

# Coordination Compounds<sup>1</sup>

## Introduction

\* Coordination compounds :

- textile dyeing
- medicinal chem
- electroplating
- industrial catalyst.
- analytical reagents

- metallurgical processes.
  - chlorophyll
  - Haemoglobin
  - Vit B<sub>12</sub>
- } C.C OF Mg, Fe and Co.

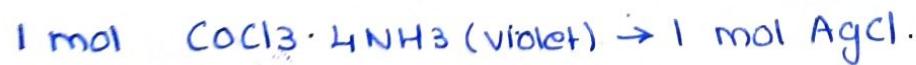
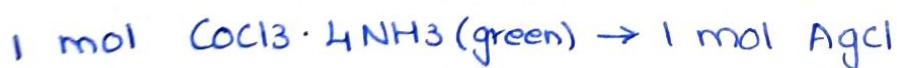
## Werner's theory of coordination compounds

- \* Alfred Werner - Swiss chemist - 1st to formulate strl. of C.C.
- \* proposed the concept of 1°, 2° valence for a metal ion.

Ex: 1° valence



- \* Exp: Series of comp. of CoCl<sub>3</sub> with NH<sub>3</sub> precipitated AgCl on addition of excess AgNO<sub>3</sub> in cold.



Here 6 grps in all (either Cl<sup>-</sup> or NH<sub>3</sub> or both) remain bonded to cobalt ion during the reac. the compounds are formulated:

Colour

Formula

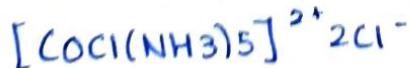
Sol. conductivity corresponds

Yellow



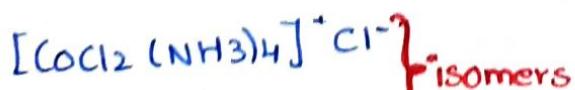
1 : 3 electrolyte

Purple



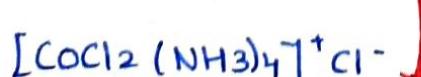
1 : 2 electrolyte

Green



1 : 1 electrolyte

Violet



1 : 1 electrolyte

} Isomers

- \* In 1898, Werner propounded his theory of C.C with 4 postulates:
- In C.C metals show two types of linkages (valences)
    - primary and secondary
  - Primary valences are normally ionisable and are satisfied by negative ions.
  - Secondary valences are non ionisable.
    - bound directly to metal.
    - equal to coordination number and is fixed for a metal.
    - satisfied by neutral molecules or negative ions.
  - Ions/groups bound by secondary linkages to the M have characteristic spatial arrangement / coordination polyhedra corresponding to different coordination no.
  - Geometrical shapes for C.C of transition metals
    - Octahedral -  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ ,  $[\text{CoCl}_2(\text{NH}_3)_4]$
    - Tetrahedral -  $[\text{Ni}(\text{CO})_4]$
    - Square Planar -  $[\text{Pt}(\text{I}_4)]^{2-}$

### Difference between :-

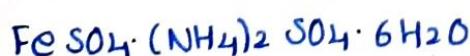
#### DOUBLE SALT

\* dissociates into simple ions in  $\text{H}_2\text{O}$  completely.

\* Ex: Potash Alum



Mohr's Salt

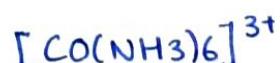


Carnallite



#### COORDINATION COMPLEX

\* doesn't dissociate into ions.



# Definitions of some imp. terms pertaining to coordination compounds:

## A) Coordination Entity

- \* central metal atom/ion bonded to fixed no. of ions/molecule
- \* Ex:  $[\text{Ni}(\text{CO})_4]$ ,  $[\text{CoCl}_3(\text{NH}_3)_3]$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$

## B) Central atom/ion

- \* the atom/ion to which fixed no. of ions/grps are bound in definite geometrical arrangement.
- \* also referred to as Lewis acids.
- \* Ex:  $[\text{NiCl}_2(\text{H}_2\text{O})_4] \rightarrow \text{Ni}^{2+}$   
 $[\text{Fe}(\text{CN})_6]^{3-} \rightarrow \text{Fe}^{3+}$ .

