

Coordination Compounds

② Ajaz Sir[©]

Coordination Compounds: Those molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in solid as well as in dissolved state. These compounds contain a central metal atom or ion surrounded by suitable number of ions or neutral molecules with the help of coordinate bonds. Thus the formation of coordinate compounds involve two things.

(a) An Acceptor, also known as central metal atom or ion which is usually a metal to which one or more of neutral molecules or anions are attached by donating pairs of electrons. eg in $[\text{Fe}(\text{CN})_6]^{3-}$, Fe^{3+} ion is Acceptor

(b) A Donor; which is an electron rich atom or molecule which can donate a pair of electrons and is known as ligand. The neutral molecules or \ominus -vely charged ions that surround the metal ion in a complex compound are known as ligands. eg in $[\text{Fe}(\text{CN})_6]^{3-}$, CN^- ion is ligand.

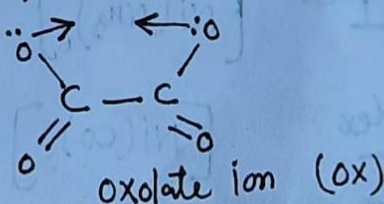
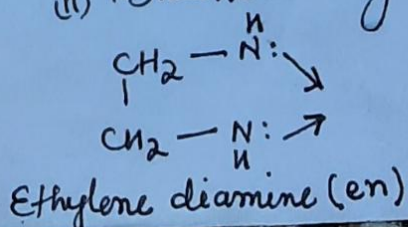
Other examples of ligands are, NH_3 , SO_4^{2-} , H_2O , Cl^- , CO etc.

Depending upon the number of donor sites, ligands may be classified as:

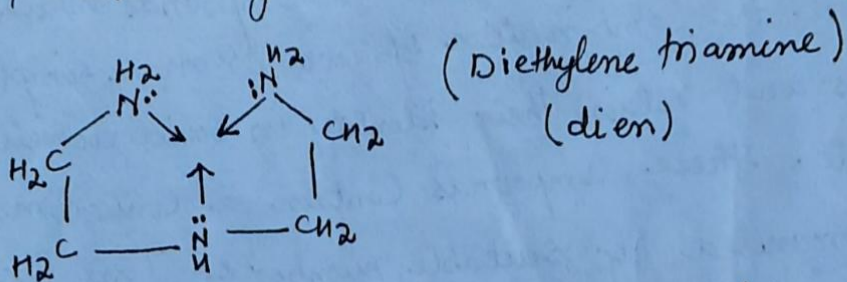
(i) Mono or unidentate ligands: These have only one donor atom

eg F^- , Cl^- , Br^- , H_2O , NH_3 , etc.

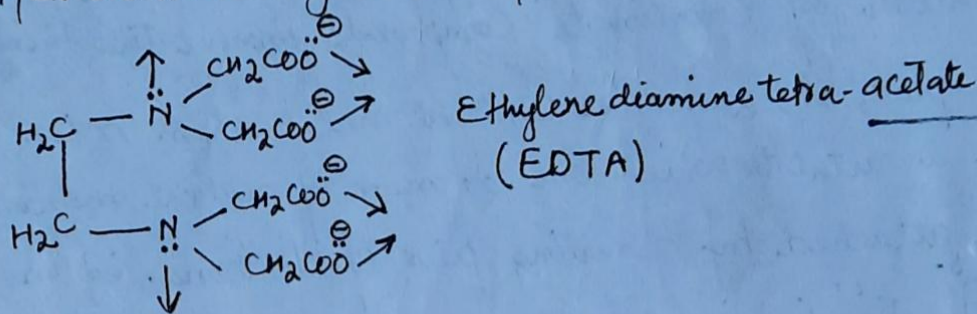
(ii) Bidentate ligands: These have two donor atoms eg



iii) Tridentate ligands: These have three donor atoms 'eg'



iv) Hexadentate ligands: Have six donor atoms 'eg'



Double Salts: These addition compounds are stable in solid state, but dissociate into their constituents when dissolved in H_2O . So these compounds retain their identity in solid state but lose their identity in aqueous state.

'eg' Mohr's salt: $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$.

Potash alum: $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Complex Ion:

It is an electrically charged species in which the central metal atom is surrounded by suitable numbers of ligands

'eg' $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_4]^{3+}$, $[PtCl_6]^{2-}$ etc.

