particles　　　　1 + 6 particles

During the formation of a chelate, the solvated metal ion in the solution reacts with a chelating agent, with the solvent molecules in the coordination sphere of the metal replaced by the chelating agent. Due to chelation, the number for particles has increased from 4 to 7, resulting in the increase in randomness of the system, thereby resulting in a positive ΔS°. Hence it causes greater complex stability.

Factors influencing the stability of chelates

1. ***Size of the chelate ring***
    - If there is no double bond in the ring, a 5-membered ring is the most stable.
    - Chelate rings having more or less than 5- members are generally less stable.
    - Consider a calcium complex with the general formula



$$(HOOCCH_2)_2N - (CH_2)_n - N(CH_2COOH)_2 \rightarrow Ca^{2+}$$

The greatest stability for the chelate is found when $n = 2$.

Value of n	**Ring size**	**Stability constant (log K)**
2	5	10.7
3	6	7.1
4	7	5.1
5	8	4.6

2. ***Number of chelate rings***
    - Greater the number of chelate rings, greater will be the stability of the complex.

- As the number of donor atoms in a chelating agent increases, the stability increases. This is due to the increase in the number of chelate rings formed by such ligands.
- Consider the stability constants of Ni^{2+} complexes with some polydentate ligands having different numbers of chelate rings.

Ligand	Chelate	log K	Increase in number of particles due to chelation	Number of rings
en	$[Ni(H_2O)_4en]$	7.9	2 to 3	1
dien	$[Ni(H_2O)_3dien]$	10.7	2 to 4	2
trien	$[Ni(H_2O)_2trien]$	14.0	2 to 5	3

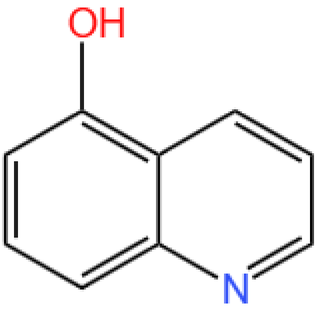
3. *Steric factor*

- The steric factor arises due to the presence of a bulky group attached to or near to a donor atom to cause mutual repulsion between the ligands and thereby weakening the metal-ligand bond. This leads to lesser stability.
- Consider the stabilities of three complexes formed by Ni^{2+} with three different chelating agents such as 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline and 4-methyl-8-hydroxyquinoline. The second stage formation constants for these complexes indicate the higher stability of the 4-methyl-8-hydroxyquinoline complex.

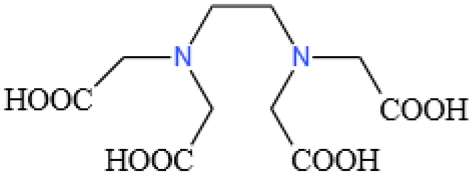
Substituent	$\log(K_1K_2)$ for Ni^{2+} complex
None	21.4
2-methyl	17.8
4-methyl	22.3

Applications of chelates in analytical chemistry

1. In qualitative analysis, nickel can be readily identified as its DMG chelate which precipitates as a rosy red solid in ammoniacal medium.
2. Magnesium, aluminium and zinc ions can also be identified as their stable and intensely coloured chelates.
3. In gravimetric analysis, magnesium, aluminium and zinc are precipitated quantitatively as their 8-hydroxyquinoline chelates called the oxinates.


8-Hydroxyquinone
(Oxine)

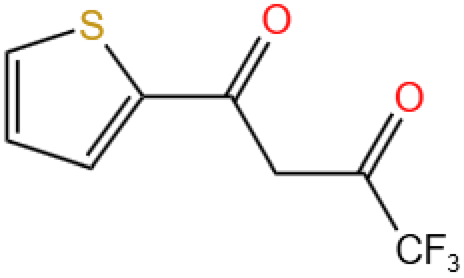
4. In volumetric analysis, certain metal chelates are used as indicators. For example, $[Fe^{II}(o\text{-}phen)_3]$ chelate called ferroin, is used as the indicator in titration of $Cr_2O_7^{2-}$, or Ce^{4+} with Fe^{2+}.
5. The formation of Ca^{2+} and Mg^{2+} - EDTA chelates is used in the determination of the total hardness of water.


EDTA
(Ethylene diamine tetraacetic acid)

6. In certain analytical separations, chelating agents are used as masking agents. A masking agent is defined as a substance that hides certain metal ions from other reagents with which their interactions are undesired. For example, in the gravimetric determination of

Ni^{2+} as its DMG complex, the interference of Fe^{3+} ion can be avoided by adding a slight excess of citric acid or tartaric acid before adding DMG and ammonium hydroxide.

7. The process of chelation is also used in the highly difficult separation of mixtures of metals, such as zirconium and hafnium. These two metals chemically resemble each other very closely. The separation of these two metals was made easy due to the discovery that the two chelates of these metals formed with thenoyltrifluoroacetone possess different solubilities in benzene.



Thenoyltrifluoroacetone

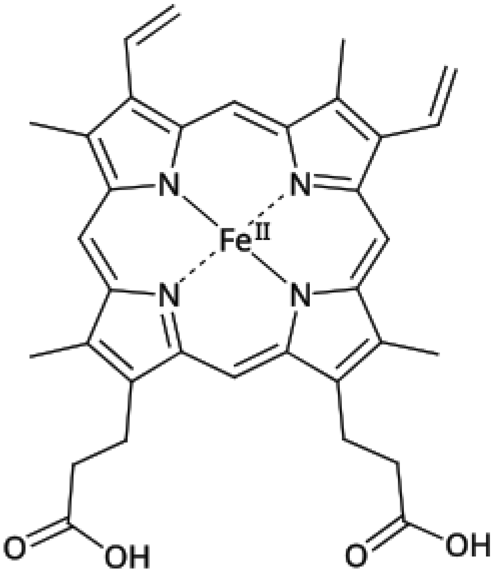
Role of chelates in living systems

<u>Haemoglobin</u>

- Haemoglobin, the red pigment in the red blood cells carries oxygen from the lungs to the tissues. It is called the respiratory pigment .
- It delivers the oxygen molecule to the myoglobin in the tissues.
- When the oxygen has been released for cell respiration, haemoglobin loses its bright red colour and becomes purple. It then combines with the waste carbon dioxide produced by the cells and deposits in the lungs so that the gas can be exhaled.
- Haemoglobin, a protein, is an iron-porphyrin chelate. This iron-porphyrin chelate is called the heme group (prosthetic group), which is a part of haemoglobin.
- Each haemoglobin molecule consists of four sub-units, each unit being a folded chain. A sub-unit consists of
    1) A protein unit (globin, a globular protein)
    2) A heme group and
    3) A histidine unit (Link between heme group and protein unit)

- The complex is octahedral having iron in 2+ oxidation state. It is coordinated to four nitrogen atoms in the porphine group, a histidine unit and a water molecule which can be replaced by molecular oxygen forming oxy-haemoglobin.

Haemoglobin	**Spin state**	**Magnetic character**	**Porphyrin ring**
Oxyhaemoglobin	Low spin	Diamagnetic	Planar
Deoxyhaemoglobin	High spin	Paramagnetic	Dome shaped with Fe^{2+} on the top

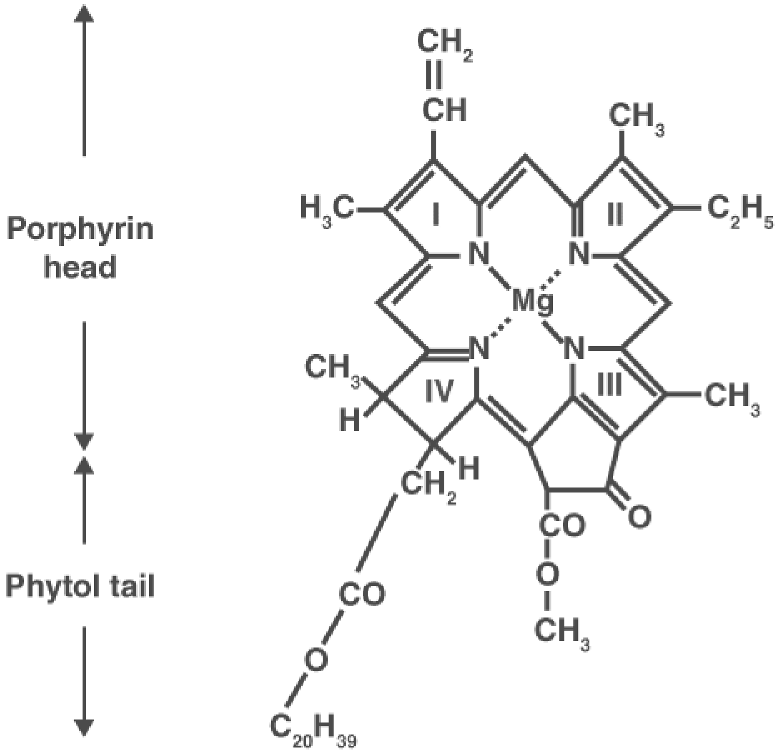


The heme group in haemoglobin

<u>Chlorophyll</u>

- Chlorophyll is a magnesium complex with tetrapyrrole belonging to the porphyrin family but with some modifications to the porphyrin ring. The modified porphyrin ring present in the chlorophyll is called chlorin.
- So, chlorophyll is a magnesium-chlorin chelate and it is the green pigment in plants.
- There are several kinds of chlorophylls that vary slightly in their molecular structure.
- In plants, chlorophyll *a* is the pigment directly responsible for the transformation of light energy into the chemical energy.

- Most photosynthetic cells contain a second type of chlorophyll also; in plants, it is chlorophyll *b*. This is able to light at different wavelengths from those absorbed by chlorophyll *a*, thus extending the range of light available for photosynthesis.
- Magnesium in the chlorophyll makes the molecule so rigid so that the energy absorbed is not lost thermally through molecular vibrations.
- Chlorophyll can convert light energy into chemical energy only when it is associated with certain proteins and embedded in a specialised membrane.
- Photosynthesis requires, in addition to chlorophyll, the help of four other metal complexes, a manganese complex, two iron complexes (cytochromes and ferredoxins) and a copper complex (plastocyanin).



Structure of chlorophyll a

- Chlorophyll *b* differs from chlorophyll *a* in having an aldehyde group (CHO) in place of the CH_3 group in ring II.

UNIT - 2

COORDINATION CHEMISTRY - II

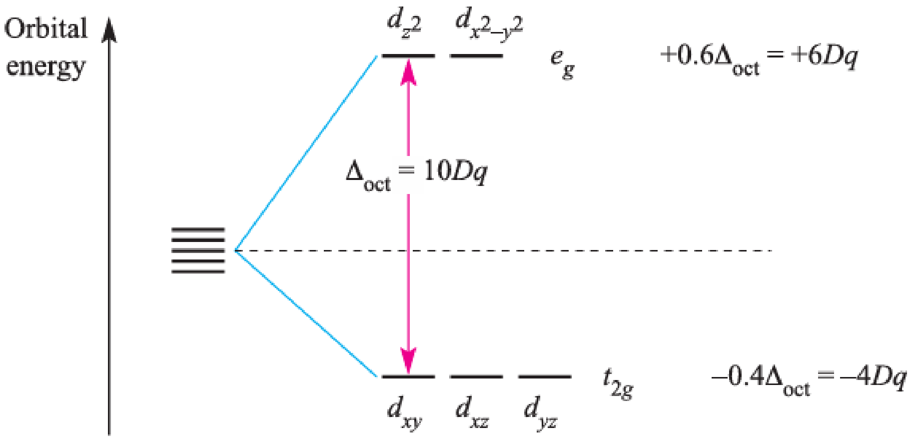
CRYSTAL FIELD THEORY

A second approach to the bonding in complexes of the d block metals is crystal field theory. Crystal field theory is an electrostatic model which predicts that the d orbitals in a metal complex are not degenerate. The pattern of splitting of the d orbitals depends on the crystal field, this being determined by the arrangement and type of ligands. The salient features of this theory are as follows:

1. Crystal Field Theory (CFT) assumes that the bond between the ligand and the central metal atom is purely ionic. i.e. the bond is formed due to the electrostatic attraction between the electron rich ligand and the electron deficient metal.
2. In the coordination compounds, the central metal atom/ion and the ligands are considered as point charges (in case of charged metal ions or ligands) or electric dipoles (in case of metal atoms or neutral ligands) and there are no metal-ligand covalent interactions.
3. The five d orbitals in an isolated gaseous metal atom/ion have the same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

Crystal field splitting in octahedral complexes

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand. Thus, the dz^2 and dx^2-y^2 orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_o (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $0.6\Delta_o$ and that of the three t_{2g} will decrease by $0.4\Delta_o$.



Crystal field splitting in an octahedral field

The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

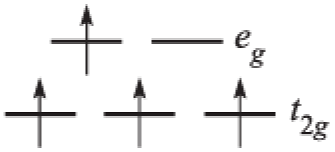
Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the d orbitals of metal ions in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the d electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule.

For d^4 ions, two possible patterns of electron distribution arise:

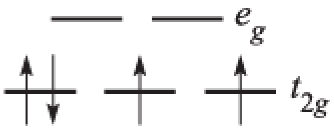
1. The fourth electron could either enter the t_{2g} level and pair with an existing electron, or
2. It could avoid paying the price of the pairing energy by occupying the e_g level.

Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

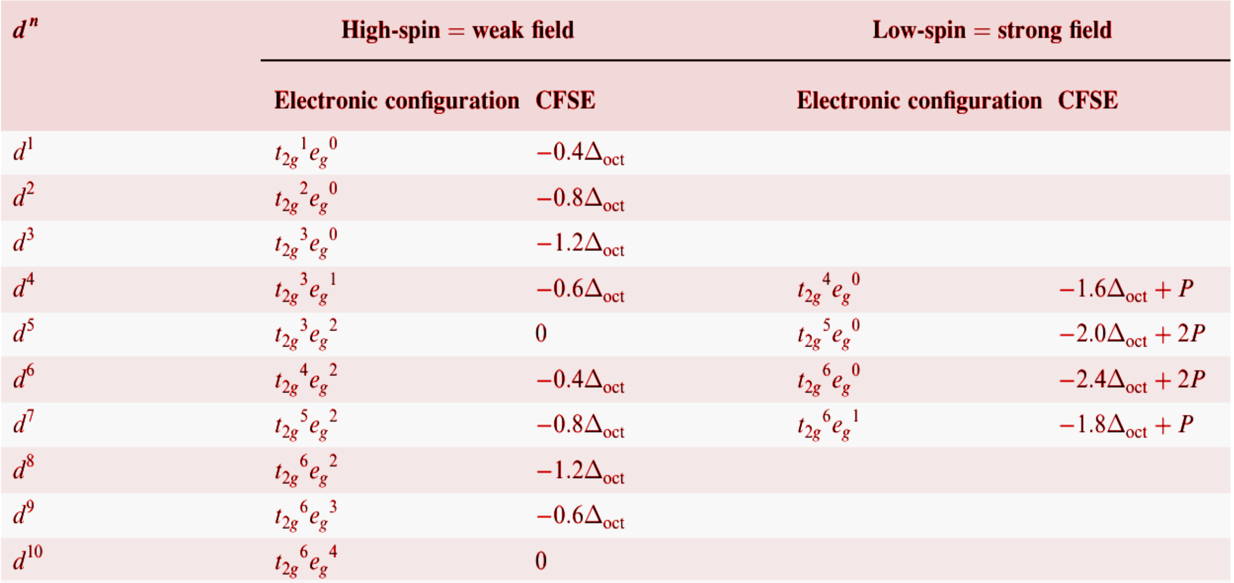
1. If $\Delta_o < P$, the fourth electron enters one of the eg orbitals giving the configuration $t_{2g}{}^3e_g{}^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.



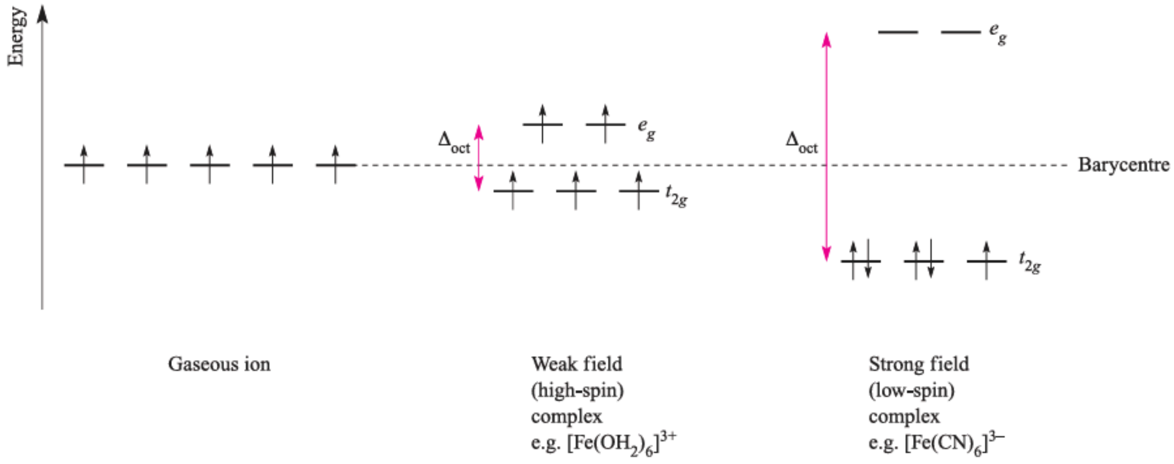
2. If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}{}^4e_g{}^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.



Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.



