CHAPTER 30

Coordination Chemistry

Addition compound

(two or more simple salt combining with fixed proportion of mass)

Double salt

* Loose their identity in aqueous solution

eg. $KCl.MgCl_2.6H_2O$ carnalite salt

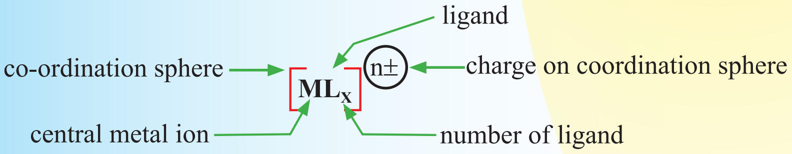
$K_2SO_4Al_2(SO_4)_3.24H_2O$ potash alum

Co-ordination compound

* Retain their indentity in aqueous solution

eg. $K_4[Fe(CN)_6]$ Potassium hexacyanidoferrate (II)

REPRESENTATION OF COMPLEX COMPOUND



Co-ordination number = Number of electron pair accepted by central metal ion.

LIGAND

Chemical species which can donates electron pair.

Classification on the Basis of Denticity

(Denticity : –Number of electron pair donated by central metal atom or ion)

Monodentate (denticity = 1) :

eg. H^-, X^-, Py, N_2, N^{3-}, N_2H_4 etc.

Bidentate (denticity = 2) :

eg. en, pn, bn, ox^{2-}, $acac^{-1}$, gly^{-1}, dmg^{-1}

Polydentate (denticity = 2):

eg. dien, trien, $EDTA^{4-}$

Ambidentate : Ligand which have more than one donor site but at the time of donation only atom can donate electron pair.

eg. : (CN^-, NC^-), (NO_2^- , ONO^-), (SCN^-, NCS^-), (OCN^-, NCO^-), ($S_2O_3^{2-}$, SO_2S^{2-})

Flexidentate ligand : Show more than one type of denticity.

eg. : CO_3^{2-}, SO_4^{2-}, CH_3COO^-

NOTES

Bidentate and Polydentate are also called chelating ligand.

Classification on the basis of electron donating and accepting tendency

Classical ligand : H_2O, NH_3 etc.

Non-classical ligand : CN^-, NO^+, NO, CO, PPh_3

π – donor ligand $\Rightarrow$ C_2H_4, C_2H_2 etc.

BONDING IN COORDINATION COMPOUND

Effective atomic number & Sidgwick rule

Total number of electron present on central metal atom or ion after accepting the electron pair from ligand.

$$K_4[\overset{+6}{Fe}(CN)_6]$$

$$EAN = 26 - (+2) + 6(2) = 36$$

- If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.
- In carbonyl complex, if EAN value = Atomic number of Noble gas then carbonyl complex is more stable.

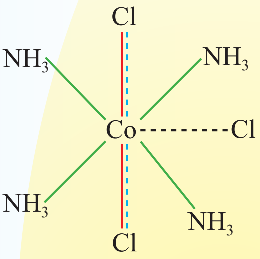
eg.	$[V(CO)_6]$	$[Cr(CO)_6]$	$[Mn(CO)_6]$
	act as oxidising agent	stable complex	act as reducing agent

Brown ring complex	**37**
Sodium nitroprusside	36
Zeise's Salt	84
$Mn_2(CO)_{10}$	36
$Fe_2(CO)_9$	36
$Co_2(CO)_8$	36

WERNER'S CO-ORDINATION THEORY

- Metals possesses two types of valencies PV & SV.
- PV is non-directional, represent by .... (doted line) is satisfied by negative charge species.
- SV is directional, represent by __________ (solid line) and satisfied by negative or neutral species.
- Now a days primary valency and secondary valency is consider as oxidation & co-ordination number respectively.