Three types:

→ Negative Complex $[Fe(CN)_6]^{3-}$

→ Positive Complex $[Ni(NH_3)_6]^{3+}$

→ Neutral Complex $[Ni(CO)_5]$

Coordination sphere: The part of complex containing the central metal atom or ion co-ordinated to different groups i.e. ligands is called inner coordination sphere. It is represented by closing the central ion with its coordinated groups in a square bracket. The portion present outside the sq. bracket is called ionisation sphere. 'eg' in the complex

$[\text{Cu}(\text{NH}_3)_4] \text{SO}_4$, the part $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is called coordination sphere, while as SO_4^{2-} part is called ionisable sphere.

Coordination Numbers The total no. of monodentate ligands or twice the number of bidentate ligands or thrice the number of tridentate ligands attached to central atom is called coordination no. 'eg' C.No. of

- (i) Pt in $\text{K}_2[\text{PtCl}_6]$ is 6 (ii) Ni in $[\text{Ni}(\text{NH}_3)_4] \text{Cl}_2$ is 4.
 (iii) Pt in $[\text{Pt}(\text{NH}_3)_3 \text{Cl}_3] \text{Cl}$ is 6 (iv) Fe in $[\text{Fe}(\text{C}_2\text{O}_4)_3]$ is 6.

Oxidation no.

The charge on a complex ion is the sum of charges on the central metal ion and its ligands 'eg' in the complex $[\text{Co}(\text{en})_2 \text{Cl}(\text{ONO})]$, the charge on central metal ion may

be calculated as:

Let charge on Co = x

$$x + 2(0) + (-1) + (-1) = 0$$

$$x + 0 - 1 - 1 = 0$$

$$x - 2 = 0$$

$$x = +2$$

Thus O. State of Co = +2

Nomenclature of following Compounds

- 1) $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2 \rightarrow$ Hexa amine nickel(II) chloride
- 2) $[\text{Co}(\text{en})_3]^{3+} \rightarrow$ Tris ethylenediamine Cobalt(III) ion.
- 3) $[\text{PtCl}_2(\text{NH}_3)_2] \rightarrow$ Diammine dichloroplatinum(II)
- 4) $[\text{Co}(\text{NH}_3)\text{Cl}(\text{en})_2]^{2+} \rightarrow$ A amine chlorobis ethylenediamine Cobalt(II) ion
- 5) $\text{K}_3[\text{Co}(\text{CN})_5\text{NO}] \rightarrow$ Potassium pentacyanonitrosyl Cobaltate (II)
- 6) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \rightarrow$ tetraaminedichloro Cobalt(II)
- 7) $[\text{Co}(\text{en})_2\text{Cl}_2]_2\text{SO}_4 \rightarrow$ dichlorobis(ethylenediamine) Cobalt(III) Sulphate.

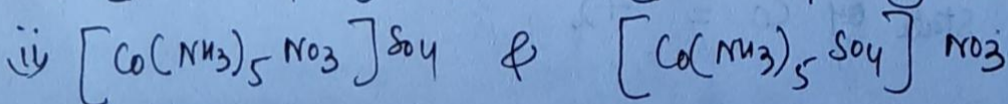
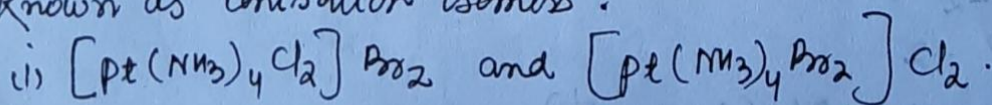
Isomerism in Co-ordination Compounds

The two or more Compounds having same chemical formula but different properties are known as isomers and the phenomenon is termed as isomerism. Isomers can be broadly classified into two classes:

(A) Structural isomers (B) Stereo isomers.

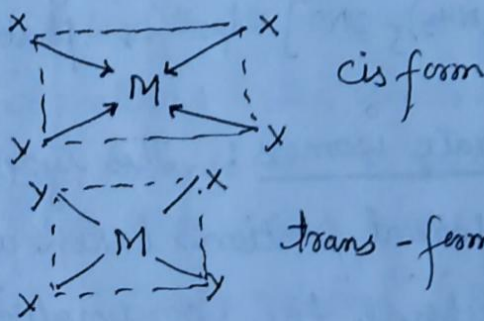
(A) Structural isomers: These are those isomers which have different structural arrangements of ligands around the central metal atom. The various types of structural isomers are as follows:

(i) Ionisation isomers: Coordination Compounds which have same molecular formula but yield different ions in solution are known as ionisation isomers.

