COORDINATION COMPOUNDS

Why the Study of Coordination Compounds?

- Natural compounds like Chlorophyll, Haemoglobin and Vitamin B_{12} are coordination compounds.
- Chlorophyll is a coordination complex of Mg^{2+}.
- Haemoglobin is a coordination complex of Fe^{2+}.
- Vitamin B_{12} or Cyanocobalamine is a coordination complex of Co^{2+}.
- The platinum complex cisplatin $[Pt(NH_3)_2Cl_2]$ is used as an antitumor agent.
- Coordination compounds are widely applied molecular or addition compounds.
- Applications covers the areas of metallurgy, biochemistry, electrochemistry, water softening, ion exchange, textile dyeing, bacteriology, & analytical chemistry

ADDITION OR MOLECULAR COMPOUNDS

- Two or more stable compounds combined in stoichiometric proportions is called an addition compound.

$$KCl + MgCl_2 + 6H_2O \longrightarrow KCl.MgCl_2.6H_2O \text{ (Carnallite)}$$

- Molecular compounds are of two types:

DOUBLE SALTS

- These are addition compounds which lose their identity when dissolved in water.
- They exist in solid state.
- Their properties are same as that of constituent compounds.
- Eg. Mohr's salt $FeSO_4(NH_4)_2\ SO_4.6H_2O$; Potash alum : $K_2SO_4Al_2(SO_4)_3.24H_2O$
- Eg. Carnallite $KCl.MgCl_2.6H_2O$ dissolved in water, dissociates into K^+, Mg^{2+}, Cl^- and H_2O.
- Aqueous solution of Carnallite answer the tests for K^+, Mg^{2+} and Cl^- ions.

COORDINATION COMPOUNDS

- Addition compounds which retain their identity in solution.
- They exist in solids as well as in solution.
- Eg. $K_4\left[Fe(CN)_6\right] \xrightarrow{\text{Aqueous solution}} 4K^+ + \left[Fe(CN)_6\right]^{4-}$
- $K_4[Fe(CN)_6]$ does not form Fe^{2+} and CN^- ions but forms $[Fe(CN)_6]^{4-}$ ion.
- Aqueous solution does not answer tests for individual ions like Fe^{2+} and CN^- .
- $[Fe(CN)_6]^{4-}$ is known as the complex ion exist as a coordination entity.

TERMS OF COMMON USAGE IN COORDINATION CHEMISTRY

COORDINATION ENTITY OR COMPLEXION ENTITY

- A central metal atom or ion surrounded by a fixed number of oppositely charged ions or neutral molecules given in square brackets.
- Eg. $[Ni(CO)_4]$, $Fe(CN)_6]^{4-}$ etc.

COMPLEX ION

- An electrically charged species which consists of a central metal ion surrounded by a group of ions or neutral molecules.
- Eg. $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$ etc.

Cationic complex

- A complex ion carrying a positive charge.
- Eg. $[Ni(NH_3)_6]^{2+}$,$[Co(NH_3)_4]^{2+}$,$[Co(NH_3)_4Cl_2]^{+}$

Anionic complex

- A complex ion carrying a negative charge
- Eg $[PtCl_6]^{2-}$, $[Fe(CN)_6]^{4-}$, $[Fe(C_2O_4)_3]^{3-}$

Neutral complex

- Eg. $[Ni(CO)_4]$, $V(CO)_5$

CENTRAL ION

- The cation to which one or more neutral molecules or anions are attached to form a complex ion.
- Eg. In the complex ion $[Cu(NH_3)_4]^{2+}$, Cu^{2+} ion is the central ion.

LIGANDS

- A species which is capable of donating electron pairs to the central metal atom or ion.
- It is a Lewis base.

DENTICITY OF A LIGAND

The number of atoms through which the ligands can donate a pair of electrons is called denticity of a ligand.

For example, denticity of ethane −1,2− diamine is 2, as it has two donor nitrogen atoms which can donate electron pairs to the central metal atom.

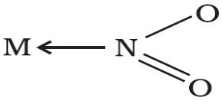
TYPES OF LIGANDS

UNIDENDATE LIGANDS

- A ligand bound to a metal ion through a single donor atom, is said to be unidendate.
- Eg. NH_3, H_2O, Cl^-, Br^-, OH^-, CO etc.

AMBIDENDATE LIGANDS

Unidendate ligands having two or more donor atoms but only one donor atom is attached to the metal during complex formation.



nitrito-N

$M \longleftarrow O — N = O$

nitrito-O

$M \longleftarrow SCN$

thiocyanato

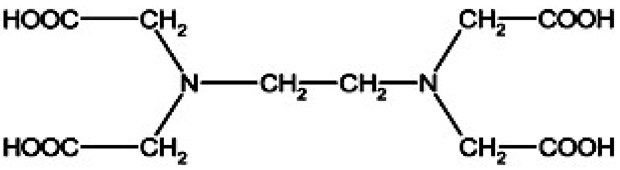
$M \longleftarrow NCS$

isothiocyanato

BIDENDATE LIGAND

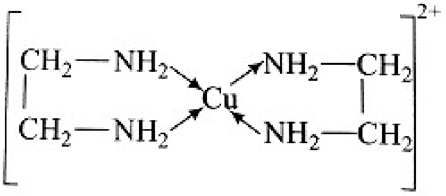
- A ligand which can bind through two donor atoms, is said to be a bidendate ligand.
- Eg. $H_2N-CH_2-CH_2-NH_2$, $^-OOC-COO^-$ etc.

