

COORDINATION CHEMISTRY

Addition compound

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

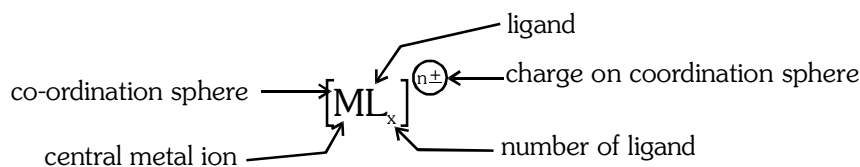
Double salt

* Loose their identity in aqueous solution
eg. $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ carnalite salt
 $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$
potash alum

C-ordination compound

* Retain their identity in aqueous solution
eg. $\text{K}_4[\text{Fe}(\text{CN})_6]$ Potassium
hexacyanidoferrate (II)

REPRESENTATION OF COMPLEX COMPOUND



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

LIGAND

Chemical species which can donate 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^- , gly^- , dmg^-

Polydentate (denticity = >2) :

eg. dien, imda²⁻, trien, nta³⁻, EDTA^{4-}

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

eg. : $(\text{CN}^-, \text{NC}^-)$, $(\text{NO}_2^-, \text{ONO}^-)$, $(\text{SCN}^-, \text{NCS}^-)$, $(\text{OCN}^-, \text{NCO}^-)$, $(\text{S}_2\text{O}_3^{2-}, \text{SO}_2\text{S}^{2-})$

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.

Classification on the basis of electron donating and accepting tendency

Classical ligand : H_2O , NH_3 etc.

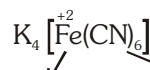
Non-classical ligand : CN^- , NO^+ , NO , CO , PPh_3 etc

$\Rightarrow \pi$ -donor ligand $\Rightarrow \text{C}_2\text{H}_4$, 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.



$$\text{EAN} = 26 - (+2) + 6(2) = 36$$

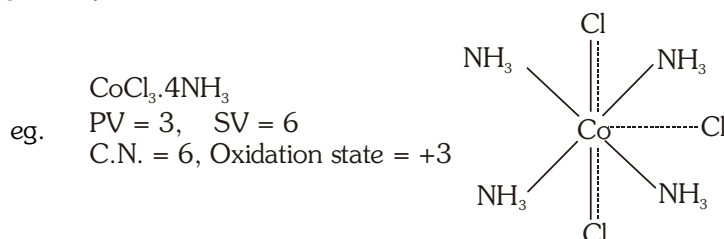
\Rightarrow If EAN value is equal to atomic number of Noble gas then complex follow sidgwick rule of EAN.

\Rightarrow In carbonyl complex if EAN value = Atomic number of Noble gas then carbonyl complex is more stable.

eg.	$[\text{V}(\text{CO})_6]$	$[\text{Cr}(\text{CO})_6]$	$[\text{Mn}(\text{CO})_5]$
	act as oxidising agent	stable complex	act as reducing agent

\Rightarrow	Brown ring complex	37
	Sodium nitroprusside	36
	Zeise's Salt	84
	$\text{Mn}_2(\text{CO})_{10}$	36
	$\text{Fe}_2(\text{CO})_9$	36
	$\text{Co}_2(\text{CO})_8$	36

- ⇒ Metals possesses two types of valencies PV & SV.
- ⇒ PV is non-directional, represent by (dotted 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.



- ⇒ Metal provide 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.

- sp^3
- Tetrahedral
- Paramagnetic
- Outer Orbital complex
- $\mu = \sqrt{8} \text{ BM}$

The diagram illustrates the crystal field splitting of the metal d-orbitals. At the top, the free ion orbitals are shown: five 3d orbitals (each containing one electron, represented by an upward and downward arrow), one empty 4s orbital, and five empty 4p orbitals. A bracket groups the 4s and 4p orbitals, with an arrow labeled dsp^2 pointing down to the complex orbitals. In the middle, the complex orbitals are shown: a lower-energy set of three orbitals (labeled t_{2g} in the original image) each containing a pair of electrons (XX), and an upper-energy set of two orbitals (labeled e_g in the original image) each containing a pair of electrons (XX). At the bottom, four cyanide ligands (CN^-) are shown with arrows pointing towards the t_{2g} orbitals, indicating the direction of ligand approach.