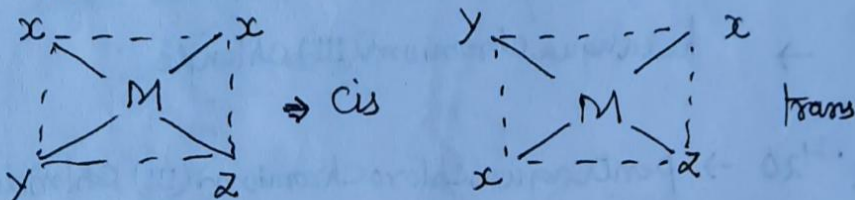


is known as trans-isomer if ligands of some kind are opposite to each other. The tetrahedral complexes don't show geometrical isomerism because the relative positions of atoms with respect to each other will be same.

Types: Mx_2y_2



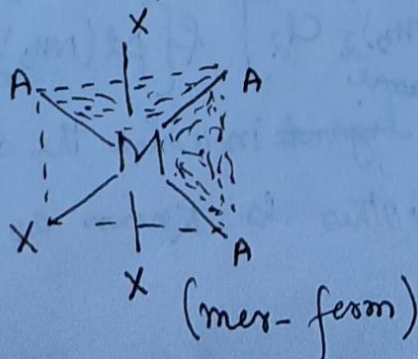
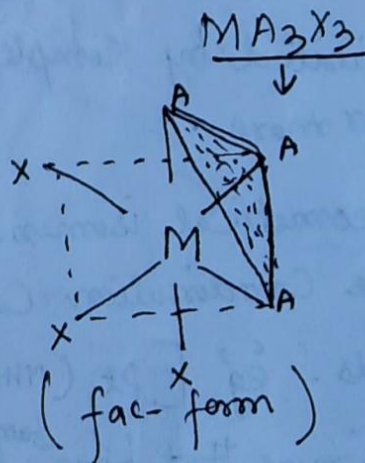
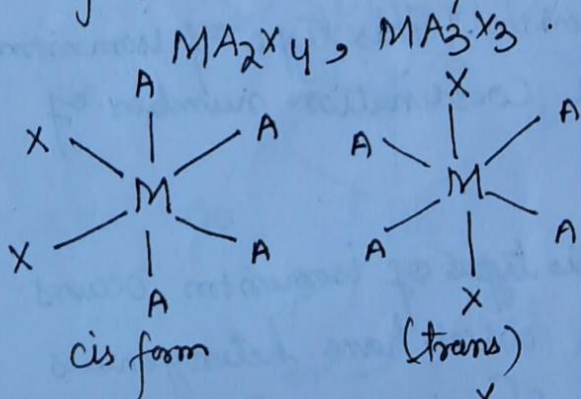
Type Mx_2yz



Geometrical isomerism in Octahedral complexes C.No.6.

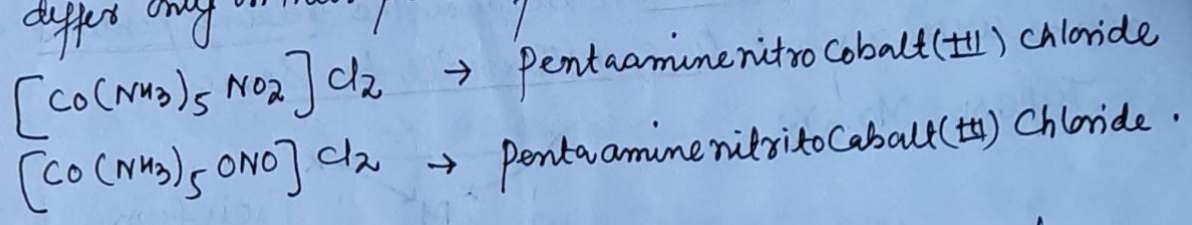
Six Co-ordination Complexes have octahedral geometry & cis-trans isomerism is possible.