POLYDENDATE LIGANDS



- Ligands which have more than two donor atoms are called polydendate ligands.
  Eg. EDTA

CHELATING LIGAND



- A bidendate or polydendate ligand which on coordination with the same central metal atom forms a ring structure is called a chelating ligand.
- The complex having a ring structure is called a chelate.

CHELATE

- A metal complex formed by a chelating ligand is called a chelate.
- The process of formation of a chelate is called chelation.

Species	Formula	Charge	Donor atom	Denticity	Name of Ligand
Ammonia	$:NH_3$	0	Nitrogen atom-one lone pair	1-unidentate	ammine
Water	$H_2:O:$	0	Oxygen atom-two lone pairs	1-unidentate	aquo or aqua
Carbon monoxide	CO	0		1-unidentate	carbonyl
Halide	X^- (Cl, Br,I)	-1	Halogen	1-unidentate	Chloro Or chlorido
Hydroxide	OH^-	-1	oxygen	1-unidentate	hydroxo
Cyanide	$:CN^-$	-1	carbon	1-unidentate	Cyano
Carbonate	CO_3^{2-}	-2		1-unidentate	carbonato
Sulphate	$SO_4{}^{2-}$	-2		1-unidentate	sulphato
Nitrite ion	NO_2^-	-1	Either N Or O at a time (ambidentate)	1-unidentate	N-nitrito OR O- nitro
Ethylene diamine	$H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$	0	Two nitrogens simultaneously	2-bidentate	en
Oxalate ion	$C_2O_4^{2-}$	-2	Two oxygens simultaneously	2-bidentate	
Ethylene diammine tetra acetic acid			Four oxygens &Two nitrogens simultaneously	6-hexadentate	EDTA

CO-ORDINATION NUMBER

- The total number of monodendate ligands attached to the central metal ion of a complex.

COORDINATION SPHERE

- The central metal ion and the ligands attached to it are enclosed in square bracket and are collectively termed as the coordination sphere.

COORDINATION POLYHEDRON

- The spatial arrangements of the ligands which are directly attached to the central metal ion is called coordination polyhedron.

OXIDATION NUMBER OF CENTRAL ATOM

- Oxidation number is as the charge that the central atom would carry if all the ligands are removed along with the electron pairs that are shared with the central atom.

HOMOLEPTIC AND HETEROLEPTIC COMPLEXES

- Complexes in which a metal is bounded to only one kind of donor groups are known as homoleptic complexes. Eg. $[Co(NH_3)_6]^{3+}$
- Complexes in which a metal is bound to more than one kind of donor groups are known as heteroleptic complexes. Eg. $[Co(NH_3)_4Cl_2]^+$

WERNER'S THEORY OF COORDINATION COMPOUNDS

The main postulates of this theory are

- In coordination compounds metals show two types of valencies-1°and 2°.
- The primary valences are normally ionisable and are satisfied by negative ions.
- Primary valency is equal to the oxidation state of the central metal ion
- The secondary valences are non ionisable.
- These are satisfied by neutral molecules or negative ions.
- The secondary valence is equal to the coordination number.
- Secondary valences will determine the stereochemistry.
- If the C.N is 4 it will be a Tetrahedral complex and if the CN is 6 it will be an Octahedral complex

NOMENCLATURE OF COORDINATION COMPOUNDS

- Name positive ion first followed by negative ion.
- Ligands are named first followed by metal ion.
- Name the metal followed by its oxidation number in Roman numeral.
- Negative ligands end in 'O'. Eg. Chlorido, bromido, cyano etc.
- Positive ligands end in 'ium'. Eg. Nitronium, Nitrosonium etc.
- Neutral ligands are named as such.
- Eg; en-Ethylene diamine, H_2O-aqua, CO-carbonyl, NO-nitrosyl, NH_3-ammine.
- Ligands are named in their alphabetical order.
- Indicate the number of ligands by prefixes di, tri, tetra etc.
- Use the prefixes bis, tris, tetrakis etc for 2,3,4 in coordination entity for other than unidentate ligands.
- In ambidentate ligand, the symbol of coordinated atom also included.
- In neutral complexes, the name of the central metal ion is unchanged.

- If the complex is a negative ion, the name of the metal ends in ‘ate’.

EXAMPLES

Write the IUPAC names of the following coordination compounds.

