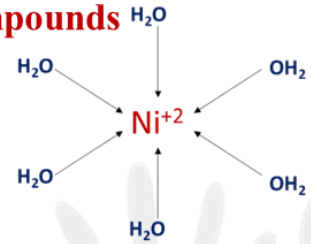
COORDINATION COMPOUNDS

A coordination complex is the product of a Lewis acid-base reaction in which neutral molecules or anions bond to a central metal atom (or ion) by coordinate covalent bonds.

General Characteristics of Electrovalent Compounds



When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out. These compounds are called molecular or addition compounds.

(A) Double Salts

Those which lose their identity in solution

$K_2SO_4.Al_2(SO_4)_3 . 24H_2O(aq) \longrightarrow K^+ + Al^{3+} + SO_4^{2-}$

(B) Coordination Compounds

Those which retain their identity in solution.

$K_4[Fe(CN)_6] \longrightarrow K^+ + [Fe(CN)_6]^{4-}$

MIND MAP

Coordination Compound

Classification of Ligands

(A) Based on charge

(i) Neutral ligands H_2O, NO, CO, C_6H_6 etc.

(ii) Positive ligands NO^+, $N_2H_5^+$

(iii) Negative ligands $\ddot{Cl}^-$, $\ddot{N}O_2^-$, $\ddot{C}N^-$, $\ddot{O}H^-$

(a) Unidentate/monodentate ligands

Ligands which donate one pair of electron to the central metal are called unidentate ligands.

(b) Bidentate ligands

Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.

(c) Polydentate ligands

A ligand that is attached to a central metal ion by bonds from two or more donor atoms.

(d) Chelating ligands

Polydentate ligands whose structures permit the attachment of two or more donor site to metal ion simultaneously, thus resulting in cyclic structure are called chelating ligands and compound formed is known as chelate compound.

(e) Ambidentate ligands

Ligands which can ligate through two different atoms present in it are called ambidentate ligands.

At a time only one atom can donate.

(f) Flexidentate Ligands

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

(C) Based upon bonding interaction between the ligand and the central atom.

(i) Classical or simple ligand

These ligand only donate the lone pair of electrons to the central atom.

(ii) Non classical or π-acid or π - acceptor ligand

These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom.

On the basis of nature of donating electron cloud these ligands are following types.

(a) σ donar π acceptor

Ex. CO, CN^-

(b) π donar π acceptor

Ex. C_2H_4, C_6H_6

MIND MAP

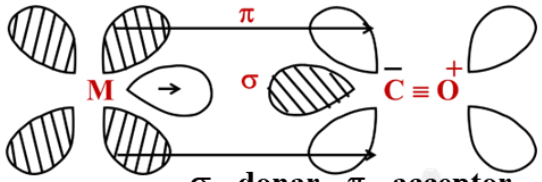
Coordination Compound

Bonding in coordination compounds

Due to presence of p acid ligands special type of bonding takes place in coordination compounds. It is known as synergic bonding.

Bonding in metal carbonyl

Ex. [Fe(CO)5] ; [Ni(CO)4] ; [Cr(CO)6]



σ - donar , π - acceptor

Organo-metallic Compounds

The compounds in which metal carbon linkage is present are known as organo-metallic compounds.

1. σ-bonded organometallic compounds

σ -bond between metal and carbon.

2. π-bonded organometallic compounds

(i) σ-donar and π-acceptor

$[Ni(CO)_4]$, $[Fe(CO)_5]$ etc.

(ii) π -donar and π-acceptor

$[Fe(C_2H_5)_2]$, $[Cr(C_6H_6)_2]$ etc.

Sidgwick Theory or Effective Atomic Number Concept (EAN)

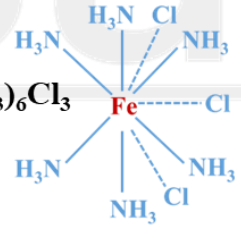
EAN = (atomic number of the metal – oxidation state of central metal) + number of electrons gained from the donor atoms of the ligands.

Werner's Co-ordination Theory

Werner's co-ordination theory was the first attempt to explain the bonding in co-ordination compounds.

Werner's Representation of Complex

(i) $Fe(NH_3)_6Cl_3$



Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.

Stereo Isomerism

They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion.

Geometrical Isomerism

(i) The ligands occupy different positions around the central metal ion.

(ii) When two identical ligands are coordinated to the metal ion from same side then it is cis isomer.

Geometrical isomers with coordination number = 4 (Square planar complexes)

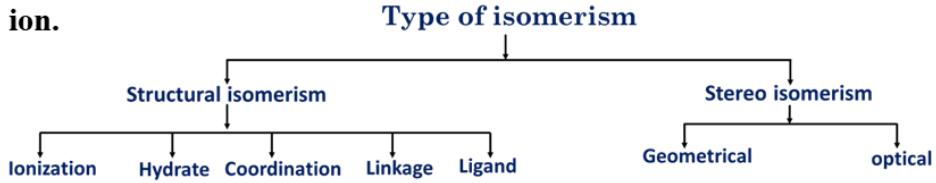
Ma_4, Ma_3b, $M(AA)_2$, $M(AA)a_2$, $M(AA)ab$, $M(AB)a_2$, $M(AA)(AB)$, $M(AA)(BB)$ can't show GI.

$[Pt(NH_3)_2Cl_2]$

Cis(Cis-platin) anti cancer

Trans

Classification of Isomerism



MIND MAP

Coordination Compound

Valence Bond Theory

(a) The metal ion under the influence of ligands can use its vacant d(n-1), ns, np, nd orbitals for hybridisation.

CN	Hybridisation	Molecular Geometry	Ex
2	sp	Linear	$[Ag(NH_3)_2]^+$ $[Ag(CN)]^-$
3	sp^2	Trigonal Planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[ZnCl_4]^{-2}$ $[FeCl_4]^-$ $[Ni(CO)_4]$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$
4	d^3s ($d=d_{xy}, d_{yz}, d_{zx}$)	Tetrahedral	

CN	Hybridisation	Molecular Geometry	Ex
4	$dsp^2(d=d_{x^2-y^2})$	Square planar	$[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^+$
5	sp^3d ($d=d_{z^2}$) or dsp^3 ($d=d_{z^2}$)	Trigonal bipyramidal	$[Fe(CO)_5]$ $[CuCl_5]^{3-}$
5	sp^3d ($d=d_{x2-y2}$) or dsp^3 ($d=d_{x2-y2}$)	Square pyramidal	$[Ni(CN)_5]^{-3}$
6	d^2sp^3 (inner orbital complex) or sp^3d^2 (outer orbital complex) in both case d-orbitals are d_{z^2} & $d_{x^2-y^2}$	Octahedral	$[Ti(H_2O)_6]^{+3}$ $[PtCl_6]^{-2}$ $(COF_6)^{-3}$

Factors Influencing the Magnitude of C.F.S.E

1. Higher the CFSE value higher will be the stability of complex
2. Chelated complexes are more stable than non-chelated complexes given the donor atoms are same
3. Same charges on the cation but the number of d-electrons is different

Crystal Field Theory

The drawbacks of VBT of coordination compounds are to a considerable extent removed by the Crystal Field Theory.

Stability of Coordination Compound

The stability of a coordination compound [MLn] is measured in terms of the stability constant (equilibrium constant, Kf).