eg Octahedral Complexes of type MA_4X_2 , MA_4XY_2

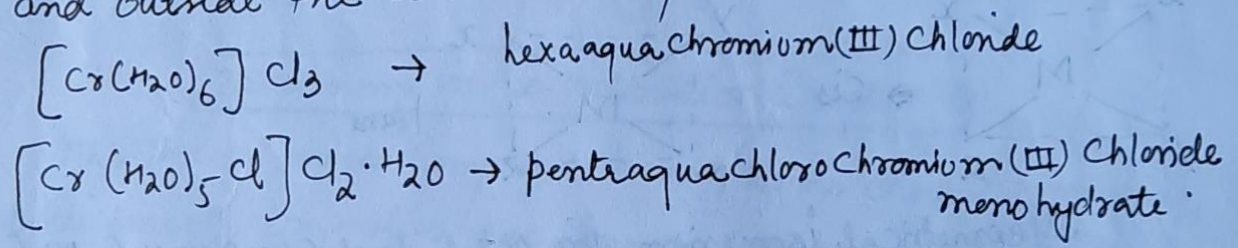


Optic
this type
molecules
Sym

(2) Linkage isomers: This type of isomerism is shown by compounds containing monodentate ligands capable of coordinating in more than one way (ambidentate ligands) & so they differ only in their point of attachment with central atom.



(3) Hydrate isomers: This type of isomerism arises because of different positions taken up by water molecules inside and outside the coordination sphere.



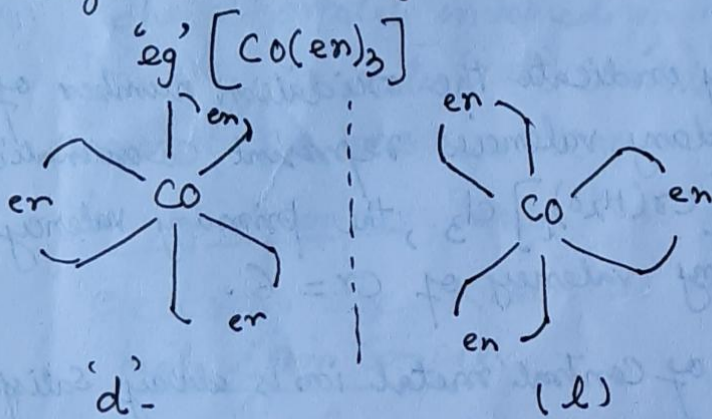
(4) Stereo isomers: Those molecules which have same molecular formula & same structural formula but differ only in spatial arrangement of ligands about the central metal atom constitute the stereo isomerism. This type of isomerism is exhibited by complexes with coordination numbers of four or more.

\rightarrow Geometrical isomerism: This type of isomerism occurs in those coordination compounds which have heterogeneous ligands. eg $[Pt(NH_3)_2Cl_2]$ & $[Pt(NH_3)_2Cl_4]$.

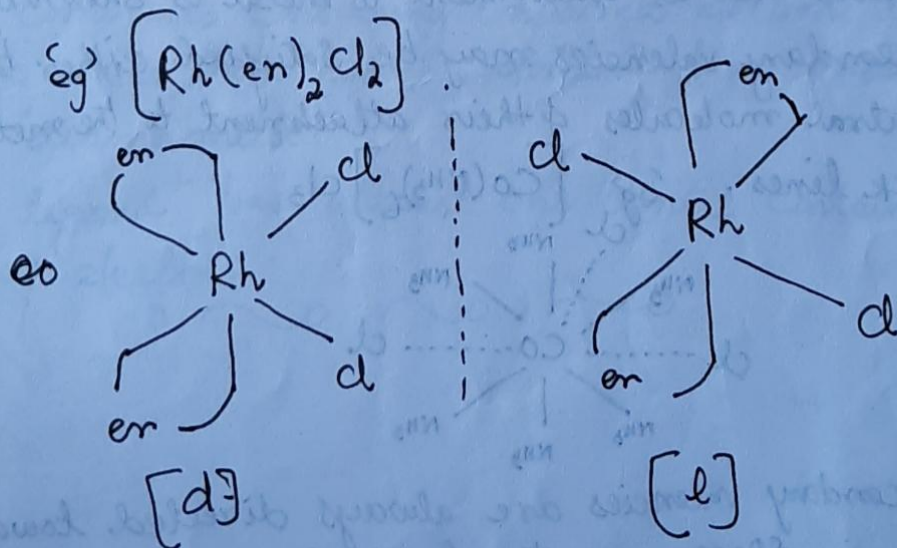
The isomers that have ^{same} ligands in which the same kind of ligands are adjacent to each other is known as Cis-isomer while

Optical isomers

This type of isomerism is exhibited by asymmetric or chiral molecules i.e. molecules which don't have elements of symmetry (plane of symmetry). These isomers are non-superimposable mirror images of each other & they resemble one another in their ~~res~~ chemical reactions & most of their physical properties except that they rotate the plane polarised light in opposite directions. The isomer which rotates the plane polarised light towards left is called "Laevorotatory" or L-(-). While that rotate plane polarised light towards right is called "Dextrorotatory" [D]-(+).