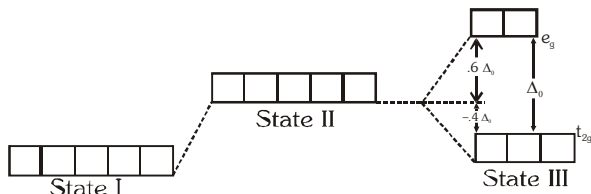
- Square planar
- Diamagnetic
- Inner Orbital complex

- Tetrahedral
- Diamagnetic
- Outer Orbital complex

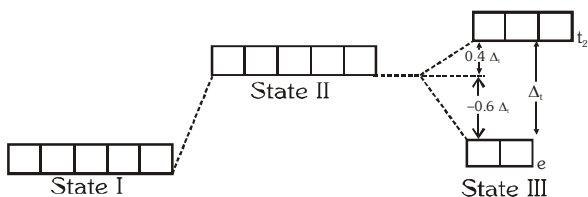
CRYSTAL FIELD THEORY

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 :

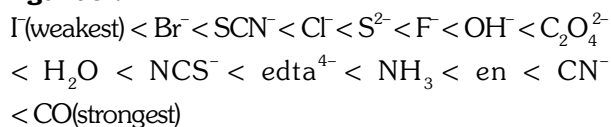


In tetrahedral :



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

➤ **Series which shows the relative strength of ligands :**



➤ **Crystal field stabilisation energy (CFSE) :**

(i) For octahedral CFSE = $[-0.4(n_{t_{2g}}) + 0.6(n_{e_g})] \Delta_o + \text{Paring energy (P.E.)} \times x$

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

(ii) For tetrahedral CFSE

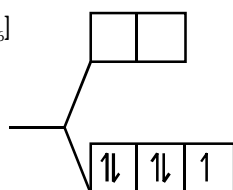
$$= [-0.6(n_e) + 0.4(n_{t_2})] \Delta_t + \text{Paring energy (P.E.)} \times x$$

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

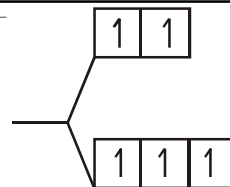
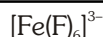
⇒ Follow Hund's Pauli & Aufbau rule.

CN-6

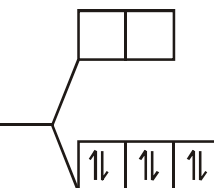
eg.



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



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



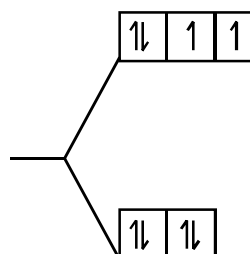
d^2sp^3 , Octahedral
 low spin complex,
 inner orbital complex,
 diamagnetic

Exeption :

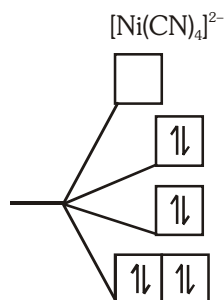
$[Co(OX)_3]^{3-}$	d^2sp^3	diamagnetic
$[Co(H_2O)_6]^{3+}$	d^2sp^3	diamagnetic
$[NiF_6]^{2-}$	d^2sp^3	diamagnetic
$[Cr(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Mn(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[Fe(NH_3)_6]^{2+}$	sp^3d^2	paramagnetic
$[CoL_6]^{4-}$ ($L = NO_2^-/CN^-$)	d^2sp^3	paramagnetic

CN-4 :

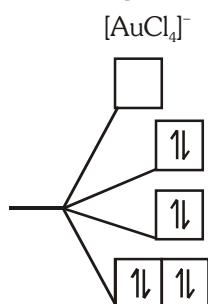
eg.