## C) Ligands

- \* the ion/molecule bound to central atom/ion.

### \* Ex:

Simple ions -  $\text{Cl}^-$

Small molecules -  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  Large molecules -  $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)$

Macromolecules - proteins

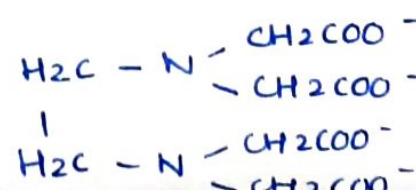
### \* Types:

1. Unidendate - bound through 1 donor ( $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ )
2. Didendate - " " 2 donors (en, ox)
3. Polydentate - " " many "  $[\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3]$ , EDTA

en - ethane - 1,2-diamine ( $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{NH}_2$ )

ox - oxalate  $[\text{C}_2\text{O}_4^{2-}]$

EDTA $^{4-}$  = ethylenediamine tetra acetate  
 (4 oxygen, 2 nitrogen)



In di- or polydentate ligand

↓

## DENDICITY

(no. of ligating grp present)

## chelate

## Ambidentate

- 2 or more donor atom simultaneously bind to single metal ion.
  - Chelate complexes are more stable
  - Ex: en which bonds to metal ion ↑ each of the 2 nitrogens.

- Either of the donor atoms ligates in the complex.



D) Coordination number (CN)

\* **ON** of a metal ion is the no. of ligand donor atoms to which the metal is directly bonded.

\* Ex:



\*only the no of sigma bonds formed by the ligand with the central ion/atom is counted.

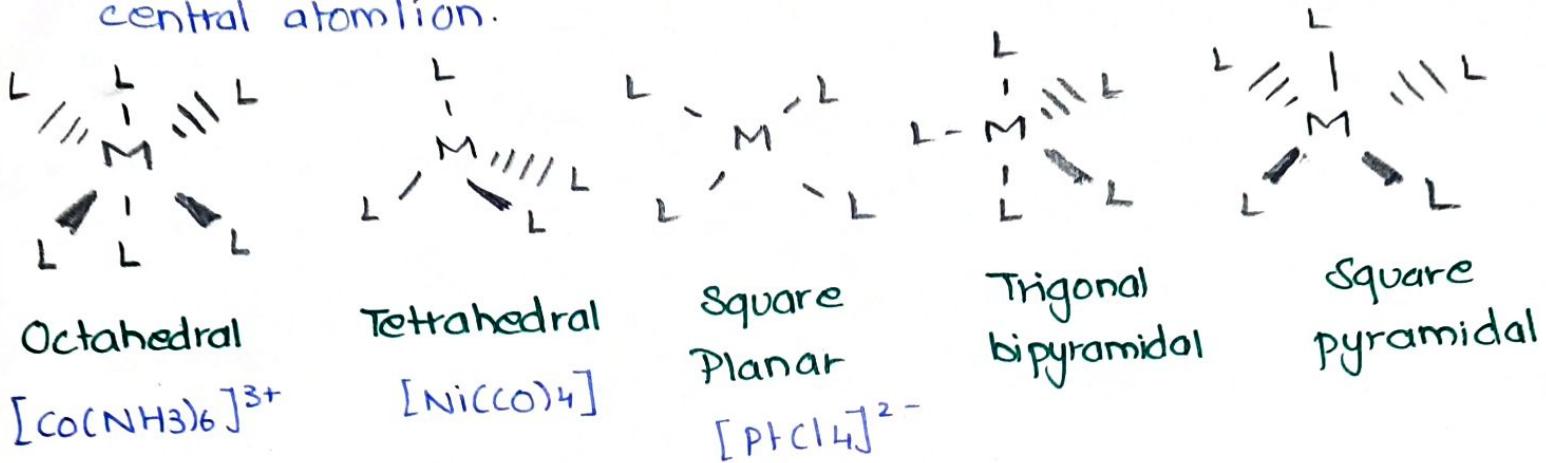
## E) Coordination Sphere

\* the central atom/ion + ligands are enclosed in the square bracket and called coordination sphere.