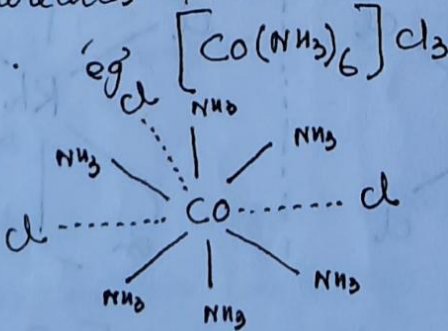
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Bonding in Co-ordination Compounds.

Werner's Theory.

Alfred Werner in 1893 proposed the first most successful theory to explain the formation and properties of co-ordination compounds in terms of their structure known as "Werner's Coordination theory", and he was awarded Nobel prize in chemistry for this theory. The ~~Salient~~ Salient features of this theory are as follows:

- (1) Metals have two types of valencies primary and Secondary (non-ionisable) (ionisable)
- (2) The primary valency indicate the oxidation numbers of metal ion whereas Secondary valencies represent co-ordination numbers of metal. eg $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, the primary valency of $\text{Cr} = 3$ & Secondary valency of $\text{Cr} = 6$.
- (3) The primary valency of central metal ion is always satisfied by anions and its attachment to metal is shown by dotted lines. The secondary valencies may be satisfied either by anions or by neutral molecules & their attachment to the metal is shown by thick lines. eg $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

- (4) The Secondary valencies are always directed towards the fixed positions in space and this leads to definite geometry of the Coordination Compound.

Bonding in Co-ordination Compounds:

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Werner's theory was the first successful attempt to describe the bonding in co-ordination compounds. However, the theory which explains the nature of bonding within the coordination sphere was proposed by Linus Pauling (1931) & is known as 'valence bond theory'. According to this theory:-

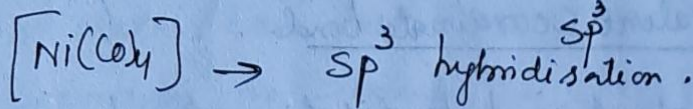
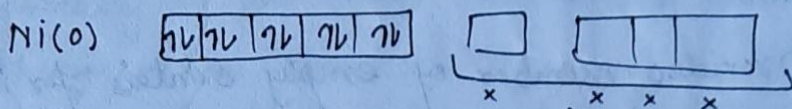
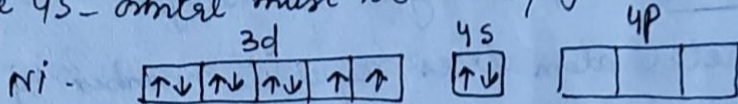
- (i) The central metal atom loses requisite number of electrons to form cation.
- (ii) The cation provides number of empty orbitals for the formation of covalent coordinate bond.
- (iii) The d-orbitals involved in hybridisation may be inner $(n-1)d$ or outer (nd) orbitals. The complex formed by using inner d electrons are known as inner orbital complex or low spin complex, while those formed by using outer d electrons are known as outer orbital complex or high spin complex.
- (iv) The complexes containing unpaired electrons are 'paramagnetic' while those which don't contain unpaired electrons are 'diamagnetic'.
- (v) Each ligand has at least one orbital containing a lone pair of electrons.



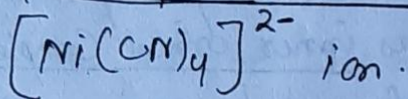
Examples to illustrate the above features of