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



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



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

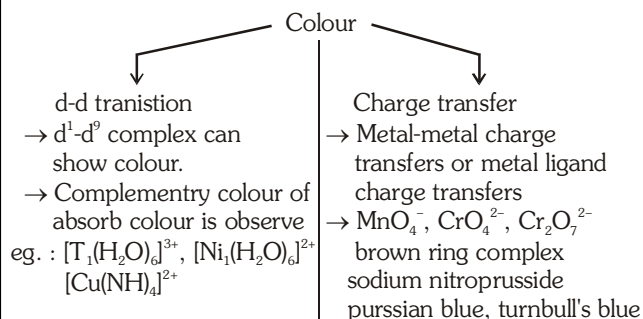
Exception :

1. d^3s hybridisation, Td , diamagnetic, inner orbital complex
eg.
 MnO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, CrO_2Cl_2 , CrO_2F_2 , VO_4^{3-}
2. Transference of electron
eg. Cu^{+2} in CN^- with L
(where $\text{L} = \text{NO}_2^- / \text{CN}^- / \text{NH}_3$ 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

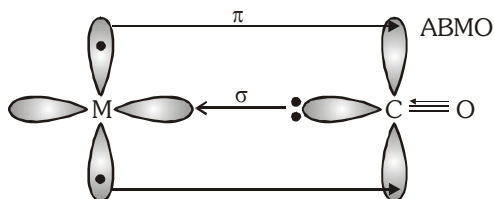


ORGANOMETALLIC COMPOUNDS

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 , $(\text{CH}_3\text{-CH}_2)_2\text{Zn}$, 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. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ etc.

Synergic bonding



IUPAC nomenclature of complex compounds :

- (A) For anionic complex (like $\text{K}_4[\text{Fe}(\text{CN})_6]$)
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 complex like $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
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 $[\text{Fe}(\text{CO})_5]$)
Name of ligands (with numeral prefix) + Common name of CMI + Ox. St. (In roman number)
eg. : Pentacarbonyl iron (0)
- (D) Rule same just apply alphabetical order when write the name of ligands.
e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
Diamminedichloroplatinum (II)

STRUCTURAL ISOMERISM

- (i) **Ionisation isomerism** : Counter ion as a ligand & ligand act as counter ion.
 $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{SO}_4 \leftrightarrow [\text{Co}(\text{H}_2\text{O})_5\text{SO}_4]\text{Cl}$
- (ii) **Hydrate isomersim** : Number of water molecule inside & outside the co-ordinate sphere are different.
 $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \leftrightarrow [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O} \leftrightarrow [\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
- (iv) **Linkage** : Exhibit when ambidentate ligand is present in co-ordination sphere.
 $[\text{NC} \rightarrow \text{Ag} \leftarrow \text{CN}]^- \leftrightarrow [\text{NC} \rightarrow \text{Ag} \leftarrow \text{NC}]^- \leftrightarrow [\text{CN} \rightarrow \text{Ag} \leftarrow \text{NC}]^-$
- (iv) **Co-ordination isomerism** : Exhibit when both are cationic & anionic complex
 $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4] \leftrightarrow [\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)_3\text{Cl}_3]$

STEREO ISOMERISM**STEREO ISOMERISM IN CO-ORDINATION COMPOUND****CN-4**

<p>* Square planar complex does not show optical isomerism.</p> <p>* Square planar complex show optical activity if the co-ordinated ligand having chiral center.</p> <p>* Square planar complex $[\text{Ma}_2\text{b}_2]^{n+}$, $[\text{Ma}_2\text{bc}]^{n+}$, $[\text{Mabcd}]^{n+}$, $[\text{M}(\text{AB})\text{cd}]^{n+}$, $[\text{M}(\text{AB})(\text{CD})]^{n+}$ show geometrical isomerism</p> <p>* $[\text{Mabcd}]^{n+}$ form two cis and one trans.</p>	<p>* Tetrahedral complex $[\text{Mabcd}]^{n+}$, $[\text{M}(\text{AB})\text{cd}]^{n+}$ $[\text{M}(\text{AB})(\text{CD})]^{n+}$ show optical isomerism</p> <p>* Tetrahedral complex does not show geometrical isomerism.</p>
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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
$\text{Ma}_3\text{b}_2\text{c}$	3	0	3
Ma_3bcd	5	1	4
$\text{Ma}_2\text{b}_2\text{c}_2$	6	1	5
$\text{Ma}_2\text{b}_2\text{cd}$	8	2	6
Ma_2bcde	15	6	9
Mabcdef	30	15	15
$\text{M}(\text{AA})(\text{BC})\text{de}$	10	5	5
$\text{M}(\text{AB})(\text{AB})\text{cd}$	11	5	6
$\text{M}(\text{AB})(\text{CD})\text{ef}$	20	10	10
$\text{M}(\text{AB})_3$	4	2	2

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