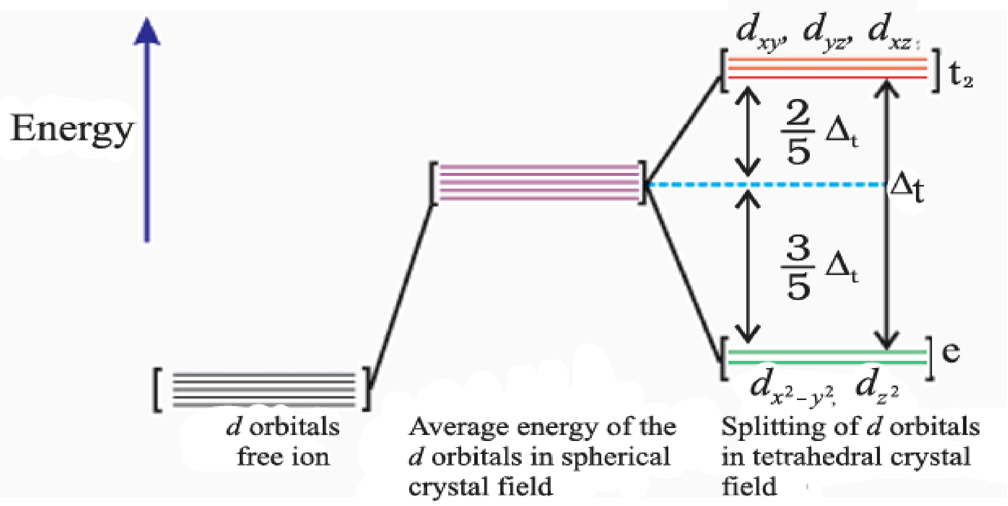
d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	**CFSE**	**Electronic configuration**	**CFSE**
d^1	$t_{2g}{}^1e_g{}^0$	$-0.4\Delta_{oct}$		
d^2	$t_{2g}{}^2e_g{}^0$	$-0.8\Delta_{oct}$		
d^3	$t_{2g}{}^3e_g{}^0$	$-1.2\Delta_{oct}$		
d^4	$t_{2g}{}^3e_g{}^1$	$-0.6\Delta_{oct}$	$t_{2g}{}^4e_g{}^0$	$-1.6\Delta_{oct} + P$
d^5	$t_{2g}{}^3e_g{}^2$	0	$t_{2g}{}^5e_g{}^0$	$-2.0\Delta_{oct} + 2P$
d^6	$t_{2g}{}^4e_g{}^2$	$-0.4\Delta_{oct}$	$t_{2g}{}^6e_g{}^0$	$-2.4\Delta_{oct} + 2P$
d^7	$t_{2g}{}^5e_g{}^2$	$-0.8\Delta_{oct}$	$t_{2g}{}^6e_g{}^1$	$-1.8\Delta_{oct} + P$
d^8	$t_{2g}{}^6e_g{}^2$	$-1.2\Delta_{oct}$		
d^9	$t_{2g}{}^6e_g{}^3$	$-0.6\Delta_{oct}$		
d^{10}	$t_{2g}{}^6e_g{}^4$	0		



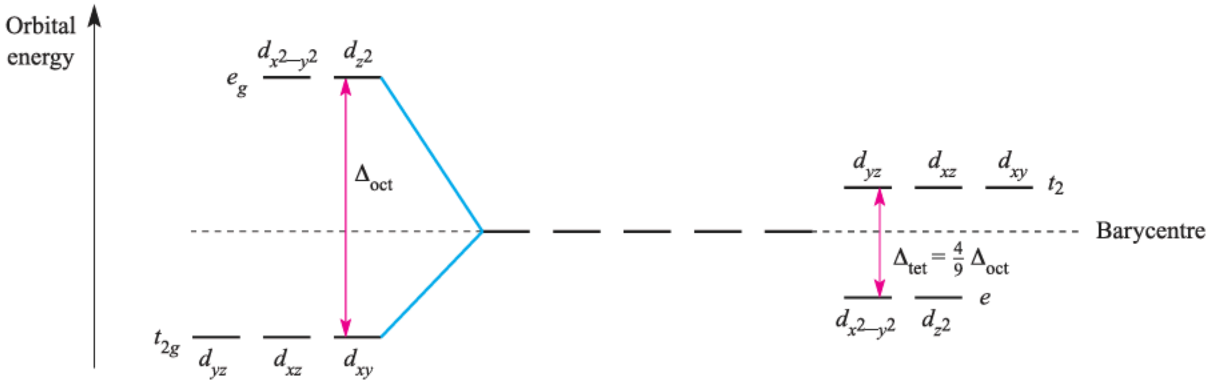
Crystal field splitting in a high-spin vs. a low-spin complexes

Crystal field splitting in tetrahedral complexes

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_O$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed. Tetrahedral complexes are almost invariably high-spin. The 'g' subscript is used for the octahedral and square planar complexes which have centre of symmetry. Since tetrahedral complexes lack symmetry, 'g' subscript is not used with energy levels.



Crystal field splitting in a tetrahedral field



Crystal field splitting in an octahedral vs. a tetrahedral field

Calculation of CFSE

1. $[Mn(H_2O)_6](NO_3)_2$

   The complex has octahedral geometry.

   The central metal ion = Mn^{2+} ($3d^5$)

   The H2O ligand is relatively weaker. Hence the high-spin complex is formed.

   Therefore, the electronic configuration becomes $t_{2g}^3e_g^2$.

   CFSE = $[(-0.4X3)+(0.6X2)]\Delta_O = (-1.2+1.2)\Delta_O = \mathbf{0\Delta_O}$

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

   The geometry of the complex is octahedral.

   The central metal ion = Fe^{2+} ($3d^6$)

   The CN- is a strong ligand. Therefore the low-spin complex is formed.

   The electronic configuration becomes $t_{2g}^6e_g^0$.

   CFSE = $[(-0.4X6)+(0.6X0)]\Delta_O + 2P = (-2.4+0)\Delta_O + 2P = \mathbf{-2.4\Delta_O + 2P}$

3. $[NiCl_4]^{2-}$

   The complex has tetrahedral geometry.

   The central metal ion = Ni^{2+} ($3d^8$).

   Since the tetrahedral complex is of high-spin, the electronic configuration becomes $e^4t_2^4$.

   CFSE = $[(-0.6X4)+(0.4X4)]\Delta_t = (-2.4+1.6)\Delta_t = \mathbf{-0.8\Delta_t}$

4. $[Co(NH_3)_2Cl_2]$

   The geometry of the complex is tetrahedral.

   The central metal ion = Co^{2+} ($3d^7$)

   The complex is of high-spin, the electronic configuration becomes $e_4t_2^3$.

   CFSE = $[(-0.6X4)+(0.4X3)]\Delta_t = (-2.4+1.2)\Delta_t = \mathbf{-1.2\Delta_t}$

Factors influencing the crystal field splitting values

1. ***Geometry of the complex***
   - The degree of splitting of d orbitals is affected by the geometry of the complex.
   - $\Delta_{sp} > \Delta_O > \Delta_t$
   - $\Delta_t = (4/9)\Delta_O$; $\Delta_{sp} = 1.3\Delta_O$

2. ***Oxidation state of the central metal ion***
   - Greater the charge on the central metal ion, greater is the attraction for the ligands.
   - Hence the ligands are drawn in more closely by the central metal ion.
   - So, they will have a greater effect in perturbing the metal d orbitals. This leads to a higher Δ value.
   - For example, the Δ_O value of $[Co(NH_3)_6]^{3+}$ is greater than that of $[Co(NH_3)_6]^{2+}$.

3. ***Principal quantum number of the d orbital***
   - Generally, the crystal field splitting is the greatest for complexes containing 5d electrons and the least for complexes containing 3d electrons.
   - This is due to the fact that the 5d orbitals extend farther into space and hence interact more strongly with the ligands leading to an increase in the amount of splitting.
   - For example, the Δ_O values
     $[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$
   - As a result of the high splitting values of second and third row transition elements (4d and 5d series), most of their complexes are exclusively low-spin (maximum

pairing of electrons) compared to the large number of both low-spin and high-spin (maximum unpaired electrons) complexes of the first row transition elements.

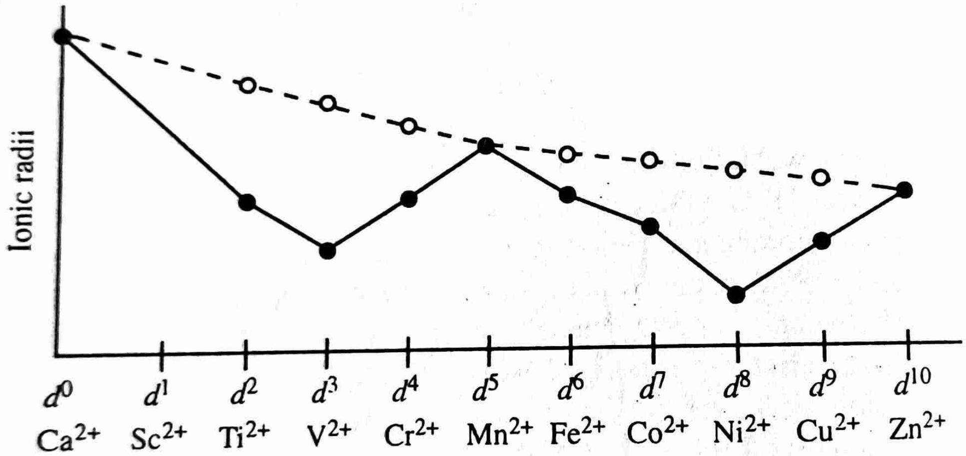
4. ***Nature of the ligands***

- The nature of the ligands also affect the degree of splitting of d orbitals.
- The ligands having less splitting ability are called *weak field ligands* whereas those with greater splitting power are known as *strong field ligands.*
- The splitting abilities of various ligands are arrived at from the spectra of their complexes.
- The ligands are arranged in the order of their increasing splitting ability.
- This series is called the spectrochemical series (since the values of splitting ability are obtained from the spectra of their complexes).
- This series is given below
  $\mathbf{I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 < en < bipy < o\text{-}phen < NO_2^- < CN^- < CO}$
- This order of increasing field strength of ligands is independent of the nature of the central metal ion and the geometry of the complex.
- Although this is the usual order, reversals occur, especially with ligands of about the same field strength.

Consequences of crystal field splitting

1. ***Ionic radii of transition metal ions***

The variation in ionic radii of divalent cations of the metals of the first transition series in their crystalline compounds, MX_2 (metal halides), where each metal ion is octahedrally surrounded by six ions, may be considered. In the absence of CFSE due to the d orbital splittings, the ionic radii of the transition metal ions should decrease gradually with increasing nuclear charge. Thus the ionic radii for M^{2+} ions are expected to decrease smoothly from Ca^{2+} to Zn^{2+} due to the increased nuclear charge. The change in size is not regular. A smooth dotted line is expected to be drawn through Ca^{2+}, Mn^{2+} and Zn^{2+} , which have d^0, d^5 and d^{10} configurations. In these cases, the d orbitals are empty, half full and full respectively. These configurations develop an almost spherical field round the nucleus. They have zero CFSE.



Variation of ionic radii with the number of d electrons

In Ti^{2+} ($t_{2g}^2e_g^0$) , the two d electrons occupy t_{2g} orbitals of lower energy, that is, the electrons occupy orbitals which are oriented between the ligands. Thus there is no shielding of the nuclear charge and the ligands are drawn closer to the nucleus. As a result, its ionic radius is less than that expected, when there was no crystal field effect.

In V^{2+} ($t_{2g}^3e_g^0$) , the effect of crystal field splitting is more prominent because now there are three t_{2g} electrons. The increased nuclear charge has an even greater effect with V^{2+} Hence its ionic radius is less than that of Ti^{2+}.

In Cr^{2+}($t_{2g}^3e_g^1$), the e_g level has one electron. This orbital is oriented in the direction of the ligand. Hence it provides good shielding to the ligands. Therefore, the ligands can no longer approach so closely and hence the ionic radius increases. The ionic radius of Cr^{2+} is more than that of V^{2+} ion. But it is still smaller than the value expected, if there were no crystal field effects.

For high spin Mn^{2+} ($t_{2g}^3e_g^2$) , each d orbital has one electron. This results in a spherical distribution of charge around the nucleus. Hence the octahedral radius of high spin Mn^{2+} has the value as expected from the consideration of nuclear charge alone. Therefore, it falls on the smooth line joining Ca^{2+} and Zn^{2+}.

The next three electrons enter the t_{2g} orbitals and hence the ionic radii again decrease for Fe^{2+} ($t_{2g}^4e_g^2$), Co^{2+} ($t_{2g}^5e_g^2$) and Ni^{2+} ($t_{2g}^6e_g^2$). In Cu^{2+}, the added electron goes to the e_g($t_{2g}^6e_g^3$). Hence its ionic radius is greater than that of Ni^{2+} but smaller than that Zn^{2+}.

Thus the shape of the curve is explained by the crystal field splitting. If there was no crystal field splitting, then a smooth curve from Ca^{2+} to Zn^{2+} through Mn^{2+} would have been obtained; but a curve with two humps is actually obtained.

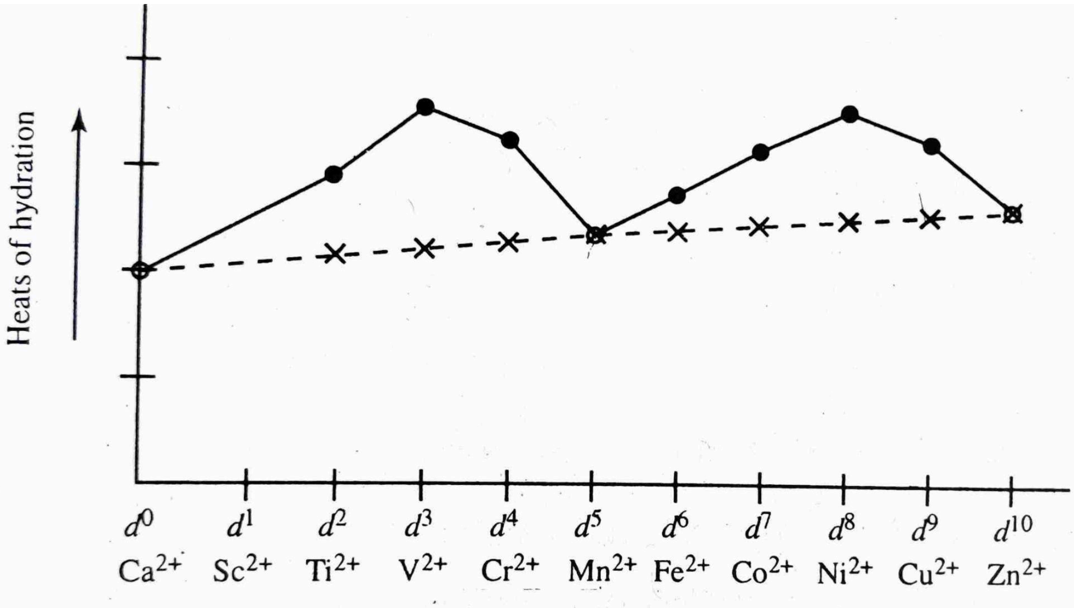
2. ***Heats of hydration of bivalent ions of first transition series***

The heat of hydration is the heat evolved in the hydration process.

$$M^{2+}_{(g)} + 6H_2O_{(1)} \rightarrow [M(H_2O)_6]^{2+} + \text{heat of hydration}$$

The negative sign indicates that heat is evolved in the hydration process. (Generally six water molecules enter the coordination sphere to form an octahedral aqua complex).

We know that the ionic radii of divalent ions of the first row transition elements decrease from Ca^{2+} to Zn^{2+}. Hence the experimental values of heats of hydration of these ions should increase regularly from Ca^{2+} to Zn^{2+}. This is because the decrease in ionic radii values brings the ligand water molecules closer to the metal, M^{2+} ions resulting in the increased electrostatic attraction between the cation and water ligands, but this expected regular increase does not occur.



Variation of heats of hydration with the number of d electrons

The ions Ca^{2+}, Mn^{2+} and Zn^{2+} have d^0, d^5 and d^{10} configurations respectively. These ions which have zero CFSE fall almost on the straight line. The distance of the other points above this line corresponds to the CFSE. The experimental values, instead of increasing regularly, show maxima at V^{2+} ($t_{2g}{}^3e_g{}^0$) and Ni^{2+} ($t_{2g}{}^6e_g{}^2$) and minima at Ca^{2+}($t_{2g}{}^0e_g{}^0$) . Mn^{2+}($t_{2g}{}^3e_g{}^2$) and Zn^{2+}($t_{2g}{}^6e_g{}^4$). These maxima and minima can be explained by the concept of CFSE. All the hexahydrate ions, $[M(H_2O)_6]^{2+}$ are high-spin octahedral complexes. For high-spin complexes, CFSE is minimum (zero) for d^0, d^5 and d^{10} ions . Hence they show minima in the graph. CFSE will be maximum (1.2 Δ_O) for d^3 and d^8 ions. Hence they correspond to maxima in the graph.