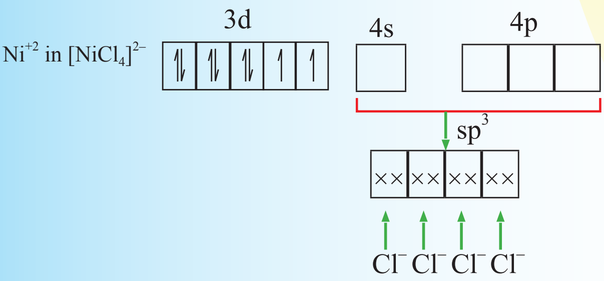
eg. $CoCl_3.4NH_3$
PV = 3, SV = 6
C.N. = 6, Oxidation state = +3



VBT

- Metal provoide hybridised vacant orbital for the acceptance of lone pair from ligand.
- Hybridisation, shape and magnetic behaviour of complex depends upon the nature of ligand.
- Strong field ligand pair up the unpaired e^- of central metal atom where as weak field ligand does not.
- If unpaired e^- present in complex then complex is paramagnetic. If unpaired e^- is absent then diamagnetic.

  eg. CN = 4 ; $[NiCl_4]^{2-}$



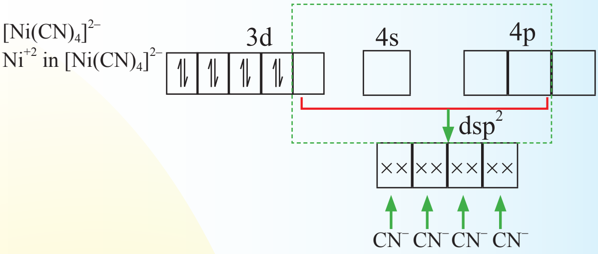
→ Sp^3

→ Tetrahedral

→ Paramagnetic

→ outer Orbital complex

→ $\mu = \sqrt{8}$ BM

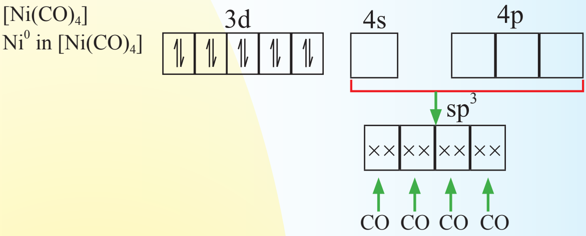


→ dsp^2

→ Square planar

→ Diamagnetic

→ Inner Orbital complex



→ sp^3

→ Tetrahedral

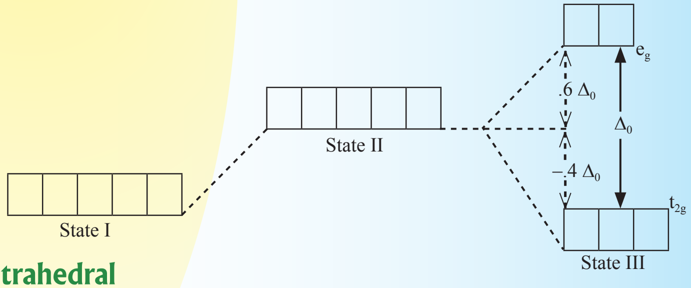
→ Diamagnetic

→ Outer Orbital complex

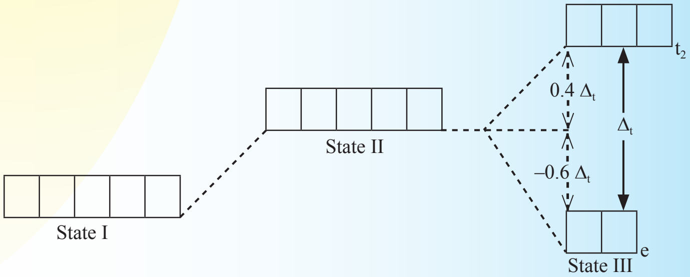
CRYSTAL FIELD THEORY

Crystal Field Theory : In the electric field of these negative charges, the five d-orbitals of the metal atom no longer have exactly same energy. Splitting of five degenerate d-orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting.

In octahedral



In tetrahedral



Orbitals which have same energy in a subshell are known as degenerate orbitals.