A) Tetrahedral Complex · $[Ni(CO)_4]$

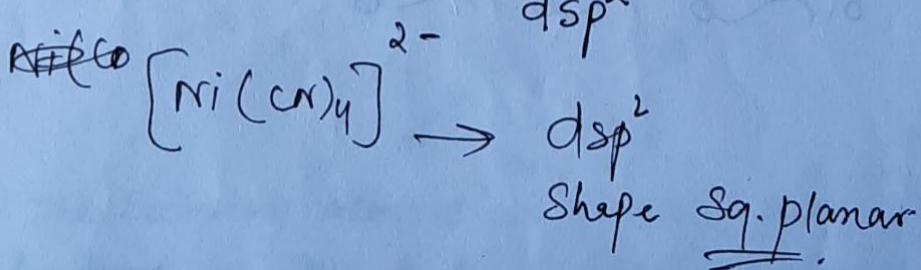
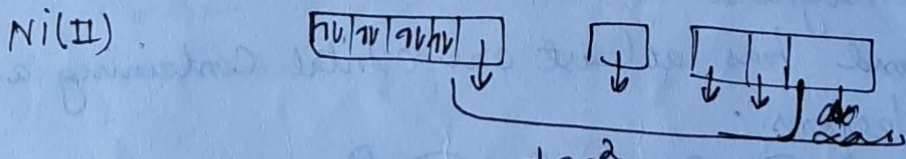
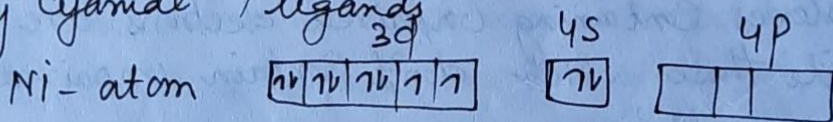
The Ni has $3d^8 4s^2$ as its outer electronic configuration. For complexes with coordination number 4, the central atom may involve sp^3 or dsp^2 type of hybridisation, for each of which the $4s$ -orbital must be empty.



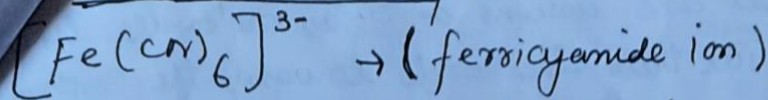
(B) Square planar · (dsp^2)



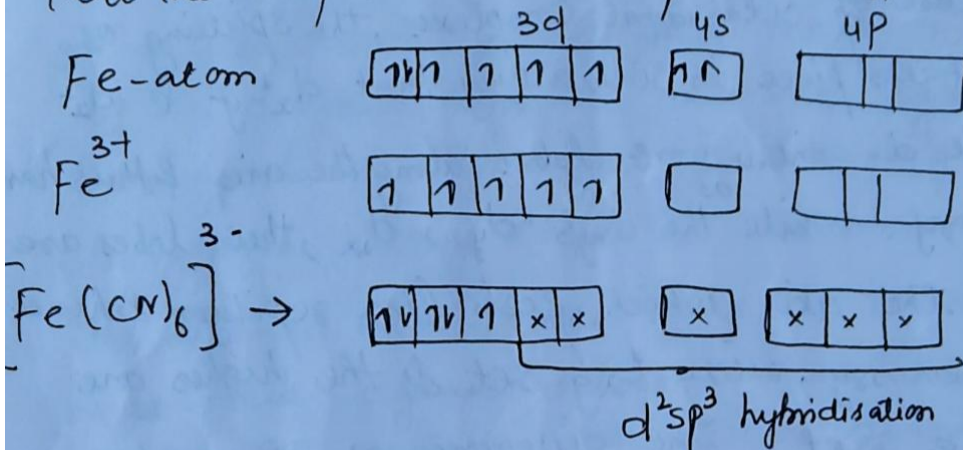
This type of hybridisation forms when one 'd' one 's' and two 'p' orbitals are empty and hence the electrons are forced to pair up for hybridisation by cyanide ligands.



Octahedral Complex.



Iron atom has electronic configuration $3d^6 4s^2$. In this complex iron is in +3 oxidation state and has electronic configuration $3d^5 4s^0$. It has been experimentally found observed that the complex has one unpaired electron.



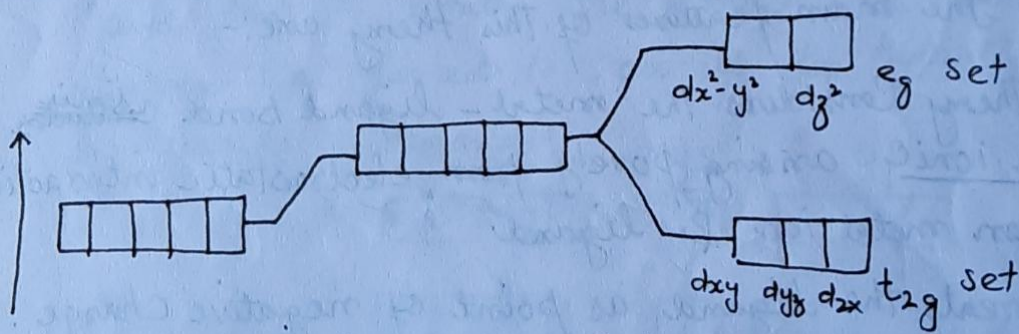
Crystal field theory

This theory was developed by Hans Bethe and Van-Vleck in 1932. The main features of this theory are:-

- (1) This theory considers the metal-ligand bond ~~covalent~~ to be ionic arising purely from electrostatic interactions between metal ion & ligand.
- (2) It treats the ligand as point of negative charge.
- (3) It considers the effect of ligands on the relative energies of the d-orbitals of central atom ion. According to this theory, in a free transition-metal ion, all the five d-orbitals have equal energies i.e. they are degenerate and this degeneracy is maintained if the -ve charge around the central metal atom forms a spherical symmetrical field.