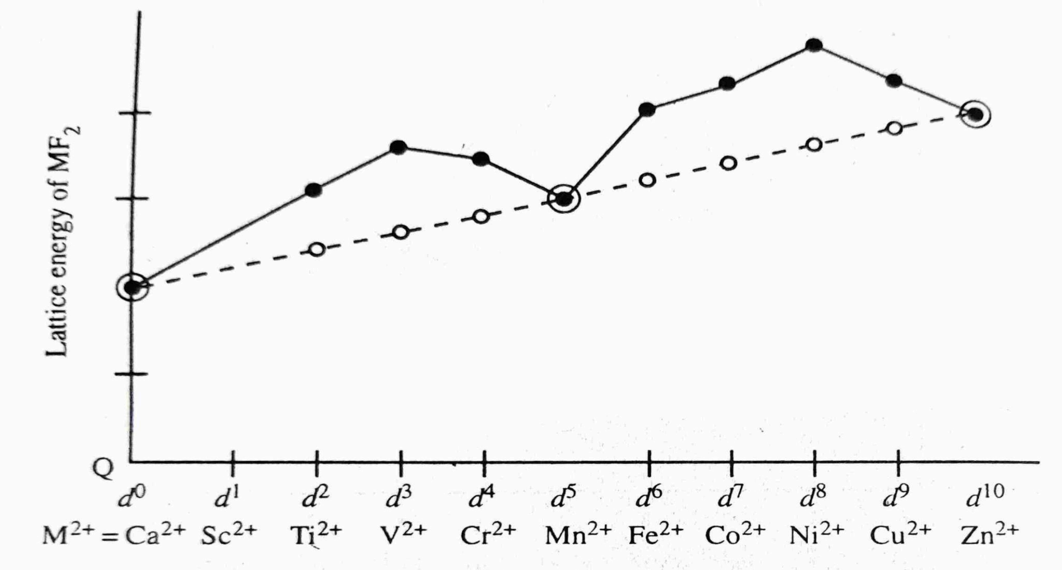
If the experimental values are corrected by subtracting the CFSE values calculated from the spectral data, then the resulting points fall almost on a straight line from Ca^{2+} to Zn^{2+} through Mn^{2+}.

Hence we conclude that if there was no crystal field splitting, then a smooth graph would have been obtained.

3. ***Lattice energy and CFSEs***

Let us consider the difluorides of transition metals of the first transition series from CaF_2 to ZnF_2. In crystalline state, these fluorides possess an octahedral arrangement of F^- ions around the M^{2+} metal ions. Since the ionic radii of M^{2+} ions are expected to decrease gradually, their lattice energies should increase gradually. This is because the lattice energy is inversely proportional to the inter-ionic distance. Since the radius of the anion is the same in all these compounds, the lattice energy should be inversely proportional to the ionic radius of the metal ion. This is actually the case as is evident from the plot of lattice energy against the number of d electrons. An almost straight line could have been drawn through the points which indicates the lattice energies of CaF_2, MnF_2 and ZnF_2.

However, the points showing the observed lattice energies of all the other bivalent metal fluorides of the series follow an irregular variation. The points showing the observed lattice energies of these fluorides lie above the points which show their theoretical lattice energies in the absence of any crystal field effects. The difference between the observed lattice energy and the theoretical lattice energy in the absence of crystal field effects gives the CFSE. From this CFSE, the crystal field splitting energy, Δ_O can be calculated. If there was no crystal field splitting of d orbitals, then a smooth graph would have been obtained.



Variation of lattice energies with the number of d electrons

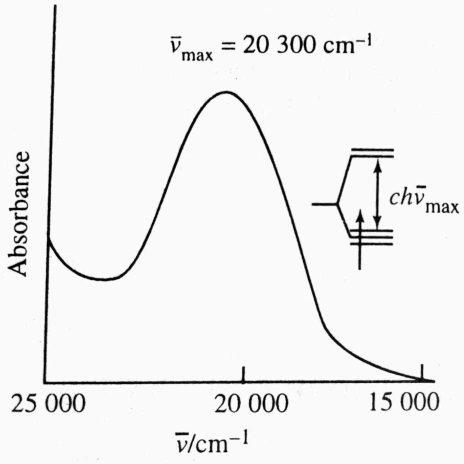
INTERPRETATION OF MAGNETIC PROPERTIES

- The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the number of unpaired electrons and hence structures adopted by metal complexes.
- A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications.
- For metal ions with up to three electrons in the d orbitals, like $Ti^{3+}(d^1)$; $V^{3+}(d^2)$; $Cr^{3+}(d^3)$; two vacant d orbitals are available for octahedral hybridisation with 4s and 4p orbitals. The magnetic behaviour of these free ions and their coordination entities is similar.
- When more than three 3d electrons are present, the required pair of 3d orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) cases, a vacant pair of d orbitals results only by pairing of 3d electrons which leaves two, one and zero unpaired electrons, respectively.
- The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions.

- However, with species containing d^4 and d^5 ions there are complications.
  1. $[Mn(CN)_6]^{3-}$ has a magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons.
  2. $[Fe(CN)_6]^{3-}$ has a magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons.
  3. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic.
- This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities.
- $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic.
- On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

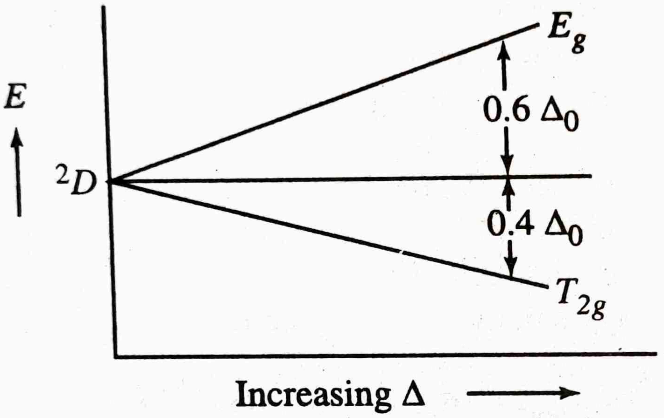
SPECTRA OF $[Ti(H_2O)_6]^{3+}$ ION

The electronic spectrum of aqueous Ti(III), d^1 species is shown below.



The electronic spectrum of $[Ti(H_2O)_6]^{3+}$

It has an absorption band at 20,400 cm^{-1} (4900 Å). It denotes the energy required to promote an electron from a t_{2g} orbital to an e_g orbital. The spectroscopic term ground state of gaseous Ti^{3+} ion is ^2D; the corresponding description of the (t_{2g}^1) and (e_g^1) configurations are T_{2g} and E_g. The T_{2g} state lies 0.4 Δ_O below, and E_g state 0.6 Δ_O above the values of the five d orbitals in a spherical field. The energy for the electronic transition $E_g \leftarrow T_{2g}$ increases as Δ_O increases. The emission is denoted as $E_g \rightarrow T_{2g}$ The energy diagram for the d^1 ion is shown below.



Energy level diagram for a d^1 ion (octahedral field)

In several cases, the λ_{max} of the lowest frequency band in the visible or ultraviolet region arises from the promotion of an electron from a t_{2g} orbital to an e_g orbital. This band in the visible region results in characteristic colours for many transition metal complexes.

In $[Ti(H_2O)_6]^{3+}$, this transition corresponds to an energy absorption of 244 kJ $mole^{-1}$. In Ti^{3+}, such a transition is spectroscopically forbidden according to the selection rule for electronic spectra $\Delta l = \pm 1$, where l is the second quantum number. However, it occurs in the complex due to the loss of the perfect octahedral symmetry by the vibrations of the ligand molecules (H_2O). This vibration also causes broadening of the absorption peak; in the absence of such vibrations absorption should be sharp producing a line. The absorption in $[Ti(H_2O)_6]^{3+}$ is weak and therefore the complex has a pale colour.

The value of Δ_O for the complex can be evaluated from its spectrum.

For $[Ti(H_2O)_6]^{3+}$, $\Delta_O = 20{,}400$ cm^{-1}. Therefore, 0.4 $\Delta_O = 8160$ $cm.^{-1} = 98$ kJ

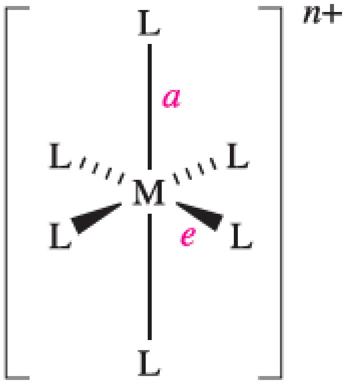
Thus, 0.4Δ_O the LFSE (ligand field stabilization energy) for this complex is 98 kJ.

The 0.4 Δ_O values have been evaluated for several ligands from the spectral absorptions. The spectrochemical series is evolved based on such spectral data. The magnitude of the splitting 0.4 Δ_O, depends on the nature of the ligands, and it affects the energy of the transition; this in turn influences the frequency of maximum absorption in the spectrum.

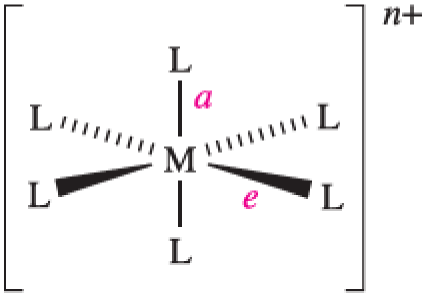
JAHN - TELLER EFFECT

The Jahn–Teller theorem states that *any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy*.

Octahedral complexes of d^9 and high-spin d^4 ions are often distorted, e.g. CuF_2 (the solid state structure of which contains octahedrally sited Cu^{2+} centres) and $[Cr(H_2O)_6]^{2+}$, so that two metal–ligand bonds (axial) are different lengths from the remaining four (equatorial).



Bond length $a > e$



Bond length $a < e$

For a high-spin d^4 ion, one of the e_g orbitals contains one electron while the other is vacant. If the singly occupied orbital is the dz^2, most of the electron density in this orbital will be concentrated between the cation and the two ligands on the z axis. Thus, there will be greater electrostatic repulsion associated with these ligands than with the other four, and therefore the complex suffers elongation ($a > e$). Conversely, occupation of the dx^2-y^2 orbital would lead to elongation along the x and y axes as in structure ($a < e$).

A similar argument can be put forward for the d^9 configuration in which the two orbitals in the e_g set are occupied by one and two electrons respectively. Electron-density measurements confirm that the electronic configuration of the Cr^{2+} ion in $[Cr(H_2O)_6]^{2+}$ is approximately $(d_{xy})^1(d_{yz})^1(d_{xz})^1(dz^2)^1$. The corresponding effect when the t_{2g} set is unequally occupied is expected to be very much smaller since the orbitals are not pointing directly at the ligands. This expectation is usually, but not invariably, confirmed experimentally. Distortions of this kind are called *Jahn–Teller* or *tetragonal distortions.*

Consequences of Jahn-Teller effect

1. 6-coordinated complexes are found to possess distorted octahedral structure due to this effect.
2. Despite having three chelate rings, $[Cu(en)_3]^{2+}$ is found to be less than $[Cu(en)_2(H_2O)_2]^{2+}$ which contains only two chelate rings. In the former case, two chelate rings make use of two elongated bonds (due to z-out) along the z-axis. These rings are under strain and hence less stable.
3. The absorption spectra of complexes having this distortion are different from the spectra of complexes having no distortion; instead of getting a single Gaussian curve, a curve with a shoulder is obtained in the spectrum due to distortion.
4. The distortion also affects the reactivity of complexes. For example, $[Cu(H_2O)_6]^{2+}$ exchanges two of its H_2O molecules on the elongated z-axis more rapidly than its four H_2O molecules in the xy-plane.

STABILITY OF COMPLEXES

Stability constants

- Coordination complexes are assumed to be formed from their constituents in aqueous solution by a stepwise replacement of coordinated H_2O molecules by ligand molecules or ions.
- The different steps involved in the formation of a complex may be represented as

$$[M(H_2O)_n] + L \overset{K_1}{\rightleftharpoons} [M(H_2O)_{n-1}L] + H_2O$$

$$[M(H_2O)_{n-1}L] + L \overset{K_2}{\rightleftharpoons} [M(H_2O)_{n-2}L_2] + H_2O$$

$$[M(H_2O)_{n-2}L_2] + L \overset{K_3}{\rightleftharpoons} [M(H_2O)_{n-3}L_3] + H_2O$$

$$[M(H_2O)L_{n-1}] + L \overset{K_n}{\rightleftharpoons} [ML_n] + H_2O$$

- The equilibrium constants involved in each step (K_1, K_2, K_3, …, K_n) are called step-wise stability constants (or) successive stability constants of the system.
- The stability constants are also known as formation constants. They are called stability constants because greater their values, greater will be the stability of the system.
- 1/K is also called the instability constant
- If the reaction takes place in a single step, then the complex formation step becomes

$$[M(H_2O)_n] + nL \overset{\beta_n}{\rightleftharpoons} [ML_n] + nH_2O$$

The equilibrium constant involved in the step β_n is called the over-all stability constant or over-all formation constant for the n^{th} stage product.

- The over-all stability constant β_n is the product of the step-wise stability constants of the system.

Stability of complexes in aqueous solutions

The stability of a complex in an aqueous solution can be influenced by the following factors:

1) ***Solvation vs. hydration***
    - ➢ For the formation of a complex in an aqueous solution, the incoming ligand should be capable of displacing the aqua ligand which hydrates the central metal ion.
    - ➢ If the M-L bond is stronger than M-OH_2 bond, then the complex formed is more stable. (L= incoming ligand)
2) ***Effect of pH***
    - ➢ Many ligands that form the complex with the metal ion are basic.
    - ➢ In acidic medium, the ligands may get protonated and lose their donor ability.
    - ➢ For example, EDTA binds strongly at higher pH, but weakly in acidic solution as carboxylate groups are protonated.
    - ➢ Therefore, lower pH reduces stability.

3) ***Competition with hydrolysis***

- ➢ Many metal ions tend to undergo hydrolysis in water.
- ➢ In that case, availability of free metal ions for complexation is reduced.
- ➢ Stronger ligands like ox, EDTA suppress hydrolysis by binding tightly.

Factors affecting the stability of a complex ion

I. ***Charge of a central metal ion***

- Greater the positive oxidation state of the central metal ion, greater will be its attraction for the ligands; hence greater will be the stability of the complex.
- Therefore, when a meta ion forms complexes with the same ligand in more than one oxidation state, the complexes of the higher oxidation states are always more stable than those of the lower oxidation states.

II. ***Size of the central metal ion***

- Keeping the charge constant, as the size of the central metal ion decreases, the specific charge per unit surface area increases.
- Hence, the metal's attraction for the ligand increases.
- Generally, stabilities of complexes increases with decrease in size of the central metal ion.

III. ***Nature of the ligand atom***

- Consider the complexes formed by the halide ions
- For most of the metals, the order of stabilities follows the sequence

$$\mathbf{F^- > Cl^- > Br^- > I^-}$$

- But this order is reversed for a few metals like Pt^{2+}, Cu^+, Ag^+, Hg^{2+} and Tl^+, where back donation from metal to ligand occurs in addition to the transfer of electrons from the ligand to the metal.

IV. ***Basicity of the ligands***

- Greater the basicity, greater will be the tendency to donate electron pairs.
- This means that the more basic ligands will form more stable complexes.

V. ***Chelating ability of the ligand***

- The stabilities of complexes are greatly increased by the coordination of polydentate ligands which form ring structures with the metal atom forming a part of the ring system.
- Such ring-structured complexes are chelates and the process of chelate formation is called chelation. The ligands forming chelates are called chelating agents.
- Due to chelation, extra stability is conferred to the complex. This is called the chelate effect.
- The chelate effect may be regarded thermodynamically as due to the favourable entropy change of the reaction.

VI. ***Chelate ring size***

- When there is no double bond in the chelate ring, generally a 5-membered ring will be the most stable.
- When there are double bonds, a 6-membered ring is the most stable.
- Any ring containing less than 5 members or more than 6 members will be less stable generally.

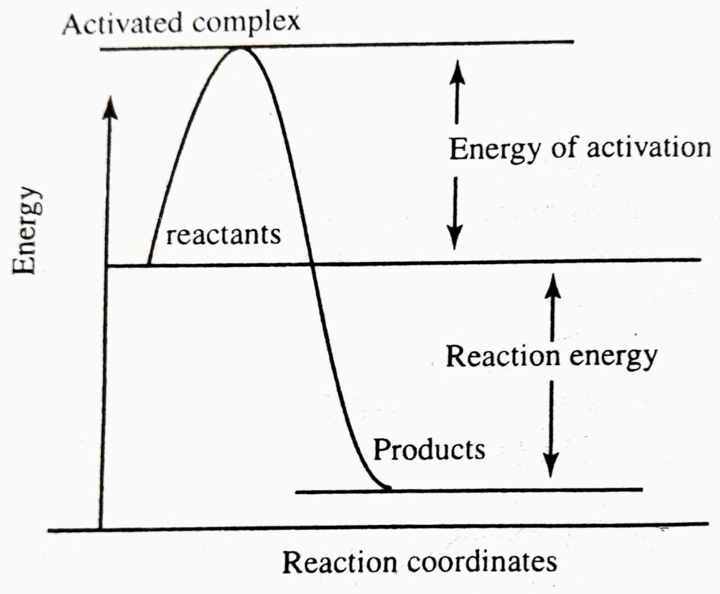
VII. ***Outer electronic configuration of the central metal ion***

- When considering the complexes containing the metal ion having similar charge and size, the metal ion having pseudo inert gas configuration **(**$(n-1)s^2p^6d^{10}$**)** forms more stable complexes than that of a metal ion having inert gas configuration **(**$(n-1)s^2p^6$**)**.
- This is due to the poor shielding of outer electrons by d electrons in a metal having pseudo inert gas configuration.