- (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (iv) $[Pt(NH_3)BrCl(NO_2)]^-$
- (ii) $K_2[Ni(CN)_4]$ (v) $[PtCl_2(en)_2](NO_3)_2$
- (iii) $[Cr(en)_3]Cl_3$ (vi) $Fe_4[Fe(CN)_6]_3$

Answers

- (i) Tetraamminediaquacobalt(III) chloride
- (ii)Potassium tetracyanonickelate(II)
- (iii) Tris(ethane–1,2–diamine) chromium(III) chloride
- (iv) Amminebromidochloridonitrito-N-platinate(II)
- (v) Dichloridobis(ethane–1,2–diamine)platinum(IV) nitrate
- (vi) Iron(III) hexacyanoferrate(II)

Write the IUPAC names of the following coordination compounds.

- (i) $[Co(NH_3)_6]Cl_3$ (iv) $K_3[Fe(C_2O_4)_3]$
- (ii) $[Co(NH_3)_5Cl]Cl_2$ (v) $K_2[PdCl_4]$
- (iii) $K_3[Fe(CN)_6]$ (vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

Answers

- (i) Hexaamminecobalt(III) chloride
- (ii) Pentaamminechloridocobalt(III)chloride
- (iii) Potassium hexacyanoferrate(III)
- (iv) Potassium trioxalatoferrate(III)
- (v) Potassium tetrachloridopalladate(II)
- (vi)Diamminechlorido(methylamine)platinum(II)chloride

Write the IUPAC Names of the following coordination compounds.

- (i) $[Pt(NH_3)_2Cl(NO_2)]$ (vi) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
- (ii) $K_3[Cr(C_2O_4)_3]$ (vii) $K_2[Zn(OH)_4]$
- (iii) $[CoCl_2(en)_2]Cl$ (viii) $K_3[Al(C_2O_4)_3]$
- (iv) $[Co(NH_3)_5(CO_3)]Cl$ (ix) $[CoCl_2(en)_2]^+$
- (v) $Hg[Co(SCN)_4]$ (x) $[Ni(CO)_4]$

Answers

- Diamminechloridonitrito-N-platinum(II)
- (ii) Potassium trioxalatochromate(III)
- (iii) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
- (iv) Pentaamminecarbonatocobalt(III) chloride
- (v) Mercury tetrathiocyanatocobaltate(III)
- (vi) Tetraamineaquachloridocobalt(III) chloride

- (vii) Potassium tetrahydroxozincate(II)
- (viii) Potassium trioxalatoaluminate(III)
- (ix) Dichloridobis(ethane-1,2-diamine)cobalt(III)
- (x) Tetracarbonylnickel(0)

ISOMERISM IN COORDINATION COMPOUNDS

- Compounds having the same molecular formula but different structural or spatial arrangements are called isomers and the phenomenon is called Isomerism.
- If the isomerism is caused by the difference in the structure it is called structural isomerism.
- If the isomerism is caused by the difference in spatial arrangements, it is called stereoisomerism.

A. STRUCTURAL ISOMERISM

1. Ionisation Isomerism

- This type of isomerism arises due to the exchange of ions between the coordination sphere of the metal ion and ions outside the coordination sphere.
- Eg. $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

2. Hydrate Isomerism

- This type of isomerism is due to the exchange of water between the inside and outside of coordination sphere. Eg. $[Cr(H_2O)_6]Cl_3$
- Eg: $[Cr(H_2O)_5Cl]Cl_2H_2O$ and $[Cr(H_2O)_4Cl_2]Cl(H_2O)_2$

3. Linkage Isomerism

- Certain ligands can donate the electron pair at two different sites and the isomerism due to this is called linkage isomerism.
- Eg. $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

4. Coordination Isomerism

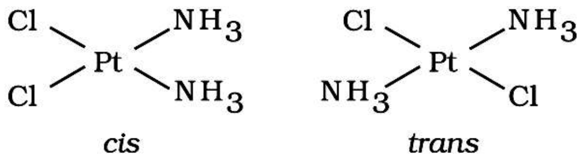
- This occurs in compounds containing both cationic and anionic complexes.
- This isomerism is due to exchange of ligands in the coordination sphere of cationic and anionic parts.
- Eg. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

B. STEREO ISOMERISM

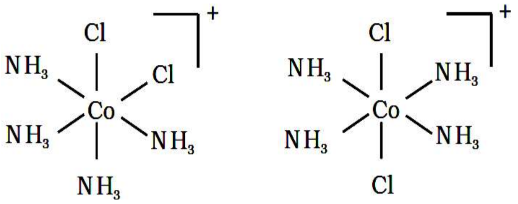
- This type of isomerism is due to the difference in spatial arrangements of ligands around the central metal.

1. Geometrical Isomerism

- This type of isomerism is due to ligands occupying different positions around the central metal.
- When two identical ligands occupy adjacent positions, the isomer is called **cis isomer.**
- When two identical ligands occupy opposite positions the isomer is called **trans isomer**.
- Square planar complexes of the type MA_2B_2 and Octahedral complexes of the type MA_2B_4 show geometrical isomerism.

