CHAPTER
5

COORDINATION CHEMISTRY

Addition compound

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

Double salt

* Loose their idenity in aqueous solution

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

$K_2SO_4^-.Al_2(SO_4)_3.24H_2O$

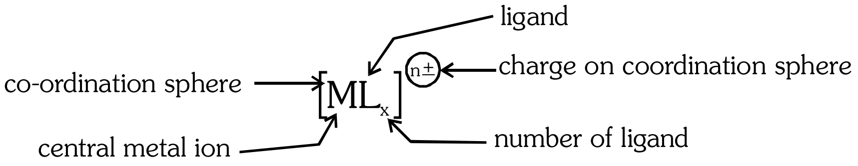
potash alum

C-ordination compound

* Retain their indenity in aqeous solution

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

Calssification of 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, $imda^{-2}$, trien, nta^{3-}, $EDTA^{4-}$

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^-

Note : Bidentate and Polydentate are also called chelating ligand.

* **Calssification on the basis of electron donating and accepting tandency**

Classsical ligand : H_2O, NH_3 etc.

Non-calssical ligand : CN^-, NO^+, NO, CO, PPh_3 etc

$\Rightarrow$ 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.

$$K_4[\overset{+2}{Fe}(CN)_6]$$

EAN = 26 – (+2) + 6(2) = 36

$\Rightarrow$ If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.

$\Rightarrow$ 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

$\Rightarrow$

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 :

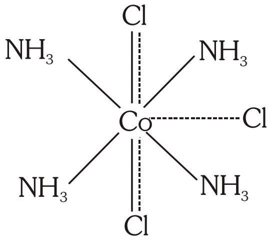
⇒ Metals possesses two types of valencies PV & SV.

⇒ 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 acceptence of lone pair from ligand.

⇒ Hybridisation, shape and magnatic behaviour of complex depends upon the nature of ligand.

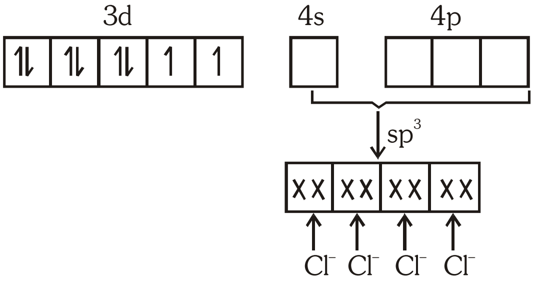
⇒ Strong field ligand pair up the unpaired e^- of central metal atom where as weak field ligand does not.

⇒ If unpaired e^- present in complex then complex is paramagnatic. If unpaired e^- is absent then diamagnatic.

eg. CN-4

$[NiCl_4]^{2-}$

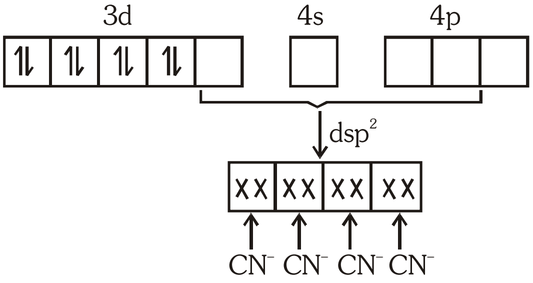
NI^{+2} in $[NiCl_4]^2$



→ sp^3
→ Tetrahedral
→ Paramagnatic
→ Outer Orbital complex
→ $\mu = \sqrt{8}$ BM

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

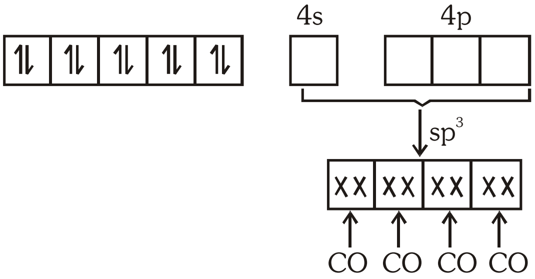
NI^{+2} in $[Ni(CN)_4]^{2-}$



→ dsp^2
→ Square planar
→ Diamagnatic
→ Inner Orbital complex

$[Ni(CO)_4]$

NI^{+2} in $[Ni(CO)_4]$

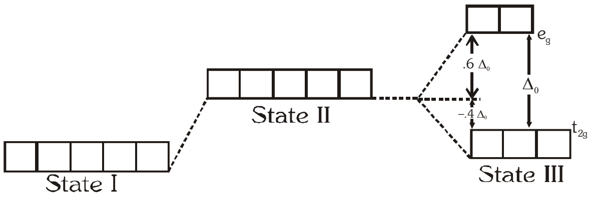


→ sp^3
→ Tetrahedral
→ Diamagnatic
→ Outer Orbital complex

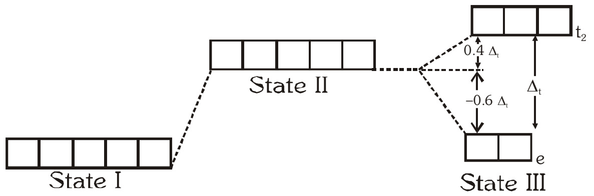
CRYSTAL FIELD THEORY

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 stablisation energy (CFSE) :**

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

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

(ii) For tetrahedral CFSE

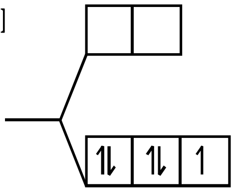
$= \left[-0.6\left(n_e\right) + 0.4\left(n_{t_2}\right)\right]\Delta_t$ +Paring energy **(P.E.)** $\times x$

where n_{t_g} = 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.