Thermodynamic stability and kinetic stability

- ➢ ***Thermodynamic stability*** : The term ‘stability’ is used without any modification.
- ➢ While considering the stability in a thermodynamic point of view, metal-to-ligand bond energies, stability constants and thermodynamic variables derived from them are taken into account.
- ➢ It is more appropriate to speak of complexes as stable or unstable.
- ➢ The thermodynamic stability of a complex depends on the difference in energy between the reactants and the products, namely the reaction energy.

- Greater the reaction energy, greater will be the thermodynamic stability.
- ***Kinetic stability*** :
- While considering stability from a kinetic point of view, the rates and mechanisms of reactions and also the energies involved in the formation of the activated complex are taken into account.
- It will be more proper to speak of complexes as being inert or labile rather than stable or unstable in the kinetic point of view
- The kinetic stability of a complex depends on the difference in energy between the reactants and the activated complex, namely the activation energy.
- Greater the activation energy, lesser will be the reaction rate, implying that the complex is inert.



The relative energies of products, reactants and activated complex of a reaction

- Stable complexes may be inert or labile and unstable complexes may be labile or inert.
- For example, $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ have roughly the same bond energy. This means that two complexes are of equal stability from the thermodynamic point of view. But $[Fe(H_2O)_6]^{3+}$ is labile and exchanges its ligands with other ligands rapidly, whereas $[Cr(H_2O)_6]^{3+}$ is inert and hence exchanges its ligands very slowly.

COMPARISON OF VBT AND CFT

ASPECT	**VBT**	**CFT**
1) Nature of bonding	Covalent (M-L overlap, hybrid orbitals)	Ionic/ electrostatic (Ligands as dipoles or point charges)
2) Main concept	Hybridization of orbitals (s,p,d)	Splitting of d-orbitals in ligand field
3) Geometry	Explained via. the type of hybridization (sp^3, dsp^2,...)	Explained via. d-orbital splitting patterns
4) Colour of complexes	Cannot be explained	Explained by d-d electronic transitions
5) Magnetic property	Depends on electron pairing in hybrid orbitals	Depends on high spin (or) low spin based on crystal field splitting
6) Stability	Not explained	Explained by CFSE
7) Limitations	Failed to account for spectra, stability and thermodynamics	Ignored the covalent nature of bonding
8) Example	i) $[NiCl_4]^{2-}$ Tetrahedral (sp^3, paramagnetic) ii) $[Ni(CN)_4]^{2-}$ Square planar (dsp^2, diamagnetic)	i) $[FeF_6]^{3-}$ - High spin ii) $[Fe(CN)_6]^{3-}$ - Low spin

UNIT - 3

ORGANOMETALLIC COMPOUNDS

METAL CARBONYLS

Metal carbonyls and their related compounds are most commonly formed by the metals in group VIII in the periodic table, and less commonly by the neighbouring transition elements in groups VII and VI. and still less commonly by certain elements in group V. They are formed by reactions involving CO and either free metals or metal salts, and are characterised as having CO groups directly bonded to the metal atoms through carbon. Transition metal carbonyls and related anions and cations are defined as complexes of the transition metal in zero or low positive or low negative oxidation state with CO.

EAN rule for metal carbonyls

- The adherence of metal carbonyls and related compounds to the EAN rule is striking. In mononuclear metal carbonyls $M(CO)_y$, the EAN of metal M is that of the next higher inert gas and is given by the relation,

  $$\mathbf{EAN = m+2y}$$

  where m is the atomic number of the metal. M. Each CO group adds two electrons.
- Examples for such carbonyls include, $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, etc.
- Let’s consider $Cr(CO)_6$

  Atomic number of Cr = 24

  Oxidation state = 0

  Electrons gained through coordination = 6X2 = 12

  Total = 36 which is the atomic number of the next higher inert gas, krypton. Thus many metal carbonyls obey the EAN rule.
- For carbonyls of the type, $M_x(CO)_y$ the relation,

$$G-\left(\frac{xm+2y}{x}\right)=x-1$$

holds good. In the above equation, G is the atomic number of the next higher inert gas and m is the atomic number of the metal M.

This relation also applies to polynuclear compounds and most of the related carbonyl compounds. The EAN rule can only be used as a guiding principle and not as a strict inviolable rule. If the central metal in a complex is present as an ion, then the EAN of the metal is derived by deducting the number of electrons lost in ion formation from the atomic number of the metal, and then adding the number of electrons gained by coordination. In many cases the EAN so calculated is equal to the atomic number of the next higher inert gas element.

Classification of metal carbonyls

- Metal carbonyls are broadly classified into two types, namely, *mononuclear* and *polynuclear* metal carbonyls.
- Mononuclear metal carbonyls are those which contain only one central metal atom. Examples for mononuclear metal carbonyls are $[V(CO)_6]$, $[Cr(CO)_6]$, $[Fe(CO)_5]$, $[Ni(CO)_4]$, etc.
- Polynuclear metal carbonyls are those which contain more than one atom. Depending upon the number of central metal atoms, polynuclear carbonyls are called binuclear, trinuclear, tetranuclear metal carbonyls.
- These polynuclear metal carbonyls are further classified into homopolynuclear and heteropolynuclear metal carbonyls.
- Homopolynuclear metal carbonyls are those which contain the same central metal atoms. For example, $[Mn_2(CO)_{10}]$, $[Fe_2(CO)_9]$, $[Fe_3(CO)_{12}]$, $[Co_2(CO)_8]$, $[Co_4(CO)_{12}]$, $[Co_6(CO)_{16}]$, etc.
- Heteropolynuclear are those which contain more than one kind of central metal atom. For example, $[Mn_2Fe(CO)_{14}]$, $[CoMn(CO)_9]$, $[Fe_2Ru(CO)_{12}]$, $[FeRu_2(CO)_{12}]$ etc.

General methods of preparation of metal carbonyls

1. ***<u>Direct combination</u>***

$$xM + yCO \rightarrow M_x(CO)_y$$

Metal carbonyls can be prepared by passing CO over finely divided metal at suitable temperature and pressure. The process can be favoured by applying high temperature and low pressure. Under these conditions, the metal becomes more active for metal carbonyl formation.

$$Fe + 5\ CO \rightarrow Fe(CO)_5 \text{ (at 200 ℃ and 200 atm)}$$

$Ni(CO)_4$, $Co_2(CO)_8$, $Mo(CO)_6$, $Ru(CO)_5$, $Rh_2(CO)_8$ are some of the metal carbonyls prepared by this method.

2. ***High pressure synthesis***

   Almost all of the known metal carbonyls have been prepared by reactions between metallic halides or sulphides or oxides and CO under pressure. Such reactions are useful especially in cases where metallic compounds are largely covalent. Generally, some free metal must be present to act as an acceptor for the non-metal. For example, $Co_2(CO)_8$ is prepared as per the equation

$$2\ CoS + 8\ CO + 4\ Cu \rightarrow Co_2(CO)_8 + 2\ Cu_2S$$

3. ***Disproportionation reaction***

   Disproportionation reactions are reactions involving self-oxidation and reduction. One part of the reactant is oxidised at the expense of the other part which gets reduced. For example, when nickel(I) cyanide is treated with carbon monoxide, $Ni(CO)_4$ and $Ni(CN)_2$ are formed

$$2\ NiCN + 4\ CO \rightarrow Ni(CO)_4 + Ni(CN)_2$$

4. ***Oxidation of metal carbonyl hydrides***

   Oxidation of metal carbonyl hydrides by MnO_2 or H_2O_2 yields metal carbonyls. For example, oxidation of iron carbonyl hydride using H_2O_2 gives the trimeric tetracarbonyl of iron.

General properties of metal carbonyls

1. Metal carbonyls are diamagnetic with the exception of $V(CO)_6$, which is paramagnetic.
2. They are generally covalent which is indicated by their volatility as well as insolubility in polar solvents and solubility in nonpolar solvents.
3. Most of the meta carbonyls are crystalline solids except $Ni(CO)_4$ and $M(CO)_5$ (M = Fe, Ru, Os) which are liquids.
4. Many are extremely toxic.

5. Many are coloured, except $Ni(CO)_4$, which is colourless.

CARBONYL	***Colour***	**CARBONYL**	***Colour***
$Fe(CO)_5$	Yellow	$Ir_4(CO)_{12}$	Yellow
$Fe_2(CO)_9$	Orange	$Co_2(CO)_8$	Orange-red
$Fe_3(CO)_{12}$	Green	$V(CO)_6$	Blue-green
$Rh_4(CO)_{12}$	Red	$Mn_2(CO)_{10}$	Golden

6. They decompose on heating to their respective metals and CO.
7. In many reactions, their properties are those of the metal and CO.
8. Many metal carbonyls react with NO to form metal carbonyl nitrosyls where NO acts as a three-electron donor.

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

9. Metal carbonyls react with alkalis to form carbonylate anions which produce carbonyl hydrides on acidification.

$$Fe(CO)_5 + NaOH \rightarrow Na[HFe(CO)_4] + CO_2$$

$$Na[HFe(CO)_4] + HCl \rightarrow [H_2Fe(CO)_4] + NaCl$$

10. Many metal carbonyls combine with halogens to form metal carbonyl halides.

$$Fe(CO)_5 + X_2 \rightarrow [Fe(CO)_4X_2] + CO$$

11. Some metal carbonyls are reduced by H_2 to form metal carbonyl hydrides.

$$Mn_2(CO)_{10} + H_2 \rightarrow 2\ HMn(CO)_5$$

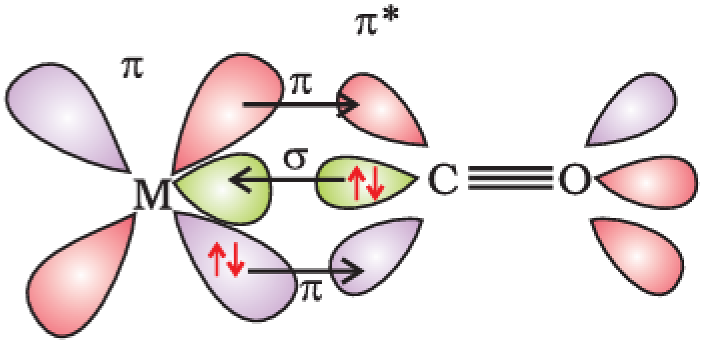
Bonding in metal carbonyls

1. ***<u>C-O bond</u>***

The idea that CO as such is in some way bound to the metal atom was postulated. The chemical evidence shows that CO is liberated in many reactions of the metal carbonyls and that the CO groups can be replaced step by step by other neutral ligands. The force constant of the CO group in metal carbonyls is not very different from that of the free CO molecule. This means that the bond character in the CO group is much the same as in the free CO molecule.

2. ***M-C bond***

The metal atoms have nine valence orbitals [nd^5, $(n+l)s^1$ and $(n+1)p^3$], and in metal carbonyls and related compounds they show a strong tendency to utilize all of them in forming bonds. Thus in $Fe(CO)_5$, five orbitals are used for the Fe-C σ bonds, the electrons of which come from the CO groups. The remaining orbitals contain tron electrons which are used in π-bonding. The overlapping of the lone pair with the carbon atom with nd, (n+1)s and (n+1)p vacant metal orbitals may be regarded as forming a M-C σ bond. Because of the low basicity of CO, this is not sufficient to explain the stability of the carbonyls. Hence, further source of bonding should exist. In all metal carbonyls, there are filled non-bonding d orbitals of the metal, which are of the correct symmetry to overlap with fairly low lying π antibonding orbitals of CO to form a M-C π bond. This formation of an additional bond by transfer of charge from the metal can be seen, not only as an additional bond, but also as a means of strengthening the original bond by the removal of the unfavourable charge separation induced by the donor σ bond. The drift of metal electrons into CO orbitals will tend to make CO as a whole negative and hence it increases its basicity, which accounts for the greater strength of a bond; at the same time the drift of electrons to the metal in the σ bond tends to make CO positive, thus enhancing the acceptor strength of the π orbitals. The effects of σ bond formation thus strengthen the π bonding and vice versa. This bonding mechanism is known as synergic interaction which accounts for a major part of the M-C bond strength in metal carbonyls and related compounds.



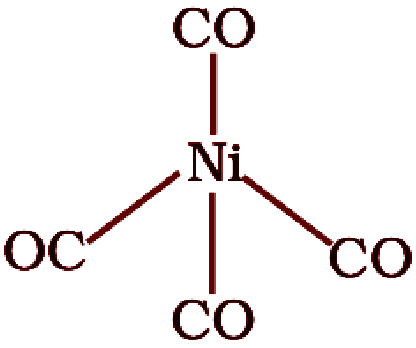
Synergic bonding

A major consequence of the presence of electrons in the π-antibonding orbitals of CO is the reduction in the bond order of the C-O bond. The C-O stretching frequency of CO itself is about 2155 cm^{-1} whereas the corresponding frequencies in terminal metal carbonyl groups lie at considerably lower values, and are generally around 2000 cm^{-1}. Any effect which decreases C-O bond order should necessarily increase M-C bond order because the two are roughly complementary to each other.

Structure and bonding in carbonyls

1. ***$Ni(CO)_4$***

   Perfect tetrahedral shape



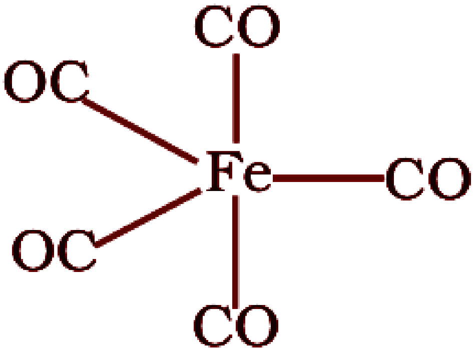
2. ***$Fe(CO)_5$***

   Trigonal bipyramidal structure.

   The axial Fe-C bond (1.806 Å) is shorter than the equatorial one (1.833 Å).

   The backbonding is more efficient in axial bonds than equatorial bonds.

   The axial and equatorial COs have two different γ_{CO} values.

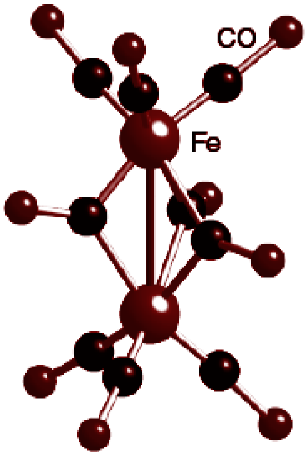


3. $Fe_2(CO)_9$

Two octahedra sharing a common face formed by the carbon atoms of 3 bridging groups.

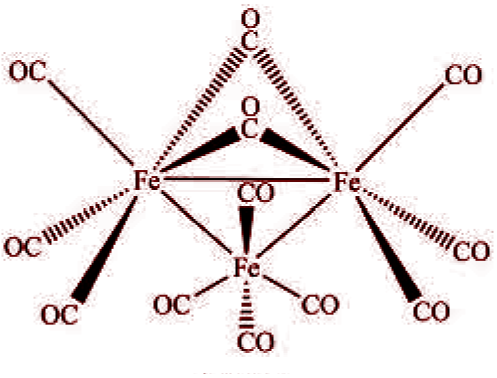
Bridging COs stabilize when backbonding is insufficient.

The Fe-Fe bond distance is 2.46 Å.



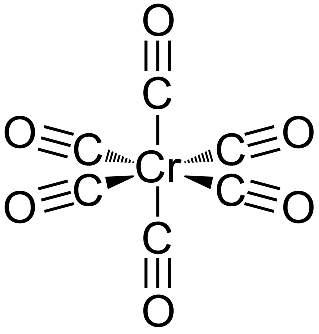
4. $Fe_3(CO)_{12}$

The structure resembles an isosceles triangle. Two Fe centres are similar and one Fe has differently bonded COs.

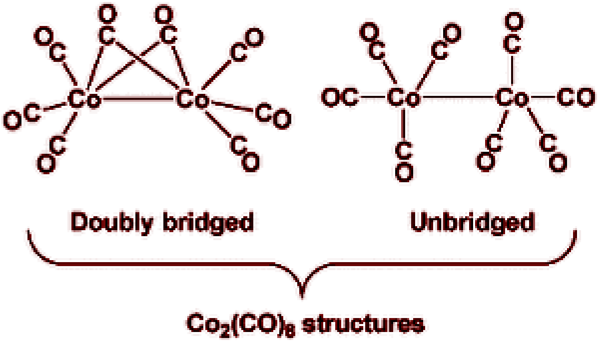


5. $Cr(CO)_6$

It has a perfect octahedral structure.



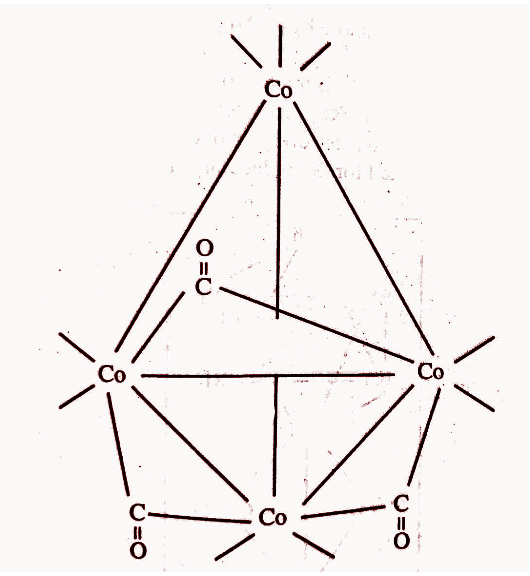
6. $Co_2(CO)_8$



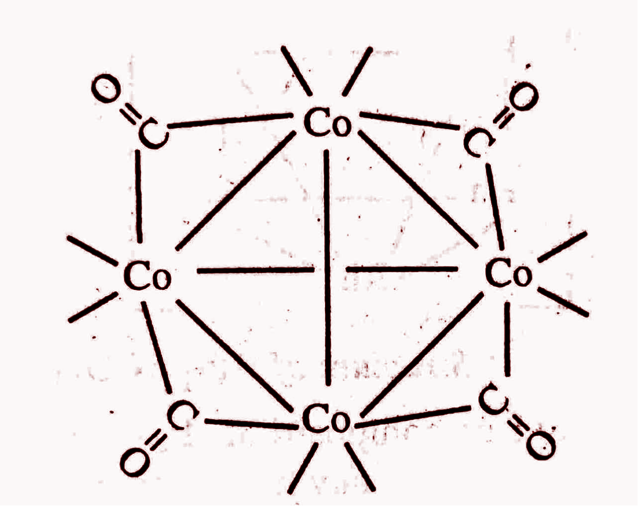
It exists in two forms. Bridged CO has lower γ_{CO} value.