Series which shows the Relative Strength of Ligands

I^- (weakest) < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < $C_2O_4^{2-}$ < H_2O < NCS^- < $edta^{4-}$ < NH_3 < en < CN^- < CO(strongest)

Crystal Field Stabilisation Energy (CFSE)

(i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{eg})]\,\Delta_0$ + Paring energy (P.E.) × x

Where $n_{t_{2g}}$ = number of electron in t_{2g} orbitals
n_{eg} = number of electron in eg orbitals
x = number of elctron pair

(ii) For tetrahedral CFSE

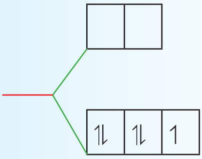
= $[-0.6(n_e) + 0.4\ (n_{t_2})\ \Delta_t$ + Paring energy **(P.E.)** × x]

where n_{t_2} = number of electron in t_2 orbitals
n_e = number of electron in e orbitals
x = number of electron pair

⇒ Follow Hund's Pauli & Aufbau rule.

CN-6

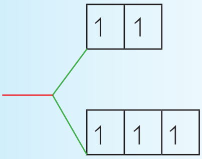
eg. $K_3[Fe(CN)_6]$
Fe^{+3}
CN^-SFL
$\Delta_0 > P$



d^2sp^3, Octahedral low spin complex, inner orbital complex, paramagnetic

$\mu = \sqrt{3}$ BM

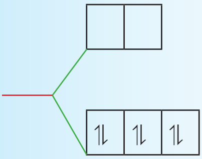
$Fe(F)_6]^{3-}$
Fe^{+3}
F^-WFL
$\Delta_0 < P$



sp^3d^2, Octahedral high spin complex, outer orbital complex, paramagnetic

$\mu = \sqrt{35}$ BM

$[IrF_6]^{3-}$
Ir^{+3}
$\Delta_0 > P$



d^2sp^3, Octahedral low spin complex, inner orbital complex, paramagnetic

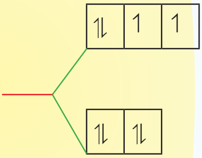
Exception

$[Co(OX)_3]^{3-}$	d^2sp^3	diamagnetic
$[Co(H_2O)_6]^{3+}$	d^2sp^3	diamagnetic
$[NiF_6]^{2-}$	d^2sp^3	diamagnetic
$[Cr(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Mn(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Fe(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[CoL_6]^{4-}$ ($L = NO_2^-/CN^-$)	d^2sp^3	paramagnetic

CN-4

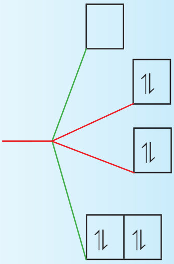
eg.

$[NiCl_4]^{2-}$



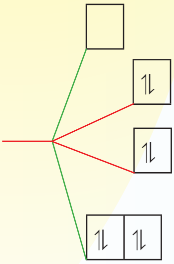
sp^3, Tetrahedral
Outer orbital complex, paramagnetic high spin complex

$[Ni(CN)_4]^{2-}$



dsp^2, Sq. planar
inner orbital complex,
paramagnetic
low spin complex

$[AuCl_4]^-$



dsp^2, Sq. planar
inner orbital complex,
paramagnetic
low spin complex,

Exception

- d^3s hybridisation, Td, diamagnetic, inner orbital complex eg.

  $MnO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, CrO_2Cl_2, CrO_2F_2, VO_4^{3-}$

- Transference of electron
  eg. Cu^{+2} in CN–4 with L
  (where L = NO_2^- / CN^- / NH_3 etc.)

Factor affecting splitting

(i) Strength of ligand
(ii) Oxidation state of central metal ion
(iii) Transition series (d-series)
(iv) Geometry (number of ligands)
(v) Chelation

Colour of complexes

Colour

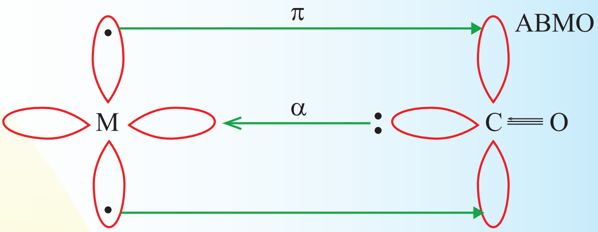
d-d transition
→ d^1-d^9 complex can show colour.
→ Complementry colour of absorb colour is observe.
eg. : $[Ti(H_2O_6)]^{3+}$, $[Ni_1(H_2O)_6]^{2+}$ $[Cu(NH)_4]^{2+}$

Charge transfer
→ Metal-metal charge transfers or metal ligand charge transfers
→ MnO_4^-, brown ring complex sodium nitroprusside purssian blue, turnbull's blue

ORGANOMETALLIC COMPOUNDS

Compounds in which the less E.N. (Ge, Sb, B, Si, P, As) central metal atoms are bonded directly to carbon atoms are called organometallic compounds.