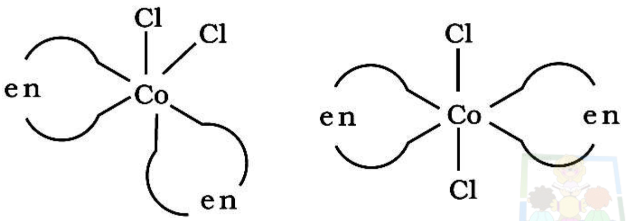


Cis and trans isomers of $[Pt(NH_3)_2Cl_2]$

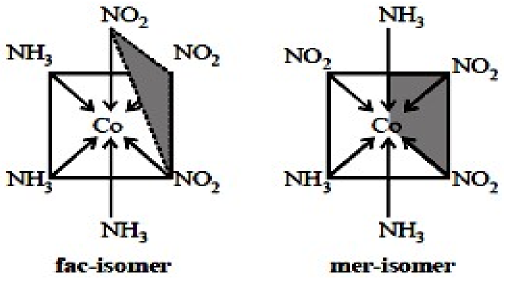


Cis and trans isomers of $[Co(NH_3)_4Cl_2]^+$

- In Type MA_3B_3, three donor ligands occupy adjacent position or similar ligands occupy the same face of an octahedron.
- The isomer is called facial or fac isomer
- similar ligands occupy the meridian of an octahedron.
- The isomer is called meridional or mer isomer
- In Type $M(AA)_2B_2$, A-bidentate ligand, in figure (en) is shown and B-unidentate, Cl is shown.



Cis and Trans isomers of $[Co(en)_2Cl_2]$

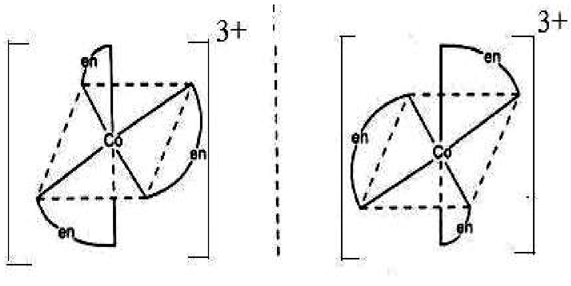


fac and mer isomers of $[Co(NH_3)_3(NO_2)_3]$

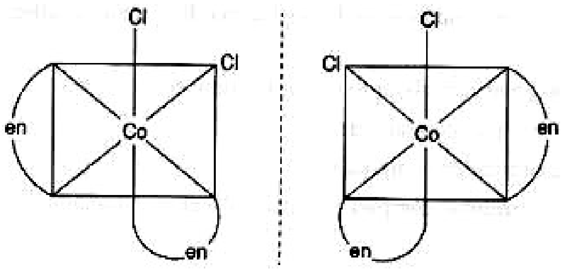
- Tetrahedral complex does not show geometrical isomerism because the relative positions of unidentate ligands attached with central metal atom are the same with respect to each other.

OPTICAL ISOMERISM

- This type of isomerism arises when a molecule of the complex is not superimposable on its mirror image.
- Eg. Octahedral complexes of the types $[Co(en)_3]^{3+}$, $[Co(en)_2Cl_2]^{2+}$
- Eg. $[Co(en)_3]^{3+}$

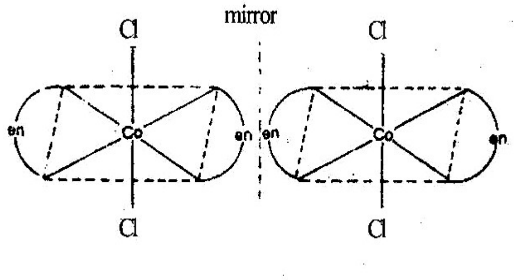


Optical isomers of $[Co(en)_3]^{3+}$



Optical isomers of cis $[Co(en)_2Cl_2]^{2+}$

- Eg. Trans $[Co(en)_2Cl_2]^+$ does not show optical isomerism since it is symmertric.



trans $[Co(en)_2Cl_2]^+$

BONDING IN COORDINATION COMPOUNDS

- To explain the properties such as colour, geometry, magnetic behaviour etc of complexes.

VALENCE BOND THEORY [VBT]

- This theory was proposed by Pauling.
- The main assumptions of this theory are
- The central metal atom in the complex provides a number of empty orbitals for the formation of coordinate bonds with suitable ligands.
- The number of empty orbitals provided is equal to the coordination number of the central ion.
- The atomic orbitals of the metal hybridise to form a set of equivalent orbitals with definite geometry such as square planar, tetrahedral, octahedral etc.
- The empty hybrid orbitals of metal ion overlap with the filled orbitals of the ligands.
- Octahedral, square planar and tetrahedral complexes are formed as a result of d^2sp^3 or sp^3d^2, dsp^2 and sp^3 hybridisation respectively.