7. $Co_4(CO)_{12}$

It exists in different forms depending on the phase.



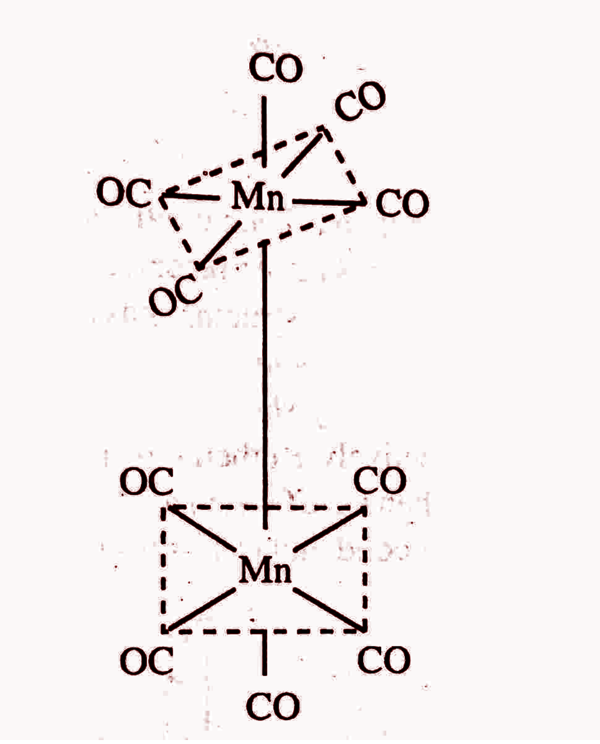
In solid state : 4 Co atoms are present at four corners of a tetrahedron



In solution

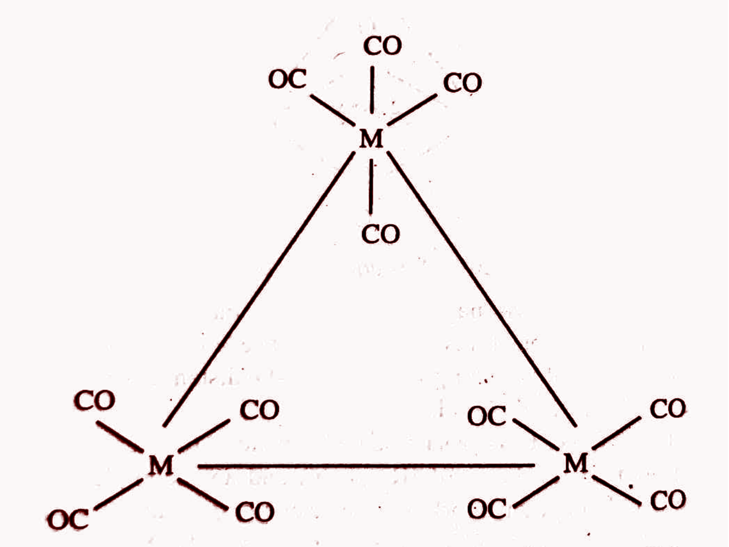
8. $Mn_2(CO)_{10}$

Two square pyramidal $Mn(CO)_5$ groups are joined by a Mn-Mn bond, each metal having an octahedral arrangement. The structure resembles two staggered octahedra sharing one corner. 4 Mn-CO equatorial bonds are bent slightly inwards in each of the octahedra (Mn atoms lie 0.12 Å out of equatorial planes of C atoms). The Mn-Mn bonds are larger than expected for a single bond . This bond provides extra electrons to reach EAN.



9. ***$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$***

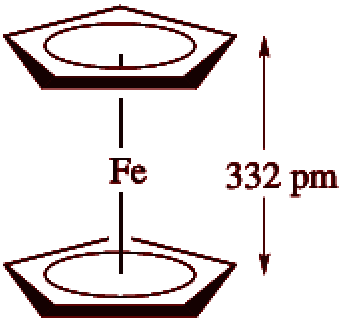
The structure is isomorphous and resembles an equilateral triangle having identical metal centres at all corners.

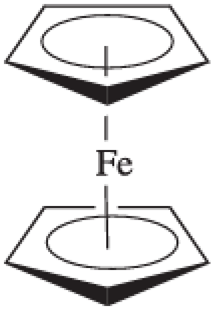


Structure of $[M_3(CO)_{12}]$ [*M = Os or Ru*]

FERROCENE - PREPARATION AND PROPERTIES

One of the best-known cyclopentadienyl complexes is the sandwich compound ferrocene, $(\eta^5\text{-Cp})_2Fe$. It is a diamagnetic, orange solid (Melting point : 446 K) which obeys the 18-electron rule. In the gas phase, the two cyclopentadienyl rings are eclipsed but the solid exists in several phases in which the rings are co-parallel but in different orientations.





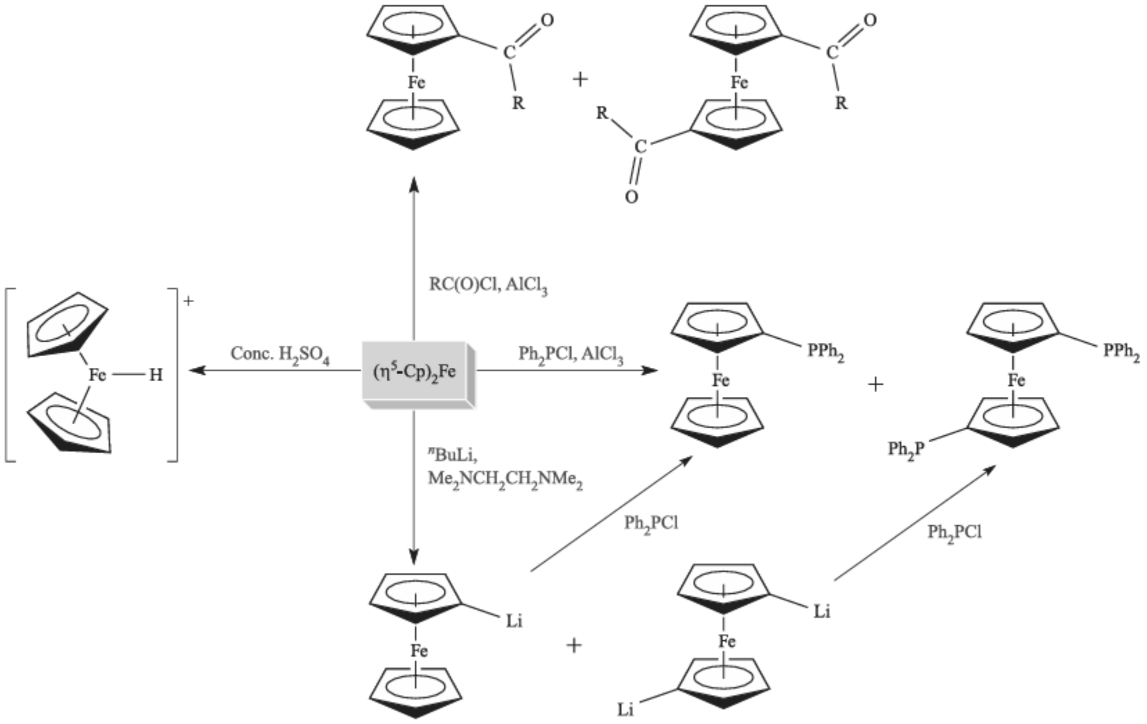
Electron count:

Fe(0) = 8 valence electrons

$2Cp^{\bullet}$ = 2 × 5 valence electrons

Total = 18 electrons

Solving the structure has been hampered by disorder problems.The barrier to rotation of the two rings is low and at 298K, there is motion even in the solid state. In derivatives of ferrocene with substituents on the Cp rings, the barrier to rotation is higher,and in $(\eta^5\text{-}C_5Me_5)_2Fe$, the two C_5 rings are staggered in both the gas and solid states. The bonding in $(\eta^5\text{-}Cp)_2Fe$ can be described in terms of the interactions between the π-MOs of the ligands and the metal 3d atomic orbitals. Ferrocene is oxidized (e.g. by I_2 or $FeCl_3$) to the paramagnetic, blue ferrocenium ion, $[(\eta^5\text{-}Cp)_2Fe]^+$. The Fc^+/Fc couple is commonly used as a convenient internal, secondary reference electrode.



Some chemical reactions of ferrocene

Uses of ferrocene

- Ferrocene acts as a fuel additive to gasoline, enhancing antiknock performance and reducing emissions.
- It functions as a high-temperature lubricant for engines and machinery, minimizing friction.
- Additionally, it stabilizes polymers like polyethylene and polypropylene against light degradation during polymerization.
- The compound excels as a catalyst in organic reactions such as oxidation, hydrogenation, and cross-coupling processes.
- Ferrocene derivatives form ligands for metal-catalyzed reactions, including Suzuki-Miyaura couplings.
- It also serves as a standard in cyclic voltammetry for electrochemical studies.
- Ferrocene derivatives create redox-active polymers, dendrimers, bioreceptors, and materials for nonlinear optics or electron beam lithography.
- In electrochemistry, it enables sensors for detecting glucose, dopamine, and heavy metals.
- It powers electrodes in redox flow batteries owing to reversible redox behavior.
- Ferrocene-based drugs target cancer, malaria, and bacterial infections, with examples like ferrocifen enhancing drug activity.
- Its Fenton chemistry supports targeted therapies via iron-mediated oxidation.
- Derivatives act as electrode mediators in blood glucose monitors.

UNIT - IV

INNER TRANSITION ELEMENTS

(LANTHANOIDS AND ACTINOIDS)

INTRODUCTION

The f-block consists of elements in which 4f and 5f orbitals are progressively filled. They are placed in a separate panel at the bottom of the periodic table. The name inner transition metals is often used to refer to the f-block elements.

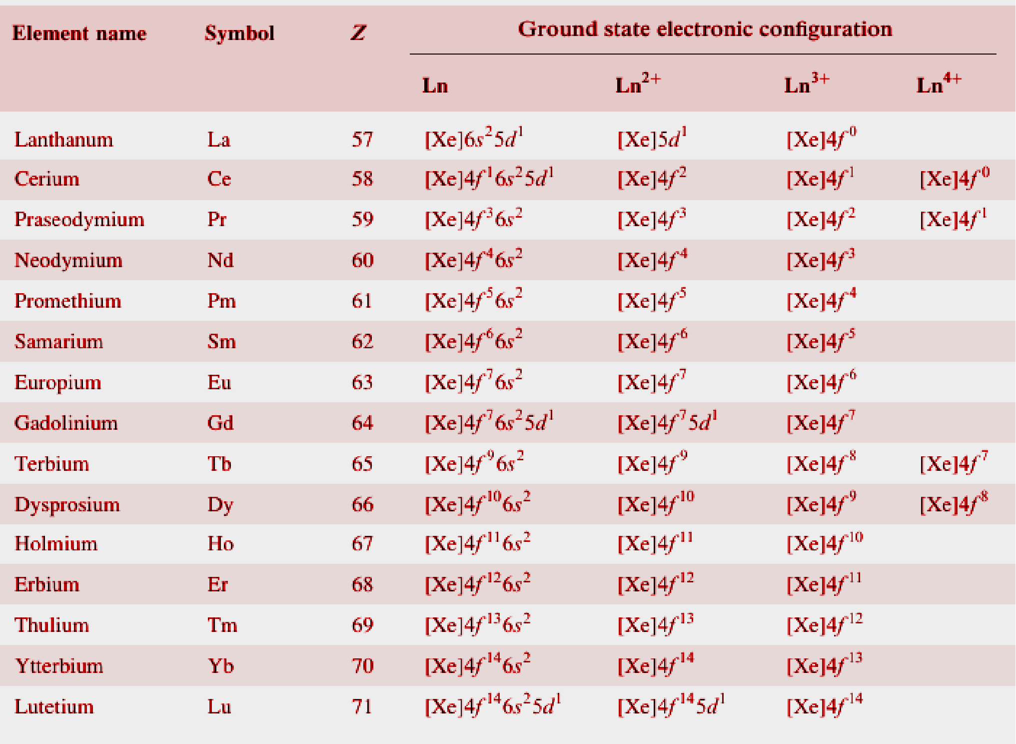
The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium). Because lanthanum closely resembles the lanthanoids, it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used. Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series. The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series. They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements. The chemistry of the actinoids is, on the other hand, much more complicated. The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study.

GENERAL CHARACTERISTICS OF F-BLOCK ELEMENTS

1. ***Electronic configuration***

In lanthanoids

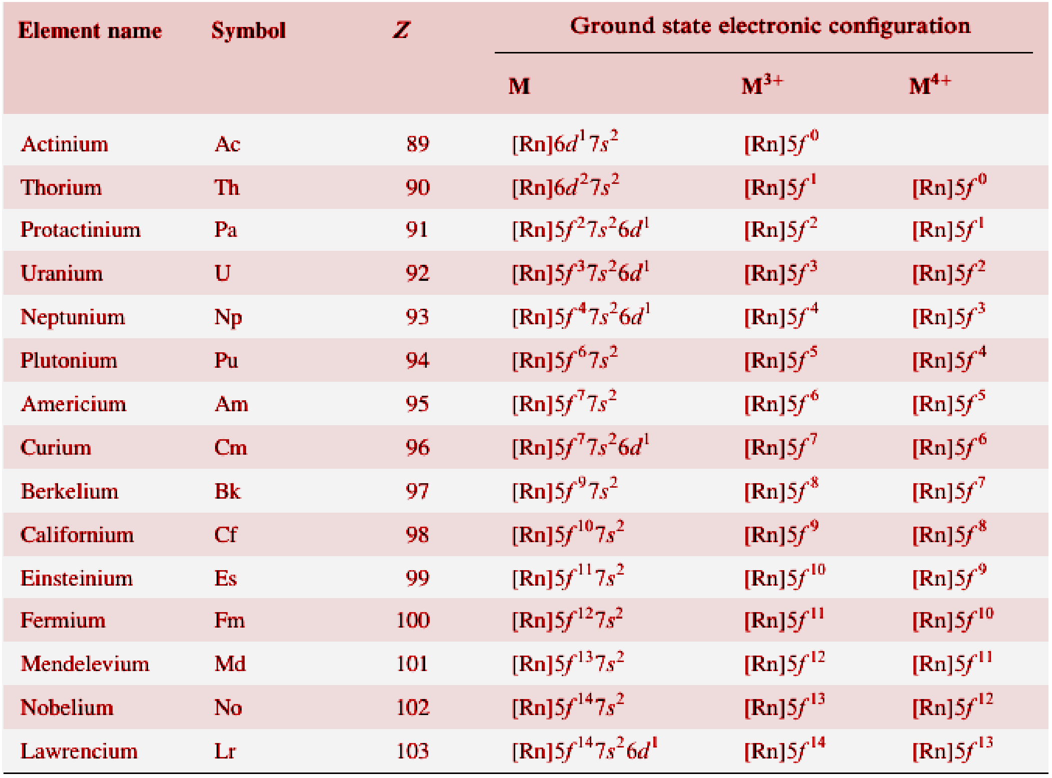
In case of *lanthanoids*, it may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level. However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form 4f n (n = 1 to 14 with increasing atomic number).



Element name	Symbol	Z	Ground state electronic configuration			
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}
Lanthanum	La	57	[Xe]$6s^2 5d^1$	[Xe]$5d^1$	[Xe]$4f^0$	
Cerium	Ce	58	[Xe]$4f^1 6s^2 5d^1$	[Xe]$4f^2$	[Xe]$4f^1$	[Xe]$4f^0$
Praseodymium	Pr	59	[Xe]$4f^3 6s^2$	[Xe]$4f^3$	[Xe]$4f^2$	[Xe]$4f^1$
Neodymium	Nd	60	[Xe]$4f^4 6s^2$	[Xe]$4f^4$	[Xe]$4f^3$	
Promethium	Pm	61	[Xe]$4f^5 6s^2$	[Xe]$4f^5$	[Xe]$4f^4$	
Samarium	Sm	62	[Xe]$4f^6 6s^2$	[Xe]$4f^6$	[Xe]$4f^5$	
Europium	Eu	63	[Xe]$4f^7 6s^2$	[Xe]$4f^7$	[Xe]$4f^6$	
Gadolinium	Gd	64	[Xe]$4f^7 6s^2 5d^1$	[Xe]$4f^7 5d^1$	[Xe]$4f^7$	
Terbium	Tb	65	[Xe]$4f^9 6s^2$	[Xe]$4f^9$	[Xe]$4f^8$	[Xe]$4f^7$
Dysprosium	Dy	66	[Xe]$4f^{10} 6s^2$	[Xe]$4f^{10}$	[Xe]$4f^9$	[Xe]$4f^8$
Holmium	Ho	67	[Xe]$4f^{11} 6s^2$	[Xe]$4f^{11}$	[Xe]$4f^{10}$	
Erbium	Er	68	[Xe]$4f^{12} 6s^2$	[Xe]$4f^{12}$	[Xe]$4f^{11}$	
Thulium	Tm	69	[Xe]$4f^{13} 6s^2$	[Xe]$4f^{13}$	[Xe]$4f^{12}$	
Ytterbium	Yb	70	[Xe]$4f^{14} 6s^2$	[Xe]$4f^{14}$	[Xe]$4f^{13}$	
Lutetium	Lu	71	[Xe]$4f^{14} 6s^2 5d^1$	[Xe]$4f^{14} 5d^1$	[Xe]$4f^{14}$	

In actinoids

All the *actinoids* are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are $[Rn]5f^7 7s^2$ and $[Rn]5f^7 6d^1 7s^2$. Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.