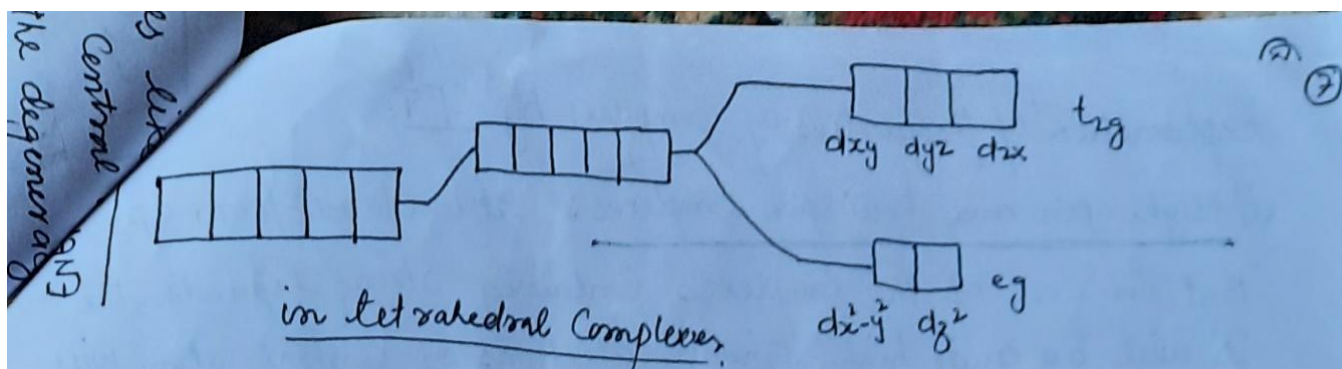
However, if ligands are anions or polar molecules like NH_3 , H_2O etc. with their -ve ends towards the central metal ion, the field no longer remains symmetrical & the degenerate set is split. This splitting depends upon the nature of the crystal field exerting its influence on central metal ion.

In case of octahedral complexes, the splitting of d-orbitals takes place in such a way that $d_{x^2-y^2}$ & d_{z^2} because these d-orbitals have lobes along the axis & thus have higher energy. While the d_{xy} , d_{yz} , d_{zx} , their lobes are in between the axis which feels less repulsion & hence have lower energy, with t_{2g} set & the higher one is called e_g set. The difference of energy between two sets is called Crystal field splitting energy (CFSE). Usually represented by Δ_o .



Splitting of d-orbitals in octahedral complex.

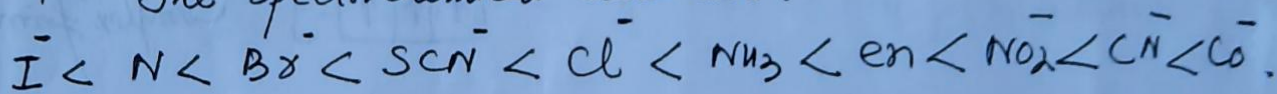
In case of tetrahedral complexes, the splitting pattern is just reverse of octahedral complexes i.e. three fold degenerate set ' t_{2g} ' set has higher energy & the two fold set ' e_g ' set has lower energy.



It has been found that for given metal ion, the magnitude of Δ_0 depends upon the nature of ligands and when the ligands are arranged in increasing order of their strength, a series known as Spectrochemical Series.

The ligands with smaller value of Δ_0 are called weak field ligands, whereas those with large value of Δ_0 are called strong field ligands.