INNER ORBITAL COMPLEX

- If the complex is formed by the use of inner d-orbitals for hybridisation, it is called inner orbital complex.
- Here, the electrons of the metal are forced to pair up.
- Hence the complex will be either diamagnetic or will have lesser number of unpaired electrons.
- Such a complex is also called **Low Spin Complex.**

OUTER ORBITAL COMPLEX

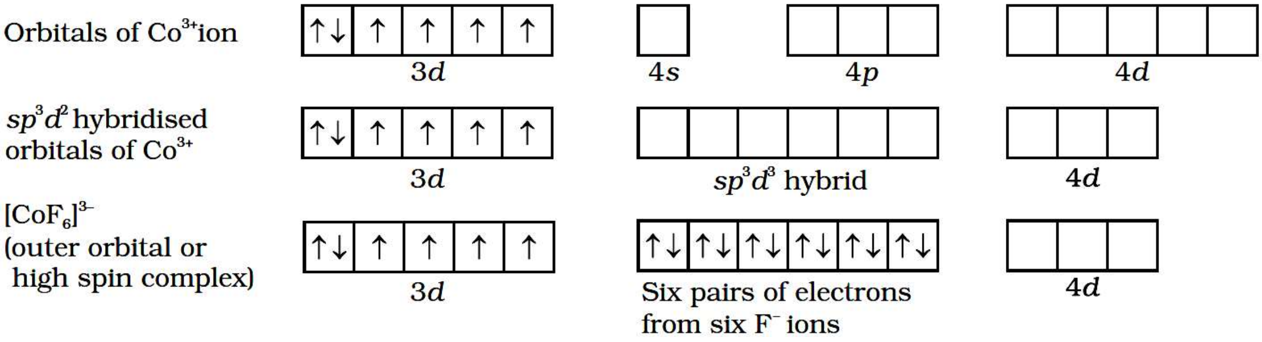
- If the complex is formed by the use of outer d orbitals for hybridisation, it is called an outer orbital complex.
- This complex will have larger number of unpaired electrons.
- Such a complex is also called **High Spin Complex.**

APPLICATIONS OF VALENCE BOND THEORY

1. $[Co(NH_3)_6]^{3+}$

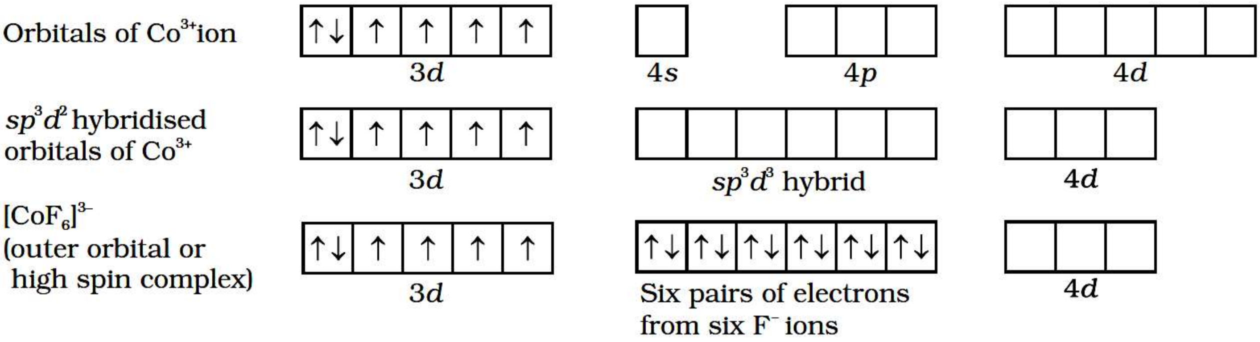
- Cobalt has the electronic configuration $3d^7 4s^2$.
- In this complex, Co is in the +3 oxidation state.

- The Co^{3+} ion is formed by the loss of two 4s and one 3d electrons.
- Since NH_3 is a strong ligand, the electrons in the 3d orbitals are forced to pair up.
- The inner d orbitals are already vacant and these two 3d, one 4s and three 4p orbitals hybridized to form six d^2sp^3 hybrid orbitals.
- Six pairs of electrons, one from each NH_3 molecule, occupy the six vacant hybrid orbitals.
- Thus, the complex has octahedral geometry and is diamagnetic.