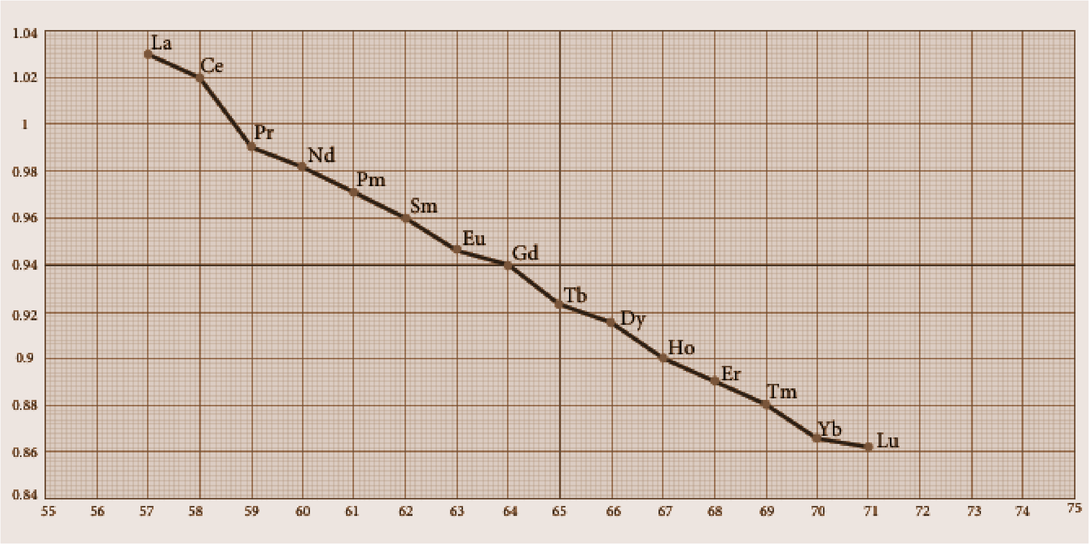
Element name	Symbol	Z	Ground state electronic configuration		
			M	M^{3+}	M^{4+}
Actinium	Ac	89	$[Rn]6d^1 7s^2$	$[Rn]5f^0$	
Thorium	Th	90	$[Rn]6d^2 7s^2$	$[Rn]5f^1$	$[Rn]5f^0$
Protactinium	Pa	91	$[Rn]5f^2 7s^2 6d^1$	$[Rn]5f^2$	$[Rn]5f^1$
Uranium	U	92	$[Rn]5f^3 7s^2 6d^1$	$[Rn]5f^3$	$[Rn]5f^2$
Neptunium	Np	93	$[Rn]5f^4 7s^2 6d^1$	$[Rn]5f^4$	$[Rn]5f^3$
Plutonium	Pu	94	$[Rn]5f^6 7s^2$	$[Rn]5f^5$	$[Rn]5f^4$
Americium	Am	95	$[Rn]5f^7 7s^2$	$[Rn]5f^6$	$[Rn]5f^5$
Curium	Cm	96	$[Rn]5f^7 7s^2 6d^1$	$[Rn]5f^7$	$[Rn]5f^6$
Berkelium	Bk	97	$[Rn]5f^9 7s^2$	$[Rn]5f^8$	$[Rn]5f^7$
Californium	Cf	98	$[Rn]5f^{10} 7s^2$	$[Rn]5f^9$	$[Rn]5f^8$
Einsteinium	Es	99	$[Rn]5f^{11} 7s^2$	$[Rn]5f^{10}$	$[Rn]5f^9$
Fermium	Fm	100	$[Rn]5f^{12} 7s^2$	$[Rn]5f^{11}$	$[Rn]5f^{10}$
Mendelevium	Md	101	$[Rn]5f^{13} 7s^2$	$[Rn]5f^{12}$	$[Rn]5f^{11}$
Nobelium	No	102	$[Rn]5f^{14} 7s^2$	$[Rn]5f^{13}$	$[Rn]5f^{12}$
Lawrencium	Lr	103	$[Rn]5f^{14} 7s^2 6d^1$	$[Rn]5f^{14}$	$[Rn]5f^{13}$

2. *Atomic and ionic sizes*

In lanthanoids

The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the lanthanoids. It has far reaching consequences in the chemistry of the third transition series of the elements. The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M^{3+} ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell. However, the shielding of one 4f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is a fairly regular decrease in the sizes with increasing atomic number.

The cumulative effect of the contraction of the lanthanoid series, known as lanthanoid contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.



Variation in atomic size of lanthanoids

In actinoids

The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

3. ***<u>Oxidation states</u>***

In lanthanoids

In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained. This irregularity (as in ionisation enthalpies) arises mainly from the extra stability of empty, half-filled or filled f subshell. Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The Eo value for Ce^{4+}/ Ce^{3+} is + 1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent. Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2 . Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion. However, Eu^{2+} is a strong reducing agent changing to the common +3 state. Similarly Yb^{2+} which has f^{14} configuration is a reductant. Tb^{IV} has half-filled f-orbitals and is an oxidant. The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

In actinoids

There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The actinoids show in general +3 oxidation state. The elements in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements. The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

4. ***Some other general characteristics***

In lanthanoids

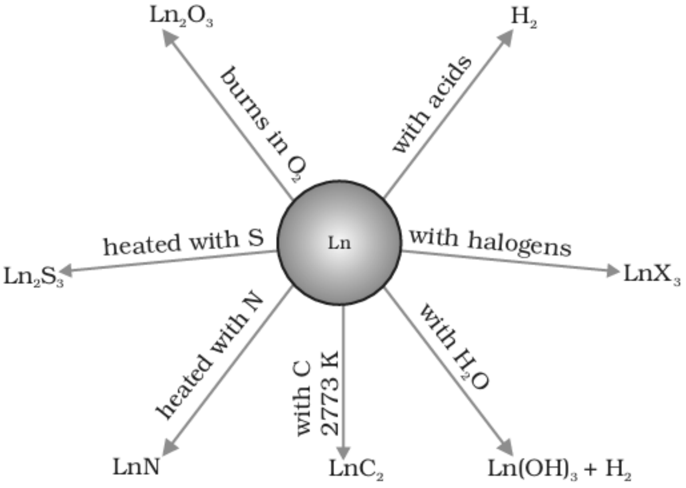
- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number, samarium being steel hard.
- Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.
- They have a typical metallic structure and are good conductors of heat and electricity.
- Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence

of f electrons. Neither La^{3+} nor Lu^{3+} ion shows any colour but the rest do so.

- ➢ However, absorption bands are narrow, probably because of the excitation within f level.
- ➢ The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.
- ➢ The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium. A detailed discussion of the variation of the third ionisation enthalpies indicates that the exchange enthalpy considerations (as in 3d orbitals of the first transition series), appear to impart a certain degree of stability to empty, half-filled and completely filled orbitals f level. This is indicated from the abnormally low value of the third ionisation enthalpy of lanthanum, gadolinium and lutetium.
- ➢ In their chemical behaviour, in general, the earlier members of the series are quite reactive, similar to calcium but, with increasing atomic number, they behave more like aluminium.
- ➢ Values for E_o for the half-reaction:

  $$Ln^{3+}_{(aq)} + 3e^- \rightarrow Ln_{(s)}$$

  are in the range of –2.2 to –2.4 V except for Eu for which the value is –2.0 V. This is, of course, a small variation.
- ➢ The best single use of the lanthanoids is for the production of alloy steels for plates and pipes. A well known alloy is mischmetall which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of mischmetall is used in Mg-based alloy to produce bullets, shells and lighter flint. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some individual Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.



Chemical reactions of lanthanoids

In actinoids

- The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.
- The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.
- The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5f electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.
- It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will

penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

BASIC DIFFERENCES BETWEEN LANTHANOIDS AND ACTINOIDS

S.No.	Lanthanoids	Actinoids
1.	Differentiating electron enters in 4f orbital	Differentiating electron enters in 5f orbital
2.	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3.	They show less tendency to form complexes	They show greater tendency to form complexes
4.	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For example, U^{3+} (red), U^{4+} (green) , UO_2^{2+}(yellow)
5.	They do not form oxo cations	They do form oxo cations such as UO_2^{2+}, NpO_2^{2+}, etc.
6.	Besides +3 oxidation states, lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states, actinoids show higher oxidation states such as +4, +5, +6 and +7.

SEPARATION METHODS OF LANTHANOIDS AND ACTINOIDS

1. ***Ion exchange chromatography***

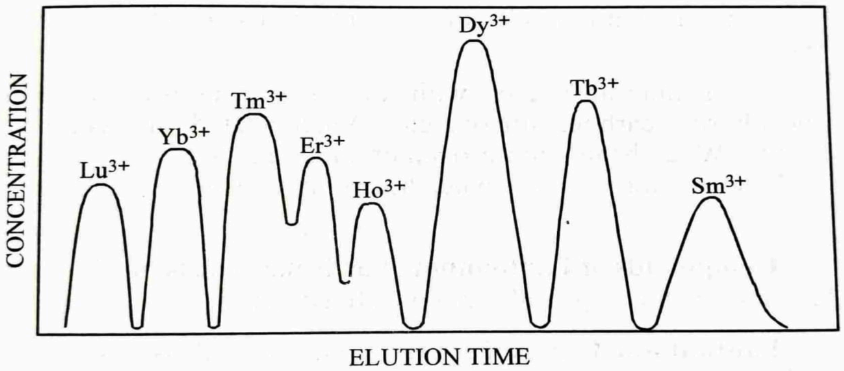
This is the most important, the most rapid and most effective general method for the separation and purification of the lanthanides. A solution of lanthanide ions is run down a column of synthetic ion-exchange resin such as Dowex-50. This is a sulphonated polystyrene and contains the functional groups $-SO_3H$. The Ln^{3+} ions are absorbed onto the resin and replace the hydrogen atom on $-SO_3H$.

$$Ln^{3+}_{(aq)} + 3H(resin)_{(s)} \rightleftharpoons Ln(resin)_{3(s)} + 3H^{+}_{(aq)}$$

The H^+ ions produced are washed through the column. Then the metal ions are eluted, that is are washed off the column in a selective manner. The eluting agent is a complexing agent, for example a buffered solution of citric acid/ammonium citrate, or a dilute solution of $(NH_4)_3(H.EDTA)$ at pH 8. Consider the citrate case. An equilibrium is set up:

$$Ln(resin)3 + 3H^+ + (citrate)^{3-} \rightleftharpoons 3H(resin) + Ln(citrate)$$

As the citrate solution flows down the column, Ln^{3+} ions are removed from the resin and form the citrate complex. A little lower down the column the Ln^{3+} ions go back onto the resin. As the citrate solution runs down the column the metal ions form complexes alternately with the resin and the citrate solution many times. The metal ion gradually travels down the column, and eventually passes out of the bottom of the column as the citrate complex. The smaller lanthanide ions such as Lu^{3+} form stronger complexes with the citrate ions than do the larger ions like La^{3+}. Thus the smaller and heavier ions spend more time in solution, and less time on the column, and are thus eluted from the column first. The different metal ions present separate into bands which pass down the column. The progress of the bands may be followed spectroscopically by atomic fluorescence. The solution leaving the column is collected by means of an automatic fraction collector in separate containers. By this means the individual elements can be separated. The metals may be precipitated as insoluble oxalates, and then heated to give the oxides.



Separation of lanthanide salts by ion-exchange chromatography

The chromatographic process is analogous to carrying out many separations or many crystallizations, but the separation is carried out on a single column. By using a long ion-exchange column the elements may be obtained 99.9% pure with one pass.

2. ***Solvent extraction method***

The heavier Ln^{3+} ions are more soluble in tri-n-butylphosphate than are the lighter Ln^{3+} ions. Their solubilities in water and ionic solvents, however, are reversed. The ratios of the partition coefficients of $La(NO_3)_3$ and $Gd(NO_3)_3$ between a solution of the metal ions in strong HNO_3 and tri-n-butylphosphate is 1 : 1.06. This difference is quite small, but by using a continuous counter-current apparatus a very large number of partitions can be performed automatically. This is much less tedious than performing 10,000 or 20,000 crystallizations. Kilogram quantities of 95% pure Gd have been obtained by this method. The technique was originally developed in the early days of atomic energy to separate and identify the lanthanide elements produced by fission of uranium.

CHEMISTRY OF THORIUM AND URANIUM

THORIUM

Thorium was discovered in 1882 in a Norwegian mineral and was named after the Scandinavian god, Thorium. Its radioactive character was established by Madam Curie and Professor Schmidt in 1898.

Occurrence : Thorium constitutes nearly 0.0012 per cent of earth's crust and is about three times more abundant than uranium. The important minerals of thorium are: thorianite (thorium oxide), thorite (thorium silicate), cheralite (silicates and phosphates of Th, Ca and Ce) and monazitę (phosphates of Ce, Y, La and Th).

Monazite sand constitutes the most important source of thorium. This is found largely in Brazil, India, Sri Lanka, U.S.A., Canada and Australia. In India, deposits of monazite sand are found on the sea coast of Kerala state.

Extraction of Thorium from Monazite : Indian monazite sand is of topmost grade in the world. Its chemical composition is as follows:

$$ThO_2 = 9.4\%,\ CeO_2 = 28.5\%,\ U_3O_8 = 0.37\% \text{ and } P_2O_5 = 25.9\%$$

Owing to the presence of rare earth impurities which in chemical properties resemble thorium, the extraction of thorium becomes quite difficult. The process of extraction involves the following steps.

1. Concentration and formation of thorium dioxide : The ore is freed from a major chunk of silicious impurities either by mechanical washing or by magnetic separation and is then treated with concentrated sulphuric acid in cast iron pans.. The resultant pasty mass is added to cold water, stirred thoroughly and then allowed to stand. Impurities such as silica and unattacked minerals settle down. The supernatant liquid which contains phosphates of thorium and rare earth elements, is syphoned off. The acid solution is partially neutralised by ammonia or alkali hydroxide or magnesia mixture when thorium, being more electropositive than the rare earths, gets precipitated as thorium phosphate alongwith comparatively smaller amounts of phosphates of rare earths. The precipitate is removed, dissolved in a minimum quantity of acid and then neutralised as before to again precipitate the phosphate of thorium. The process is repeated several times and in this way the amount of phosphates of rare earths is reduced considerably.

The precipitate of thorium phosphate obtained as above is dissolved in nitric acid (about 6M) and treated with potassium iodate in the presence of hydrogen peroxide when thorium gets precipitated as thorium iodate. The rare earth phosphates remain in solution.

The precipitate of thorium iodate is dissolved in hydrochloric acid and reprecipitated as thorium oxalate to eliminate zirconium.

The thorium oxalate is then ignited to get thorium dioxide, ThO_2.

2. Preparation of thorium metal : The preparation of thorium from thorium dioxide is rather difficult because the metal is highly reactive in its molten state. The various methods employed for the recovery of the metal are briefly discussed below.

1. Thorium dioxide, obtained as above, is heated at 950℃ with calcium in a steel bomb using calcium chloride as a flux.

$$ThO_2 + 2Ca \rightarrow 2CaO + Th$$

2. In another method, thorium dioxide is first converted into thorium chloride or thorium fluoride by heating with carbon in a current of chlorine or fluorine.

$$ThO_2 + 2C + 2Cl_2 \rightarrow ThCl_4 + 2CO$$

$$ThO_2 + 2C + 2F_2 \rightarrow ThF_4 + 2CO$$

The thorium chloride or fluoride is then reduced with electropositive metals such as Na, Ca and Mg.

$$ThCl_4 + 4Na \rightarrow Th + 4NaCl$$

$$ThF_4 + 2Ca \rightarrow Th + 2CaF_2$$

Zinc chloride is used as a flux during reduction with calcium.

3. Electrolytic method : In this method, metallic thorium is obtained by electrolysing a fused mixture of ThF_4-KC1-NaCl employing a lead cathode and a graphite anode. Electrolysis is carried out at a temperature of 800℃ employing a current density of 70 amperes per kilogram of the electrolyte. Thorium is deposited as a powder on the cathode and is scraped off from time to time. The powder is washed with dilute nitric acid, dried and converted into ingots.

4. Pure thorium can also be obtained by heating the crude metal powder in iodine vapours to form volatile thorium iodide which is isolated and thermally decomposed on an incandescent filament at about 1100 - 1200℃ to yield pure thorium.

$$Th \text{ (crude)} + 2I_2 \rightarrow ThI_4$$

$$ThI_4 \rightarrow Th \text{ (pure)} + 2I_2$$

Properties : Thorium has a high melting point of 1750℃. It exists in amorphous as well as crystalline states. At very low temperatures it has super conductivity though at ordinary temperatures, the conductivity is very low.