- σ-bonded compounds formed by nontransition elements.
  R-Mg-X, $(CH_3–CH_2)_2$ Zn, Ziegler natta catalyst, etc.
- π-bonded organometallic compounds are generally formed by transition elements e.g. Zeise's salt, ferrocene, dibenzene chromium, etc.
- σ-and π-bonded organometallic compounds : Metal carbonyls compounds formed between metal and carbon monoxide belong to this class. $Ni(CO)_4$, $Fe(CO)_5$ etc.



IUPAC nomenclature of complex compounds

- **For anionic complex (like $K_4[Fe(CN)_6]$)**
  Common name of normal cation (without numeral prefix) + name of ligands (with numeral prefix) + latin name of CMI along with suffix ate + oxidation state (in roman number).
  eg. : Potassium hexacyanoferrate (II)
- **For cationic complex like $[Cu(NH_3)_4]SO_4$**
  Name of ligands (with numeral prefix) + Common name of CMI + oxidation state (In roman number) + Name of anion (without numeral prefix)
  eg. : Tetraammine copper (II) sulphate.
- **For neutral complex (like $[Fe(CO)_5]$)**
  Name of ligands (with numeral prefix)
  + Common name of CMI + oxidation state (In roman number)
  eg. : Pentacarbonyl iron (O)
- **Rule same just apply alphabetical order when write the name of ligands**
  e.g. $[Pt(NH_3)_2Cl_2]$
  Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

- **Ionisation isomerism :** Counter ion as a ligand & ligand act as counter ion.
  $[Co(H_2O)_5Cl]SO_4 \rightarrow [Co(H_2O)_5SO_4]Cl$
- **Hydrate isomersim :** Number of water molecule inside & outside the co-ordinate sphere are different.
  $[Cr(H_2O)_6]Cl_3 \leftrightarrow [Cr(H_2O)_5Cl]Cl_2.H_2O \leftrightarrow [Cr(H_2O)_4Cl_2]Cl.2H_2O$
- **Linkage :** Exihibit when ambidentate ligand is present in co-ordination sphere.
  $[NC \rightarrow Ag \leftarrow CN]^- \leftrightarrow [NC \rightarrow Ag \leftarrow NC]^- \leftrightarrow [CN \rightarrow Ag \leftarrow NC]^-$
- **Co-ordination isomerism :** Exihibit when both are cationic & anionic complex
  $[Pt(NH_3)_4]\ [PtCl_4] \leftrightarrow [Pt(NH_3)_3Cl]\ [Pt(NH_3)Cl_3]$

STEREO ISOMERISM

Stereo Isomerism in Co-ordination Compound

CN-4

- Square planar complex does not show optical isomerism.
- Square planar complex show optical activity if the cooridinated ligand having chiral center.
- Square planar complex
  $[Ma_2b_2]^{n\pm}$, $[Ma_2bc]^{n\pm}$, $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$
  $[M(AB)(CD)]^{n\pm}$ show geometrical isomerism
- $[Mabcd]^{n\pm}$ form two cis and one trans.
- Tetrahedral com plex $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$ $[M(AB)(CD)]^{n\pm}$ show optical isomerism
- Tetrahdral complex does not show geometrical isomerism.

CN-6

Number of Possible Isomers for Specific Complexes

Formula	Number of stereoisomers	Pairs of Enantiomers	Number of G.I.
Ma_4b_2	2	0	2
Ma_3b_3	2	0	2
Ma_4bc	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	5	1	4
$Ma_2b_2c_2$	6	1	5
Ma_2b_2cd	8	2	6
Ma_2bcde	15	6	9
Mabcdef	30	15	15
M(AA)(BC)de	10	5	5
M(AB)(AB)cd	11	5	6
M(AB)(CD)ef	20	10	10
$M(AB)_3$	4	2	2

NOTES

Uppercase letter represent chelating ligands and lowercase letter represent monodentate ligands.