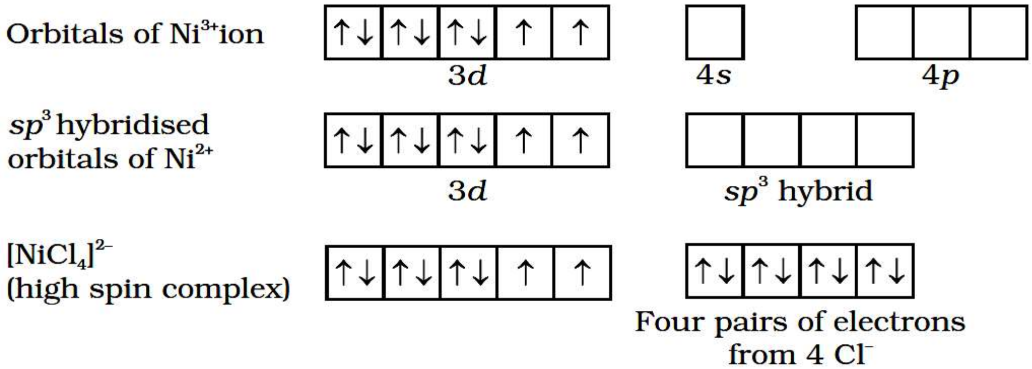
2. $[CoF_6]^{3-}$

- Cobalt has the electronic configuration $3d^7 4s^2$.
- In this complex, Co is in the +3 oxidation state.
- The Co^{3+}ion is formed by the loss of two 4s and one 3d electrons.
- Since Fluoride is a weak ligand, the electrons in the 3d orbitals are not disturbed and the outer 4d orbitals are used for hybridization.
- The six orbitals, one 4s, three 4p and two 4d orbitals hybridized to form six sp^3d^2 hybrid orbitals.
- Six pairs of electrons, one from each fluoride ions occupy the six hybrid orbitals.
- Thus, the complex has octahedral geometry and is paramagnetic.



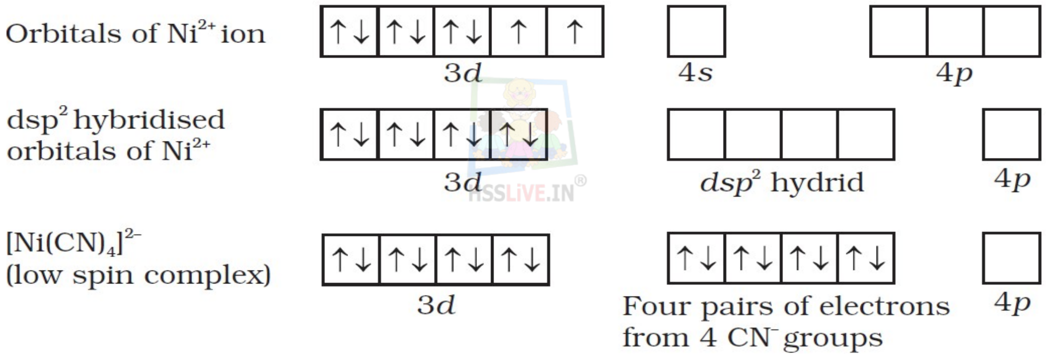
3. $[NiCl_4]^{2-}$

- Nickel has the electronic configuration $3d^8 4s^2$.
- Nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$.
- Since Chloride is a weak ligand, the electrons in the 3d orbitals are not disturbed.
- The four orbitals, one 4s, three 4p orbitals hybridized to form four sp^3 hybrid orbitals.
- Four pairs of electrons, one from each chloride ions occupy the four hybrid orbitals.
- Thus, the complex has tetrahedral geometry and is paramagnetic.



4. $[NiCN_4]^{2-}$

- Nickel has the electronic configuration $3d^8 4s^2$.
- In this complex nickel is in +2 oxidation state.
- The Ni^{2+} ion has the electronic configuration $3d^8$.
- Since Cyanide is a weak ligand, the electrons in the 3d orbitals are forced to pair up.
- The four orbitals, one 3d, one 4s and two 4p orbitals hybridized to form four dsp^2 hybrid orbitals.
- Four pairs of electrons, one from each cyanide ions occupy the four hybrid orbitals.
- Thus, the complex has a square planar geometry and is diamagnetic.



LIMITATIONS OF VALENCE BOND THEORY [VBT]

- It fails to explain the detailed magnetic properties.
- It does not explain the colour exhibited by coordination compounds.
- It does not give a quantitative interpretation of the thermodynamic and kinetic
- stabilities of Coordination compounds.
- It does not distinguish between weak and strong ligands.

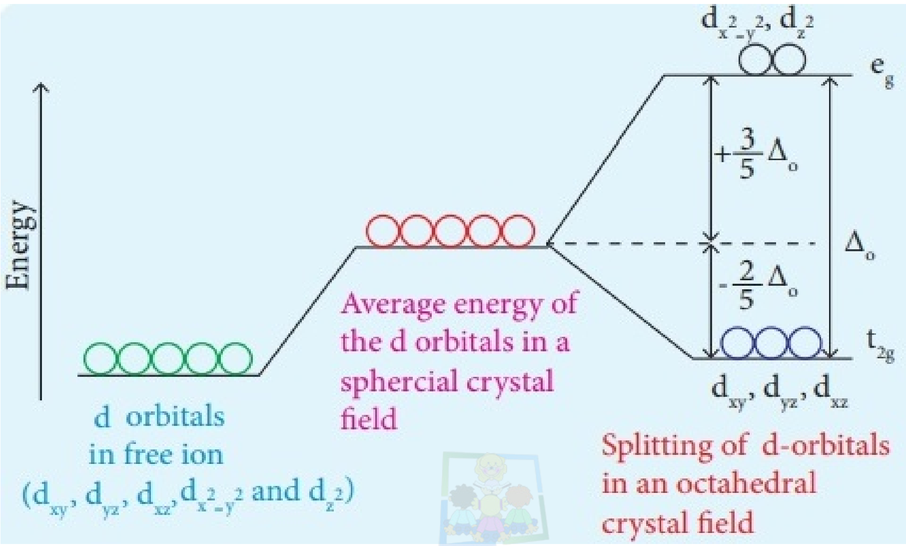
CRYSTAL FIELD THEORY [CFT]

CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEXES

- In an isolated gaseous metal ion, the five d orbitals are degenerate.
- In an octahedral complex six ligands approach the central metal ion along the three Cartesian axes.
- As the ligands approach, at first there is an increase in the energy of d orbitals.
- The orbitals lying along the cartesian axes, dx^2-y^2 and dz^2, get repelled more strongly than the orbitals directed in between the axes, dxy, dxz and dyz.
- As a result, the energy of the dx^2-y^2 and dz^2 orbitals is increased and the energy of dxy,

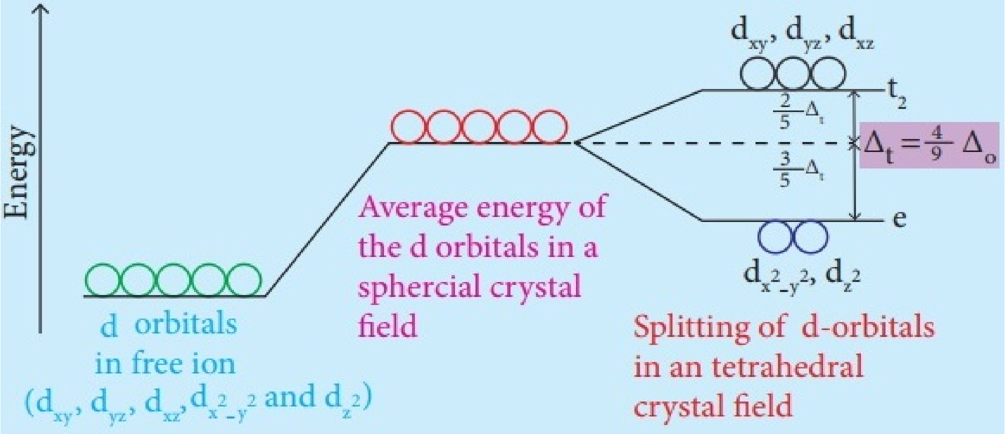
dxz and dyz orbitals is decreased.

- Thus, the five d orbitals which were originally degenerate in the free metal ion are split into two levels
- (i) the doubly degenerate level called eg level which is of higher energy and
- (ii) the triply degenerate level called t_{2g} level which is of lower energy.
- **The splitting of the five d orbitals into eg and t_{2g} energy levels by the approaching ligands is called the crystal field splitting.**
- The energy difference between t_{2g} and eg levels is called crystal field splitting energy and is denoted as Δo or 10Dq.



CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEXES

- The tetrahedral arrangement of the four ligands around the central metal ion is related to a cube.
- The metal ion is at the centre of the cube.
- Four of the eight corners of the cube are occupied by the ligands.
- The dx^2-y^2 and dz^2 orbitals (e orbitals) point along the x, y and z directions (face centres).
- The dxy, dxz and dyz orbitals (t_2 orbitals) point in between x, y and z directions (edge centres).
- The direction of approach of ligands does not coincide exactly with either e or t_2 orbitals.
- The dxy, dxz and dyz orbitals are pointing close to the direction in which ligands are approaching.
- As a result, the energy of these t_2 orbitals increases much more than the energy of the e orbitals.
- Thus, the d orbitals split into two levels.
- (i) the triply degenerate t_2 orbitals of higher energy and
- (ii) the doubly degenerate e orbitals of lower energy.
- $\Delta_t = 4/9\ \Delta_o$



SPECTROCHEMICAL SERIES

- It is a series in which the ligands are arranged in the increasing order of magnitude of crystal field splitting.
  - $I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 <$ en $< NO_2^- < CN^- <$ CO

COLOUR IN COORDINATION COMPOUNDS

- The crystal field splitting of d orbitals produces the energy difference Δ.
- This energy difference is usually very small.
- Thus, promotion of electrons from lower to higher d level (d−d transition) results from the absorption of light of higher wavelength in the visible region and the complex appears coloured.
- Depending on the wavelengths of light absorbed, the complex will have different colours.
- The d−d transition account for the colour of the complex ions and their complexes.

MAGNETIC PROPERTIES

- Coordination compounds have partially filled d orbitals.
- Hence, they exhibit magnetic properties.
- The magnetic moment of a substance depends on the number of unpaired electrons.
- i.e., the greater the number of unpaired electrons, the more is the magnetic moment.
- The magnetic moment is given by the equation, $\mu=\sqrt{n(n+2)}$

QUESTION

1. Calculate the magnetic moment of

i) $[FeF_6]^{3-}$

Electronic configuration of Fe is $[Ar]3d^6 4s^2$

Oxidation state of Fe in $[FeF_6]^{3-}$ is x.

i.e., $x-6=-3$, $x=+3$

Electronic configuration of $Fe^{3+}=[Ar]3d^5$

Fluoride is a weak field ligand

No. of unpaired electrons in $Fe^{3+}=5$

Magnetic moment, $\mu = \sqrt{n(n+2)}$, $\mu = \sqrt{5(5+2)}$, $\mu = \sqrt{35}$ =5.92 BM