Thorium undergoes transformation from a face centred cubic structure to a body centred cubic at about 1400℃. It forms many intermetallic compounds of the type $ThMn_2$, $ThMn_{1.2}$, Th_7Co_3, Th_7Fe_3, ThNi, Th_2Cu, $ThCu_2$, etc.

When heated in air, it burns brilliantly with emission of sparks forming the dioxide.

$$Th + O_2 \rightarrow ThO_2$$

The metal is fairly strongly electropositive in character. It resembles lanthanide metals in its chemical reactivity. Thus, when exposed to air, it gets tarnished. It is attacked by oxygen at 250℃, by nitrogen at 800℃ and by water at its boiling point.

It combines with hydrogen vigorously when heated, forming thorium hydride.

$$Th + 2H_2 \rightarrow ThH_4$$

It is attacked only slowly by dilute hydrofluoric, nitric and sulphuric acids but not by dilute hydrochloric acid. It is, however, attacked slowly by concentrated hydrochloric acid. Hot and concentrated hydrochloric acid gives a black residue approximating to the composition $ThO_{1.3}Cl_{0.3}H_{1.3}$. It is rendered passive when placed in strong nitric acid. Thorium is radioactive and yields a series of disintegration products (Thorium series).

Uses :

1. The most important and strategic use of thorium is in the manufacture of fuel rods for atomic reactors.
2. Its oxide, ThO_2, finds wide application in the preparation of incandescent gas mantles. These mantles consist of a mixture of 99 per cent thorium oxide and 1 per cent cerium oxide. The small amount of cerium oxide is essential because otherwise thorium oxide itself gives only poor light.
3. Thorium salts find wide application as medicines in the treatment of cancer.
4. Thorium nitrate is used for the titration of fluorides using methyl red as the indicator.

URANIUM

Uranium was discovered by Klaproth in 1789 in a specimen of pitchblende. Metallic uranium was prepared in 1840 by Peligot by the reduction of anhydrous uranium tetrachloride with potassium in a closed platinum crucible.

Occurrence : Uranium is widely distributed in a variety of rocks as well as in sea water. The latter contains about 2 x 10^{-6} g of uranium per litre. Important ores of uranium are pitchblende (or uranite) and carnotite. Other ores are: fergusonite, samarskite, autosite and uronophane.

Extraction of Uranium : The first step in the extraction of uranium is the isolation of pure uranium oxide from the ores.

1. Isolation of Uranium Oxide, U_3O_8, from Uranium Ores :

a) Uranium Oxide from Pitchblende : Uranium oxide from pitchblende ore is obtained by two processes.

First Process : The first process involves the following steps:

1. The ore is crushed to a fine powder and concentrated by gravity process.
2. The concentrated ore is roasted in a reverberatory furnace in the presence of excess air to remove sulphur, arsenic and other volatile impurities

3. The roasted ore which contains U_3O_8 is mixed with sodium carbonate and sodium nitrate and the whole mass is heated to fusion resulting in the formation of sodium uranate.

$$U_3O_8 + 3Na_2CO_3 + 1/2O_2 \text{ (from NaNO3)} \rightarrow 3Na_2UO_4 + 3CO_2$$

4. The fused mass is extracted with hot water and the solution is treated with an excess of ammonium carbonate when impurities such as aluminium, nickel, cobalt and manganese get precipitated as basic carbonates while uranium remains in solution as ammonium uranyl carbonate, $(NH_4)_4UO_2(CO_3)_3$.

5. The solution is neutralised with dilute sulphuric acid and evaporated to dryness when ammonium diuranate, $(NH_4)_2U_2O_7$, is obtained as a heavy yellow precipitate. On calcination, the diuranate yields uranium oxide, U_3O_8.

$$3(NH_4)_2U_2O_7 \rightarrow 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$

Alternatively, the roasted ore (after step 2) is heated with dilute sulphuric acid for about 16-24 hours in the presence of an oxidising agent, such as MnO_2. This oxidises the U_3O_8 present in the roasted ore to soluble uranyl sulphate, UO_2SO_4. When ammonium carbonate is added to the solution, ammonium uranyl carbonate, $(NH_4)_2UO_2(CO_3)_3$, is crystallised out which on ignition gives U_3O_8.

$$UO_2SO_4 + 3(NH_4)_2CO_3 \rightarrow (NH_4)_4UO_2(CO_3)_3 + (NH_4)_2SO_4$$

$$3(NH_4)_4UO_2(CO_3)_3 \rightarrow U_3O_8 + 9CO_2 + 12NH_3 + 6H_2O + 12O_2$$

Second Process : Klaproth's Process

In this process, the pitchblende ore is treated with nitric acid or aqua regia and the resulting solution is evaporated to dryness. The dry mass is then extracted with hydrochloric acid. The filtrate is then treated with nitric acid and neutralised with ammonium carbonate. On boiling this solution, uranium, zinc and cobalt get precipitated as oxides. The precipitate is again treated with hydrochloric acid when the oxides of zinc and cobalt get dissolved leaving behind the oxide of uranium which is insoluble in HCl.

b. Uranium Oxide from Carnotite Ore : Uranium oxide from the carnotite ore is obtained as follows:

The powdered mineral is fused with potassium bisulphate and the cold mass is extracted with water. The solution is subjected to crystallisation when crystals of double sulphates of vanadium and uranium are obtained. The crystals are treated first with zinc and sulphuric acid and then with ammonia and ammonium carbonate when all the vanadium present gets completely precipitated as carbonate which is removed by filtration. The filtrate containing ammonium diuranate is evaporated to dryness and then ignited to get the black oxide of uranium, U_3O_8.

2. Production of the Metal from the Oxide

From the black oxide of uranium, U_3O_8, the metal is obtained as follows.

1. The oxide is heated with charcoal or hydrogen when it is reduced to the uranium dioxide, UO_2. It cannot be reduced further to uranium on heating with hydrogen even at such a high temperature as 2500°C.

2. The dioxide is heated with chlorine when yellow crystalline uranyl chloride, UO_2Cl_2, is obtained.

$$UO_2 + Cl_2 \rightarrow UO_2Cl_2 \text{ (Uranyl chloride)}$$

3. Uranyl chloride is heated with carbon while a stream of chlorine continues to pass. This results in the formation of uranium tetrachloride, UCl_4, which sublimes readily.

$$UO_2Cl_2 + Cl_2 \rightarrow UCl_4 + O_2$$

4. Finally, the uranium tetrachloride is heated with sodium to get metallic uranium.

$$UCl_4 + 4Na \rightarrow U + 4NaCl$$

Alternatively and more conveniently, uranium dioxide, UO_2, obtained as above is treated with hydrofluoric acid to get uranium tetrafluoride, UF_4, which is reduced by magnesium to get the metal.

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O2Mg$$

$$UF_4 + 2Mg \rightarrow U + 2MgF_2$$

Yet another method is to reduce the uranium dioxide, UO_2, by calcium hydride at 980°C or by aluminium (Goldschmidt process).

$$3UO_2 + 4A1 \rightarrow 3U + 2Al_2O_3$$

Physical properties : Uranium has a silvery-white luster. It melts at 1132°C and is malleable and ductile. Its specific gravity is 19.05. It forms a wide range of intermetallic compounds such as U_6Mn, U_6Ni, USn_3, etc. It has several isotopes of which ^{235}U and ^{233}U are important for nuclear energy.

Chemical properties : Chemically, uranium is highly reactive. It easily gets tarnished in moist air to form the oxide.

It burns in oxygen at 170°C with a brilliant flame forming U_3O_8.

It reacts with steam between 150-250° C to form a mixture of oxide and hydride.

$$7U + 6H_2O \rightarrow 3UO_2 + 4UH_3$$

It dissolves readily in dilute hydrochloric acid. In nitric acid it dissolves at a moderate rate while in sulphuric acid and hydrofluoric acid, the rate of dissolution is very slow.

It does not react with alkalies.

It combines directly with halogens. It burns in fluorine forming green volatile tetrafluoride. It catches fire in chlorine at 180°C and in bromine at 240°C forming the corresponding halides. It reacts with iodine vapours at 260° C to form the tetraiodide, UI_4.

It reacts with hydrogen at 600° C under pressure to form the well defined hydride, UH_3.

Uses :

1. The most important use of uranium is in the production of nuclear energy by the process of nuclear fission.
2. Uranium salts find use in textile industry, ceramic industry as well as in medicine.

COMPOUNDS OF F-BLOCK ELEMENTS

1. *Ceric ammonium sulphate* $Ce(NH_4)_4(SO_4)_4 . 2H_2O$

Preparation :

$$CeO_2 + 2H_2SO_4 \rightarrow Ce(SO_4)_2 + 2H_2$$

$$Ce(SO_4)_2 + 2(NH_4)_2(SO_4)_2 + 2H_2O \rightarrow Ce(NH_4)_4(SO_4)_4 . 2H_2O$$

Properties :

- Orange coloured crystalline solid
- Strong oxidizing agent

Uses :

- Used in analytical chemistry (redox titrations, volumetric analysis)
- Used as an oxidizing agent
- Used in industrial process such as chlorine production

Advantages :

- The solution of ceric ammonium sulphate is stable for long periods of time, unaffected by light or heat.

- It is versatile such that it can be used for the titration of reducing agents in solutions with high concentration of HCl, unlike $KMnO_4$.

2. ***Thorium dioxide** ThO_2*

Thorium forms only one stable oxide, viz., the dioxide, ThO_2. Its high heat of formation (-1226.5 kJ) speaks for its high stability.

It exists in amorphous as well as crystalline forms. The amorphous form is obtained by heating the metal in air or by igniting its nitrate. The crystalline form is obtained by heating the amorphous oxide with potassium orthophosphate.

Preparation :

This may also be obtained by fusing thorium fluoride with sodium carbonate.

$$ThF_4 + 2Na_2CO_3 \rightarrow ThO_2 + 2CO_2 + 4NaF$$

ThO_2 can also be obtained from monazite sand.

Properties :

Thorium dioxide melts at 3000°C and boils at 4400°C. It is slightly soluble in water and dilute acids but readily soluble in hot concentrated sulphuric acid. It is highly refractory.

When heated strongly with boron and carbon, it forms the boride and the carbide, respectively.

Uses :

Thoria (ThO_2) is used mainly in the preparation of gas mantles. It is also used as a refractory material as well as a catalyst in many organic reactions. It finds use in welding operations, in X-ray machines and also in medicines.

3. ***Uranyl acetate** UO2(C2H3O2)2.2H2O*

Preparation :

It is prepared by dissolving uranium trioxide in acetic acid.

Properties :

It is a yellow crystalline solid, soluble in water.

Uses :

It is used as a reagent for the estimation of phosphate as it gives yellow precipitate of uranyl ammonium phosphate, $UO_2(NH_4)PO_4$ when mixed with a phosphate solution. The end point is detected by using potassium ferrocyanide as the external indicator. It is also used for the detection of sodium which is precipitated as its double salt with zinc or magnesium having the formula $NaMg[UO_2(C_2H_3O_2)_3]_3.9H_2O$.

UNIT - 5

INORGANIC POLYMERS

Inorganic polymers are giant molecules composed of atoms other than carbon. These atoms are linked together mainly by covalent bonds. Some common examples of inorganic polymers are polyphosphazines, polyphosphates, polymeric sulphur nitride, polycarboranes, silicones and a majority of silicate minerals.

GENERAL PROPERTIES OF INORGANIC POLYMERS

- With a few exceptions (such as sulphur), inorganic polymers do not burn. They only soften or melt at high temperatures.
- Inorganic polymers which have cross-linked structures with a high density of covalent bonds are generally stiffer and harder than the organic polymers.
- The chain segments between cross links in polymers having cross-linked structures are usually short and stiff. Consequently, these structures are not flexible enough to permit intercalation of solvent molecules. As a result there are very few inorganic polymers which swell reversibly imbibing solvent molecules.
- Most of the inorganic polymers are built up of highly polar repeat units. These polymers would, therefore, dissolve only in polar solvents. Most of these polymers, however, react with the solvents. There are thus only a few inorganic polymers which actually dissolve in appropriate solvents.
- Inorganic polymers are generally much less ductile than the organic polymers. Thus, while organic polymers such as polyethylene can extend by about 20 per cent or more before fracture, inorganic polymers break even when extended by about 10 per cent.
- Inorganic polymers can usually be obtained in pure crystalline as well as in pure amorphous forms. Organic polymers, on the other hand, have structures which are partly crystalline and partly amorphous.
- Inorganic polymers, in general, are stronger, harder and more brittle than the organic polymers.

Classification Of Inorganic Polymers Based On The Element In The Backbone

There is a very wide variety of inorganic polymers, important amongst which are :

I. Phosphorus-based Polymers

II. Sulphur-based Polymers

III. Boron-based Polymers

IV. Silicon-based Polymers and

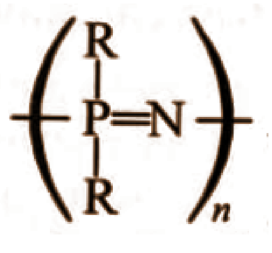
V. Coordination Polymers

PHOSPHORUS BASED POLYMERS

The phosphorus-based polymers can be divided into two categories, viz., the chain polymers and the network polymers, depending upon the type of linkage involved between their atoms. Polyphosphazines and polyphosphonitrilic chloride fall under the category of phosphorus based chain polymers.

1. ***Polyphosphazines***

   These polymers have the general structure

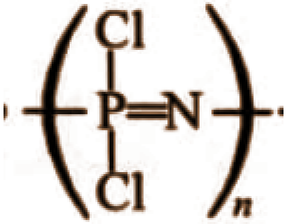


$$\left(-\overset{\displaystyle R}{\underset{\displaystyle R}{\overset{|}{\underset{|}{P}}}}=N- \right)_n$$

   Where R usually stands for Cl, OCH_3 and OC_2H_5.

   The polymers with R with Cl are known as polyphosphonitrilic chlorides and those with R as OCH_3 and OC_2H_5 are, respectively known as polydimethoxy and polydiethoxyphosphazines.

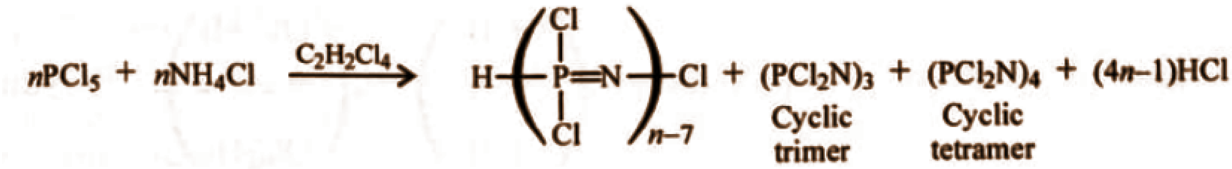
2. ***Polyphosphonitrilic chlorides***



$$\left(-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}- \right)_n$$

These polymers constitute what is known as inorganic rubber. They exhibit high elasticity and can be stretched several-fold with almost complete recovery. However, they undergo degradation under normal atmospheric conditions more rapidly than do the organic rubbers. Hence these polymers do not find much commercial use.

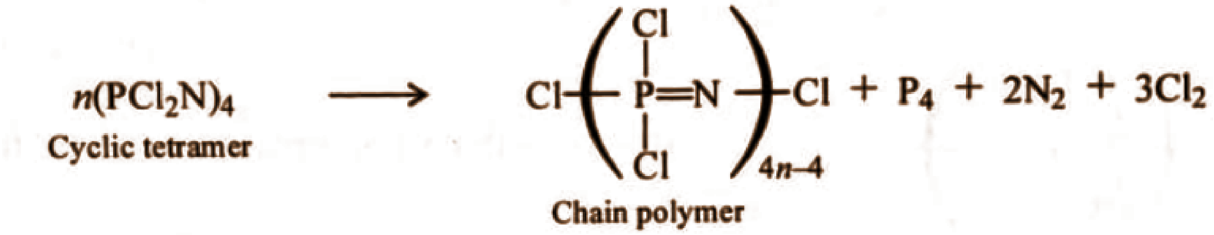
Polyphosphonitrilic chlorides can be prepared as follows :



$$n\mathrm{PCl_5} + n\mathrm{NH_4Cl} \xrightarrow{\mathrm{C_2H_2Cl_4}} \mathrm{H}\left(\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N} \right)_{n-7}\mathrm{Cl} + \underset{\text{Cyclic trimer}}{(\mathrm{PCl_2N})_3} + \underset{\text{Cyclic tetramer}}{(\mathrm{PCl_2N})_4} + (4n-1)\mathrm{HCl}$$

The above reaction yields a mixture of cyclic trimers and tetramers along with a series of linear polymers. The linear polymerisation is terminated by H and Cl atoms.

The cyclic trimer or tetramer, when heated in vacuum at 250℃, changes into a chain polymer.