The Spectrochemical Series are:



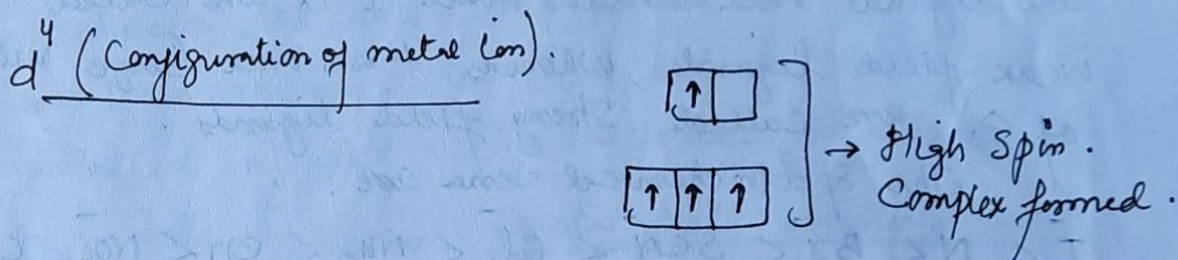
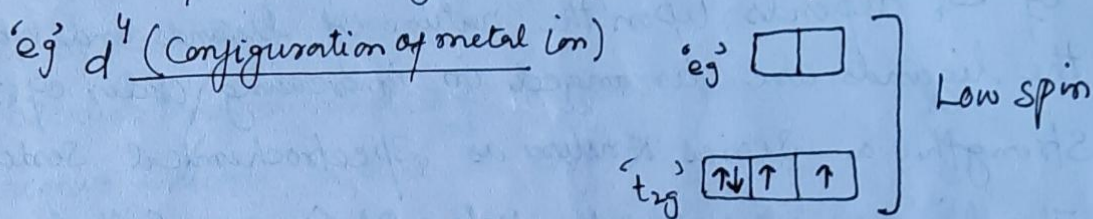
Factors affecting the magnitude of orbital splitting energy

- (i) Oxidation state of metal ion: Higher the oxidation state of central metal ion, larger the value of Δ .
- (ii) Nature of metal ion: on the d-block elements as we move from 3d - 4d - 5d elements, the Δ_0 value increases & hence the tendency to form low spin increases.
- (iii) Nature of ligands: Strong field ligands cause greater splitting > weak field ligands cause smaller splitting.

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Explanation of properties of Complexes by CFT.

(i) High spin and Low spin Complexes: It is clear from CFS, that in case of the complexes containing strong ligands, the Δ will be quite high & hence electrons of central atom will pair up the low d-orbitals formed during splitting & thus such complexes will generally be low spin complexes.



(2) Colour of Complexes: The value of Δ_0 for most of complexes is of same order of magnitude as the energy of photon of visible light. It is therefore possible for transition-metal complexes to absorb light which there by excite electrons from lower energy d-orbitals to higher energy d-orbitals. So the colour of the complex will be complimentary to the colour absorbed from white light to cause such excitation.

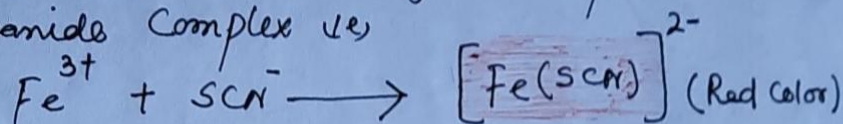
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Applications of Co-ordination Complexes: (8)

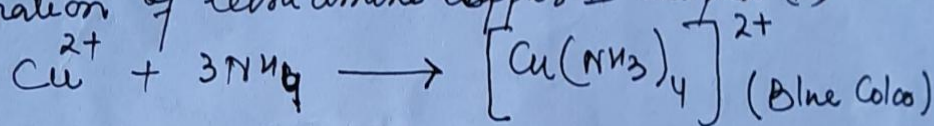
The Co-ordination Compounds constitute the minerals, plants, present in animals, biochemistry, water softening, electrochemistry, analytical chemistry etc & so are of great importance. Some of important applications of co-ordination complexes are:-

1) In analytical chemistry:

a) Fe^{3+} ions can be detected by means of red coloured sulphocyanide complex i.e.



b) Cu-salts give deep blue colour with NH_3 due to formation of tetra amine copper II complex i.e.



2) In biological process:

a) The green colouring matter of plants called chlorophyll is a complex of Mg(II) , which act as catalyst for photosynthesis.

b) Vitamin- B_{12} (Cyanocobalamin) is complex of Co(II) which acts as enzyme in the formation of RBC, which is used in treatment of pernicious anaemia.

c) Haemoglobin: It is a red pigment in blood & is complex of Fe(II) & it transport oxygen from lungs to the parts of body.

d) The complex $\text{cis}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ known as cis-platin is used in treatment of cancer.

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