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

Electronic configuration of Fe is $[Ar]3d^6 4s^2$

Oxidation state of Fe in $[Fe(CN)_6]^{4-}$ is x.

i.e., $x-6=-4$, $x=+2$

Electronic configuration of $Fe^{2+}=[Ar]3d^6$

Cyanide is a strong field ligand

No. of unpaired electrons in $Fe^{2+}=0$

Magnetic moment, $\mu = \sqrt{n(n+2)}$, $\mu = \sqrt{0(0+2)}$, $\mu = \sqrt{0} = 0$

2. Question: Teacher asked two students to write the electronic configuration of d^4 system using CFT.

Student 1 : $t_2g^3\ eg^1$

Student 2 : $t_2g^4\ eg^0$.

Suggest which student gives correct configuration. Justify your answer

Answer:

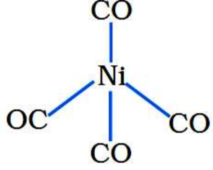
- Both students gave the correct configuration. The electronic configuration is decided by CFSE Δ_O and pairing energy P.
- If $\Delta_0 < p$, the fourth electron enters in one of the orbitals giving $t_2g^3\ eg^1$.
- Ligands with $\Delta_0 < P$ are known as weak field ligands and form high spin complexes or hypoligated complex.
- If $\Delta_0 > P$, it becomes more energetically favourable for the 4th electron to occupy a t_2g orbital configuration $t_2g^4 eg^0$.
- Ligands which produce this effect are known as strong field ligands and form low spin complexes or hyper ligated complexes

LIMITATIONS OF CRYSTAL FIELD THEORY

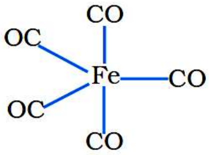
- The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds.
- According to CFT, anionic ligands should exert the greatest splitting effect.
- But actually, the anionic ligands are found at the low end of the Spectrochemical series.
- CFT does not take into account the covalent character of bonding between the ligand and the central metal atom.

BONDING IN METAL CARBONYLS

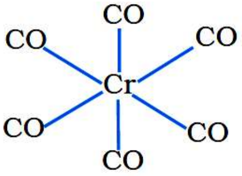
- Organometallic compounds in which CO acts as the ligand are called Metal Carbonyls.
- The organometallic compounds which contain only carbonyl ligands are called homoleptic carbonyls.
- Examples are $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mn_2(CO)_{10}$ etc.



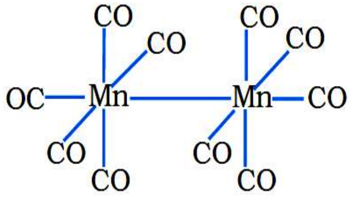
$Ni(CO)_4$
Tetrahedral



$Fe(CO)_5$
Trigonal bipyramidal

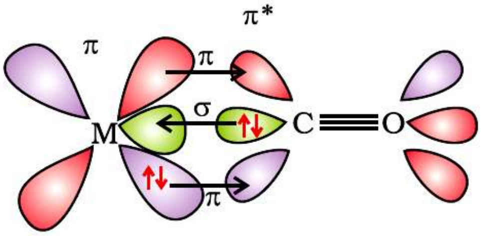


$Cr(CO)_6$ Octahedral



$[Mn_2(CO)_{10}]$

- The metal-carbon bond in metal carbonyls possess both s and p character.
- The **M–C σ bond** is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal.
- The **M–C π bond** is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding **π*** orbital of carbon monoxide.



Synergic bonding

- The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.
- This type of bonding is called **synergic bonding.**

STABILITY OF COORDINATION COMPOUNDS

- The stability of a complex is a measure of the strength of the metal-ligand bond.
- Thus, stronger the metal ligand bond, the greater is the thermodynamic stability of the complex.
- The stability of a complex may also be defined as a measure of its resistance to the replacement of one ligand by another.
- The reaction between metal ion M^{a+} and ligand L^{x-} may be represented by the equilibrium, $M^{a+} + nLx^{-} \rightleftharpoons [MLn]^{b+}$
- Where a^+, $x-$ and b^+ are the charges on the metal, the ligand and the complex ion respectively.
- The stability constant (K) of the complex is given as $K = \dfrac{[MLn]^{b+}}{[M^{a+}][Lx^{-}]^{n}}$
- Thus, greater the value of stability constant, the greater is the stability of the complex.

IMPORTANCE AND APPLICATIONS OF COORDINATION COMPOUNDS

- Hardness of water is estimated by simple titration with Na_2EDTA.
- The noble metals like gold and silver are extracted by the formation of their cyano complexes.
- Metals can be purified by the formation and subsequent decomposition of coordination compounds.
- Many medicines are complexes.
- Complexes are used in electroplating.
- Coordination compounds are used as catalysts for many industrial processes.
- Coordination compounds are of great importance in biological systems like chlorophyll, haemoglobin, cyanocobalamine etc.