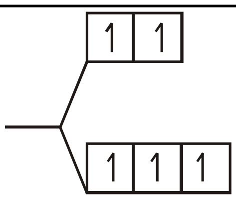
CN-6

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



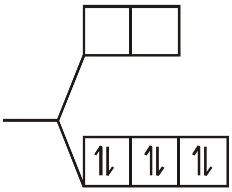
d^2sp^3, Octahedral
low spin complex,
inner orbital complex,
paramagnatic
$\mu = \sqrt{3}$ BM

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



sp^3d^2, Octahedral
high spin complex,
outer orbital complex,
paramagnatic
$\mu = \sqrt{35}$ BM

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



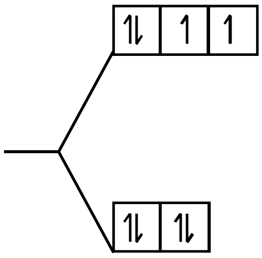
d^2sp^3, Octahedral
low spin complex,
inner orbital complex,
diamagnatic

Exeption :

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

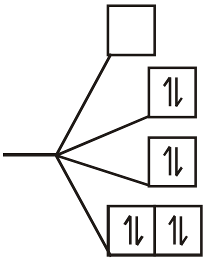
CN-4 :

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



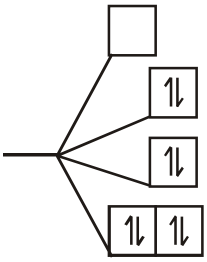
sp^3, Td
outer orbital complex,
paramagnatic
high spin complex

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



dsp^2, sq. planar
inner orbital complex,
diamagnatic
low spin complex

$[AuCl_4]^-$



ds^2, sq. planar
inner orbital complex,
diamagnatic
low spin complex,

Exception :

1. d^{3}s hybridisation, Td, diamagnetic, inner orbital complex
   eg.
   $MnO_4^-, CrO_4^{2-}, Cr_2O_7^{2-}, CrO_2Cl_2, CrO_2F_2, VO_4^{3-}$
2. Tranference 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 tranistion
→ d^1-d^9 complex can show colour.
→ Complementry colour of absorb colour is observe
eg. : $[T_1(H_2O)_6]^{3+}$, $[Ni_1(H_2O)_6]^{2+}$
$[Cu(NH)_4]^{2+}$

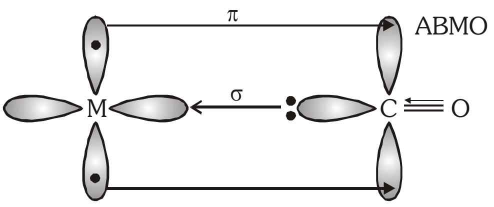
Charge transfer
→ Metal-metal charge transfers or metal ligand charge transfers
→ MnO_4^-, CrO_4^{2-}, $Cr_2O_7^{2-}$
brown ring complex
sodium nitroprusside
purssian blue, turnbull's blue

ORGANOMETALLIC COMPOUDS

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, $(CH_3–CH_2)_2Zn$, 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.

Synergic bonding



IUPAC nomenclature of complex compounds :

(A) 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 + Ox. St (in roman number).

eg. : Potassium hexacyanoferrate (II)

(B) For cationic comlex like $[Cu(NH_3)_4]SO_4$

Name of ligands (with numeral prefix) + Common name of CMI + Ox. St (In roman number) + Name of anion (without numeral prefix)

eg. : Tetraammine copper (II) sulphate.

(C) For neutral complex (like $[Fe(CO)_5]$

Name of ligands (with numeral prefix)
+ Common name of CMI + Ox. St.
(In roman number)

eg. : Pentacarbonyl iron (O)

(D) Rule same just apply alphabetical order when write the name of ligands.

e.g. $[Pt(NH_3)_2Cl_2]$
Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

(i) **Ionisation isomerism :** Counter ion as a ligand & ligand act as counter ion.
$[Co\ (H_2O)_5Cl]\ SO_4 \leftrightarrow [Co(H_2O)_5\ SO_4]\ Cl$

(ii) **Hydrate isomersim :** Number of water molecule inside & outside the co-ordinate sphere are different.
$[Cr(H_2O)_6]Cl_3 \leftrightarrow [Cr\ (H_2O)_5\ Cl]\ Cl_2.H_2O \leftrightarrow [Cr\ (H_2O)_4\ Cl_2]\ Cl.2H_2O$

(iv) **Linkage :** Exihibit when ambidentate ligand is present in co-ordination sphere.
$[NC \rightarrow Ag \leftarrow CN]^- \leftrightarrow [NC \rightarrow Ag \leftarrow NC]^- \leftrightarrow [CN \rightarrow Ag \leftarrow NC]^-$

(iv) **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 co-ordinated 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 complex $[Mabcd]^{n\pm}$, $[M(AB)cd]^{n\pm}$ $[M(AB)(CD)]^{n\pm}$ 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_4bc	2	0	2
Ma_3b_3	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

Note: Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.