

#### **Addition compound**

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

#### . Double salt

\* Loose their idenity in aqueous solution eg. KCl.MgCl<sub>2</sub>.6H<sub>2</sub>O carnalite salt K<sub>2</sub>SO<sub>4</sub><sup>-</sup>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.24H<sub>2</sub>O potash alum

CHAPTER

#### **Co-ordination compound**

 Retain their indenity in aqueous solution
 eg. K<sub>4</sub>[Fe(CN)<sub>6</sub>] 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<sup>-</sup>, X<sup>-</sup>, Py, N<sub>2</sub>, N<sup>3-</sup>, N<sub>2</sub>H<sub>4</sub> etc.

**Bidentate** (denticity = 2) :

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

**Polydentate** (denticity = -2):

eg. dien, imda<sup>-2</sup>, trien, nta<sup>3-</sup>, EDTA<sup>4-</sup>

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



Bidentate and Polydentate are also called chelating ligand.

Classification on the basis of electron donating and accepting tendency Classical ligand : H<sub>2</sub>O, NH<sub>3</sub> etc.

**Non-classical ligand :** CN<sup>-</sup>, NO<sup>+</sup>, NO, CO, PPh<sub>3</sub>

 $\pi$  – donor ligand  $\Rightarrow$  C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> 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.

$$K_{4}[\ddot{F}e(CN)_{6}]$$
  
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) <sub>6</sub> ]	$[Cr(CO)_6]$	$[Mn(CO)_6]$	
	act as oxidising	stable	act as reducing	
	agent	complex	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 stisfied by negative or neutral species.
- Now a days primary valency and secondary valency is consider as oxidation & co-ordination number respectively.



#### 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<sup>-</sup> present in complex then complex is paramagnetic. If unpaired e<sup>-</sup> is absent then diamagnatic.

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





#### **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



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

#### Series which shows the Relative Strength of Ligands

 $[ (weakest) < Br^{-} < SCN^{-} < Cl^{-} < S^{2-} < F^{-} < OH^{-} < C_{2}O_{4}^{2-} < H_{2}O < NCS^{-} < edta^{4-} < NH_{3} < en < CN^{-} < CO(strongest)$ 

#### **Crystal Field Stabilisation Energy (CFSE)**

- (i) For octahedral CFSE =  $[-0.4(n_{t_{12}}) + 0.6(n_{eg})] \Delta_0 + Paring energy (P.E.) \times x$ 
  - Where  $n_{t_{2g}} =$  number of electron in  $t_{2g}$  orbitals
    - $n_{eg}$  = number of electron in eg orbitals

x = number of elctron pair

- (ii) For tetrahedral CFSE
  - =  $[-0.6(n_e) + 0.4 (n_{t_1}) \Delta_t + Paring energy (P.E.) \times x]$
  - where  $\mathbf{n}_{t_2} = \text{number of electron in } t_2 \text{ orbitals}$

 $n_e =$  number of electron in e orbitals

x = number of electron pair

 $\Rightarrow$  Follow Hund's Pauli & Aufbau rule.

CN-6



# Exception

$[Co(OX)_3]^{3-}$	d <sup>2</sup> sp <sup>3</sup>	diamagnetic
$[Co(H_2O)_6]^{3+}$	d <sup>2</sup> sp <sup>3</sup>	diamagnetic
$\left[\mathrm{NiF}_{6}\right]^{2-}$	d <sup>2</sup> sp <sup>3</sup>	diamagnetic
$\left[\mathrm{Cr(NH}_{3})_{6}\right]^{2+}$	$sp^{3}d^{2}$	paramagnetic
$\left[\mathrm{Mn}(\mathrm{NH}_3)_6\right]^{2+}$	sp <sup>3</sup> d <sup>2</sup>	paramagnetic
$[Fe(NH_3)_6]^{2+}$	sp <sup>3</sup> d <sup>2</sup>	paramagnetic
$[\text{CoL}_6]^{4-}(\text{L} = \text{NO}_2^{-}/\text{CN}^{-})$	d <sup>2</sup> sp <sup>3</sup>	paramagnatic

[NiCNl<sub>4</sub>]<sup>2-</sup>

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#### **CN-4**



dsp<sup>2</sup>, Sq. planar inner orbital complex, paramagnetic low spin complex,

#### Exception

• d<sup>3</sup>s hybridisation, Td, diamagnetic, inner orbital complex eg.

 $MnO_{4}^{-}, CrO_{4}^{2-}, Cr_{2}O_{7}^{2-}, CrO_{2}Cl_{2}, CrO_{2}F_{2}, VO_{4}^{3-}$ 

• 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

- $\rightarrow$  d<sup>1</sup>-d<sup>9</sup> 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<sub>4</sub>, 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<sub>3</sub>-CH<sub>2</sub>)<sub>2</sub> 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)<sub>4</sub>, Fe(CO)<sub>5</sub> etc.



# **IUPAC nomenclature of complex compounds**

- For anionic complex (like K₄[Fe(CN)<sub>6</sub>])
  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<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>

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)<sub>5</sub>]) 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<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] 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.

 $[\mathrm{NC} \to \mathrm{Ag} \leftarrow \mathrm{CN}]^{-} \leftrightarrow [\mathrm{NC} \to \mathrm{Ag} \leftarrow \mathrm{NC}]^{-} \leftrightarrow [\mathrm{CN} \to \mathrm{Ag} \leftarrow \mathrm{NC}]^{-}$ 

• **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<sub>2</sub>b<sub>2</sub>]<sup>n±</sup>, [Ma<sub>2</sub>bc]<sup>n±</sup>, [Mabcd]<sup>n±</sup>, [M(AB)cd]<sup>n±</sup>

  [M(AB)(CD)]<sup>n±</sup> show geometrical isomerism
- [Mabcd]<sup>n±</sup> form two cis and one trans.
- Tetrahedral com plex [Mabcd]<sup>n±</sup>, [M(AB)cd]<sup>n±</sup>[M(AB)(CD)]<sup>n±</sup> show optical 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 <sub>3</sub> b <sub>3</sub>	2	0	2					
Ma <sub>4</sub> bc	2	0	2					
Ma <sub>3</sub> b <sub>2</sub> c	3	0	3					
Ma <sub>3</sub> bcd	5	1	4					
$Ma_2b_2c_2$	6	1	5					
Ma <sub>2</sub> b <sub>2</sub> cd	8	2	6					
Ma <sub>2</sub> bcde	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) <sub>3</sub>	4	2	2					

• Tetrahdral complex does not show geometrical isomerism.

NOTES

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