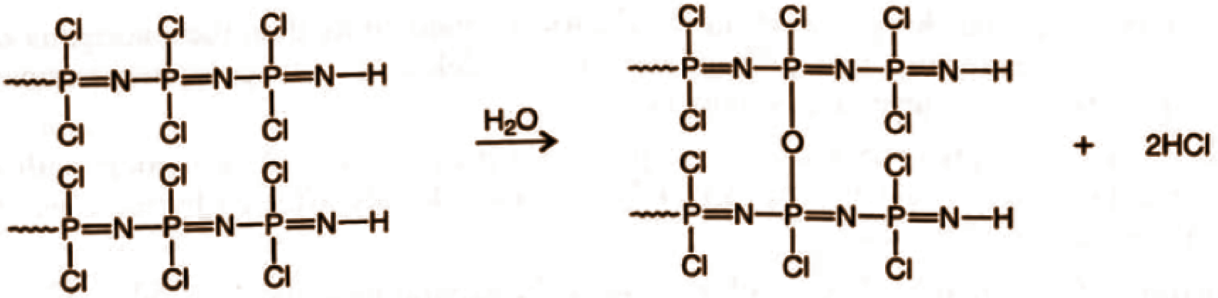


$$\underset{\text{Cyclic tetramer}}{n(\mathrm{PCl_2N})_4} \longrightarrow \underset{\text{Chain polymer}}{\mathrm{Cl}\left(\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N} \right)_{4n-4}\mathrm{Cl}} + \mathrm{P_4} + 2\mathrm{N_2} + 3\mathrm{Cl_2}$$

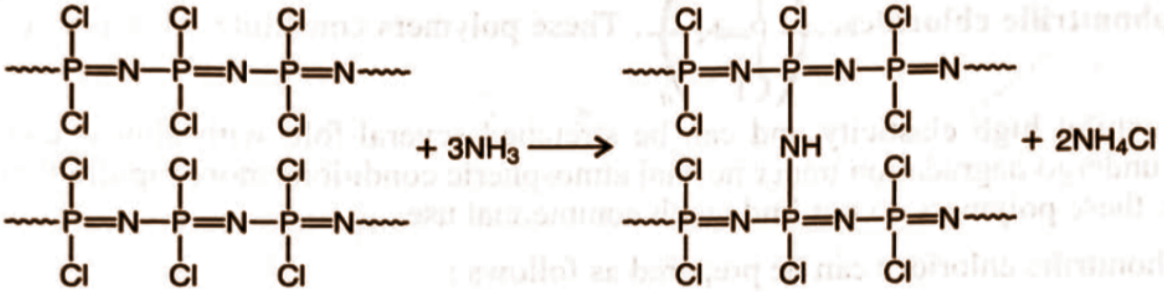
The resulting chain polymer is somewhat cross-linked and hence has limited solubility in inorganic solvents. Polyphosphonitrilic chloride is at least as good an elastomer as vulcanised rubber.

The freshly prepared polyphosphonitrilic chlorides are soluble in chloroform but insoluble in petroleum ether. When the solutions are allowed to stand, the polymers get cross-linked and slowly gel.

When samples of highly elastic inorganic rubber are stored in absence of air, there is no change in their elastic properties. However, storage in air makes the material brittle. This is due to the action of water present in air in forming oxygen bridges between the chains so that there is reduction in average length of chain segments at lattice sites, as shown below.



The Cl atoms of polymerising units of polyphosphonitrilic chloride can be replaced by other substituents such as OCH_3, OC_2H_5, etc. These substituted polyphosphazines are generally chain polymers. But, when polyphosphonitrilic chloride reacts with ammonia it produces cross-linked polymers, as shown below :



Applications of phosphorus based polymers

- The long chain vitreous sodium phosphate polymers are employed in the food processing industry. Their use in this industry is based on the interaction of phosphates with proteins.
- The short chain vitreous phosphate polymers are used for deflocculation of proteins.
- The potassium Kuroll's salt is employed in the manufacture of sausages to prevent water loss.
- The sodium Maddrell's salt is used as a polishing agent in dental surgery.
- The borophosphate glasses are used for manufacturing optical lenses.

SULPHUR BASED POLYMERS

A large number of sulphur-based polymers are now known. These include linear chain polymers as well as network polymers. The most important linear chain polymers are polymeric sulphur and polymeric sulphur nitride. The important network polymers comprise of chalcogenide glasses.

1. ***Polysulfide***

- Sulphur based inorganic polymer with the general formula $(\text{-S-S})_n$ in their backbone.
- It is made up of zig-zag chains of sulphur atoms.
- Preparation

  Addition of elemental sulphur to sulphide solution results in the formation of a polysulfide.

  $$S^{2-} + nS \rightarrow S_{n+1}^{2-}$$
- Properties
  - ➢ Yellow to amber colour
  - ➢ Brittleness increases as chain length increases.
  - ➢ Resistant to many solvents, but undergoes oxidation in the presence of strong oxidizing agents.
  - ➢ Lower elasticity but good chemical resistance.
- Applications
  - ➢ Used as sealants for fuel tanks, aircraft windows and joints.
  - ➢ As vulcanizing agents in rubber industry
  - ➢ Inhibits corrosion by forming protective sulphide layers on metal surfaces.
  - ➢ Used as cathode materials in Li-S batteries
  - ➢ Polysulfide of calcium is used as a fungicide in agriculture
  - ➢ Polysulfides can be added to lubricants to increase resistance against wear and oxidation.

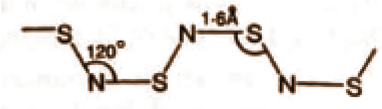
2. ***Polymeric sulfur nitride***

Polymeric sulphur nitride was first prepared in 1910 by Burt by passing vapours of S_4N_4 over silver gauze or silica wool at 100-300°C. In 1973, Labes and coworkers synthesised crystalline polymeric sulphur nitride in the form of bundles of fibres and found that the material possesses metallic conductivity in a direction parallel to the length of the fibre.

Pure $(SN)_n$ can be prepared by passing S_4N_4 vapour over silver wool at 220°C. The gaseous S_2N_2 formed is condensed to solid state by passing through a liquid nitrogen-cooled trap. It is then sublimed into an ice-cooled trap from which it is slowly allowed to warm up to room temperature. The S_2N_2 during this process of slow warming, gets polymerised to $(SN)_n$.

Polymeric sulphur nitride consists of layers of fibres stacked parallel to one another. The polymer shows metallic conductivity and metallic ductility. It is soft and malleable. The polymer is slowly attacked by moisture when exposed to it for several months. It decomposes in vacuum at 140°C to give sulphur and nitrogen.

The structure of the polymer comprises of nearly planar chains of S-N bonds of approximately the same length (1.6 Å). The structure of a portion of the polymer is as shown.



The electrical conductivity of the polymer $(SN)_n$ is in the range of 1200-3700 S cm^{-1} and increases 50-200 times when the temperature is lowered to 4.2 K. It has been found recently that the polymer becomes a superconductor at 0.26 K. The polymer is the first example of a non-metallic superconductor.

SILICON BASED POLYMERS

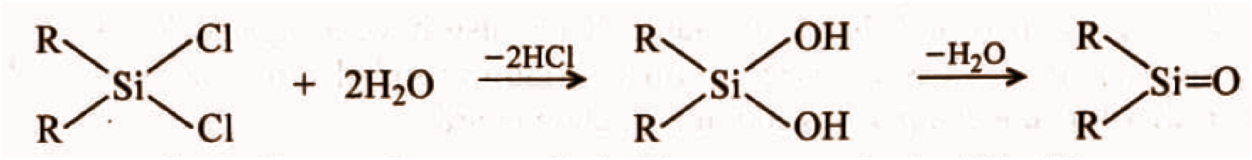
Silicones

Silicon-based polymers constitute the most important class of inorganic polymers. These include organopolysiloxanes, commonly known as silicones.

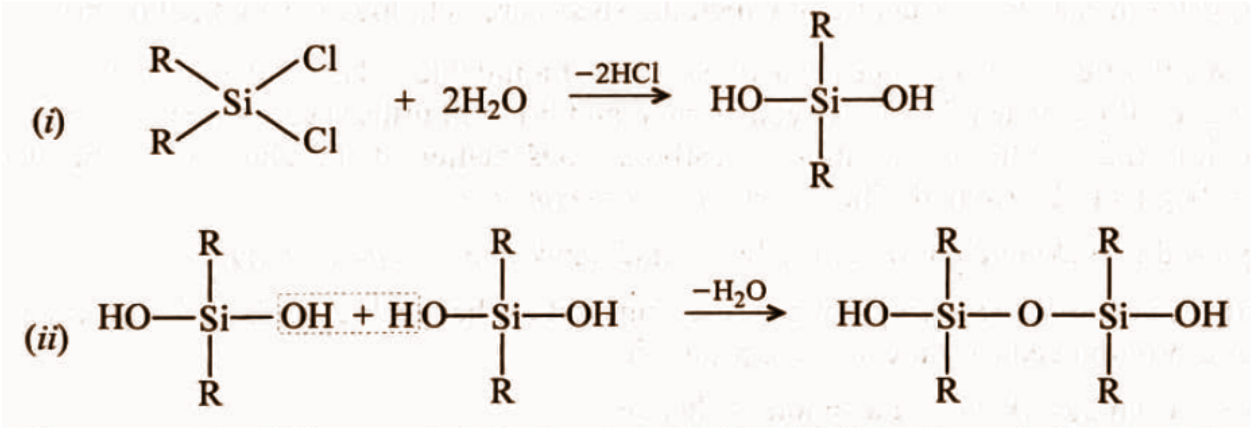
Silicon tetrachloride, when fully hydrolysed, gives silica which has a stable three-dimensional structure.

$$SiCl_4 + 4H_2O \xrightarrow{-4HCl} Si(OH)_4 \xrightarrow{-2H_2O} SiO_2$$

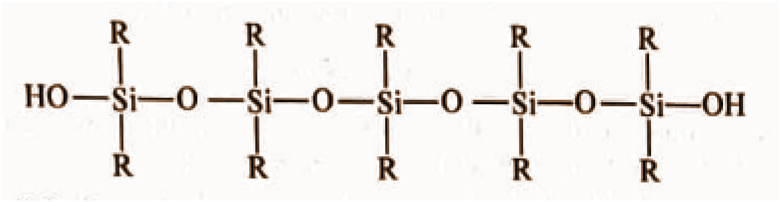
However, when an alkyl substituted chlororsilane (which can be obtained from $SiCl_4$ by Grignard reaction) is subjected to similar hydrolysis, we do not get the alkyl silicon compound according to the following expected reaction :



On the contrary, long chain polymers, called silicones, are obtained in this process. For example, in the case of dialkyl dichlorosilane, the reaction proceeds as follows :

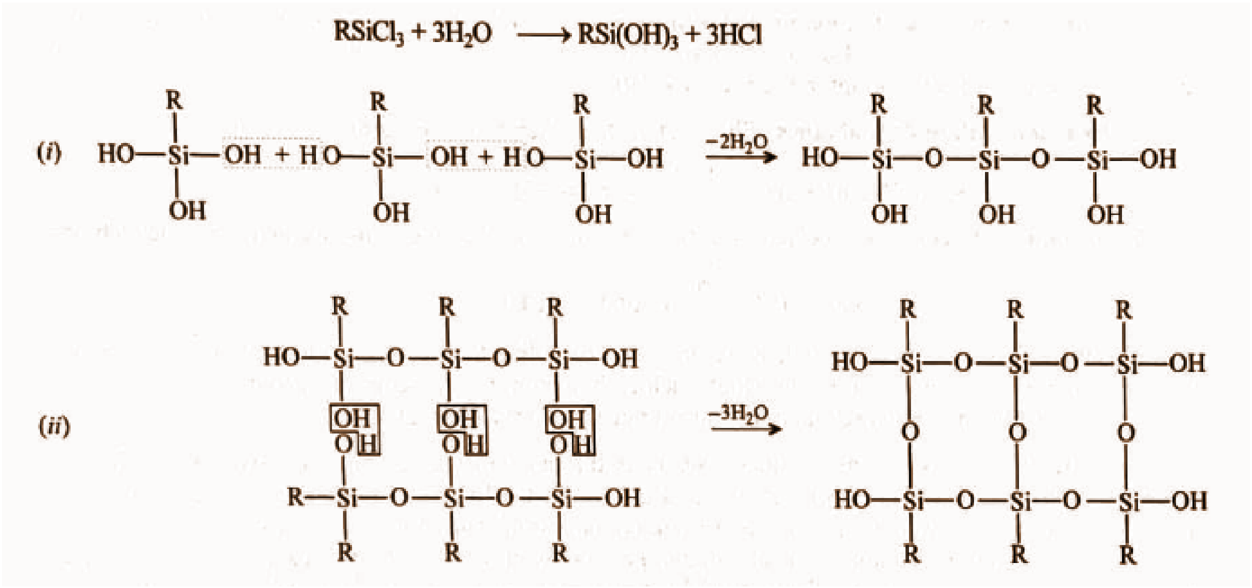


Since an active OH group is left at each end of the chain, polymerisation reaction continues and the length of the chain continues to increase giving a long chain product.



$$HO-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-OH$$

A complex cross-linked polymer is obtained on the hydrolysis of mono alkyl trichlorosilane as shown below.



It is evident that the structure can be extended in two dimensions to any length in any manner.

The silicones are, evidently, organosilicon polymers. It may be noted that unlike carbon atoms which cannot hold more than one hydroxyl group, the silicon atom in the compound RSi(OH)3 can hold three hydroxyl groups. It is this property of silicon that makes the formation of organosilicon polymers possible.

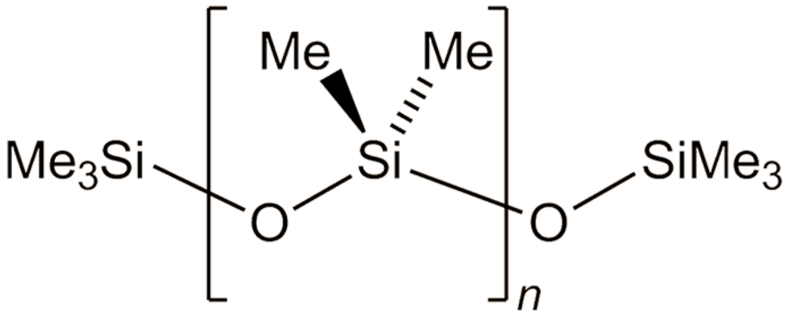
As mentioned above, the organosilicon polymers grow further by reaction with other molecules containing one silicon atom. Thus, straight chain or cross-linked polymers are obtained. Depending upon the length of the chain and the nature of groups attached to the silicon atom, they can be obtained in the form of oils, viscous fluids, resins or even rubber-like solids.

Properties and Uses of Silicones

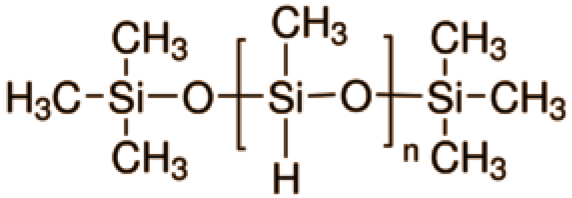
- Silicone oils are highly stable and non-volatile even on heating. They are, therefore, used for high-temperature oil baths, high vacuum pumps, etc. They do not become too viscous on cooling and are, therefore, used for low-temperature lubrication for which purpose hydrocarbon oils, which become too viscous on cooling, cannot be used. They are also used as greases, varnishes and resins which can be applied even at as low a temperature as - 40°C.
- Silicones are also water-repellents and are good insulators. They are, therefore, used for waterproofing and in electrical condensers.

- They are excellent insulators for electric motors and other electric appliances as they can withstand high temperatures.
- The rubber-like silicones retain their plasticity even at low temperatures and resist chemical attack. They are mixed in paints to make them damp-resistant. They are also used for waterproofing and for a variety of other purposes.

Polydimethylsiloxane

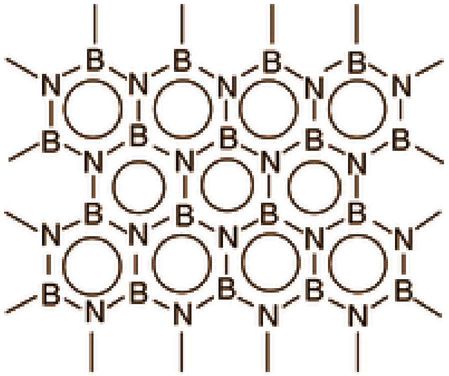


Polymethylhydrosiloxane

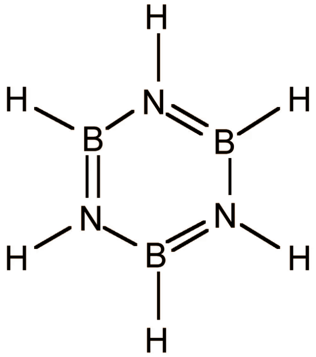


BORON BASED POLYMERS

Borazine polymers



- Borazine polymers are B-N based inorganic polymers derived from borazine ($B_3N_3H_6$). Borazine polymers refer to the polymeric analogues of borazine.



- Polymers arise from ring-opening polymerization, covalent bonding to polymer chains (e.g., via B or N sites with hydroxyl/amino groups), or use as cross-linkers.
- The resulting polymer can either be linear or cross linked.
- The B-N bonds are strong and thermally stable. The B-N bond is analogous to the Si-O bond in silicone backbones but has greater thermal stability.
- All the bonds have partial double bond character due to π-delocalization.
- <u>Properties</u>
  - ➢ Colourless solid
  - ➢ High thermal stability
  - ➢ Resistant to acids, bases and oxidants
  - ➢ Insulating
  - ➢ Hard and brittle (Ceramic like)
- <u>Applications</u>
  - ➢ Borazine polymers act as precursors for boron nitride $(BN)_n$, which is used to produce high temperature ceramic, lubricant and insulating materials.
  - ➢ Boron nitride acts as an excellent insulator with high thermal conductivity.
  - ➢ Used for heat resistant coatings on metals and ceramics.