\* ionisable ion outside the bracket - counter ion.  
For example - concentration

## F) Coordination polyhedron

\* spatial arrangement of ligand atoms directly attached to central atom/ion.



## G) Oxidation No. of Central Atom

\* charge it would carry if all the ligands are removed along with the  $\sigma$  pairs that are shared with central atom.

\* represented by roman numeral in parenthesis.

\* Ex:  $[\text{Cu}(\text{CN})_4]^{3-} \rightarrow \text{Cu(I)}$

## H) Homoleptic and heteroleptic complexes

\* Complexes in which a metal is bound to only one kind of donor groups - Homoleptic  $[\text{Co}(\text{NH}_3)_6]^{3+}$

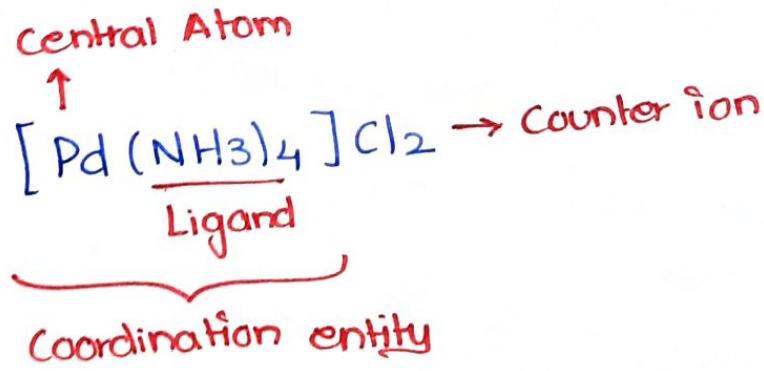
\* Complexes in which a metal is bound to more than one kind of donor groups - Heteroleptic  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

## Some common ligands & their charge:

Ligand	Formula	Donor Atom	charge
Water	$\text{H}_2\text{O}$	O	0
Ammonia	$\text{NH}_3$	N	0
Pyridine	$\text{C}_6\text{H}_5\text{N}$	N	0
carbonyl	CO	O	0
Nitrosyl	NO	N	0
Triphenyl phosphine	$(\text{C}_6\text{H}_5)_3\text{P}$	P	0

Halide ion	$x^-$	$x$	-1
Hydroxide ion	$\text{OH}^-$	O	-1
Cyanide ion	$\text{CN}^-$	N or C	-1
Nitro	$\text{NO}_2^-$	N	-1
Nitrito	$\text{ONO}^-$	O	-1
Oxide ion	$\text{O}^{2-}$	O	-2
Thiocyanate	$\text{SCN}^-$	S or N	-1
Acetate	$\text{CH}_3\text{COO}^-$	O	-1
Carbon monoxide	CO		0
Sulphate ion	$\text{SO}_4^{2-}$	O	-2
en		O	
ox			-2
EDTA			-4

### Note



- Oxi. no. of Pd  $\Rightarrow x + 0 - 2 = 0 \quad \therefore x = 2$
- homoleptic
- CN = 4.

## Nomenclature of coordination compounds

### i) Formulas of mononuclear coordination entities

1. Central Atom is listed first.
2. Ligands are listed in alphabetical order.
3. Polydendate ligands are also listed alphabetical. For abbreviated ligands, first letter of abbreviation is used.
4. Enclosed in square brackets. Ligands abb. or polyatomic are enclosed in parenthesis.
5. There should be no space b/w ligands & metal in coordination sphere.
6. Charge is indicated outside the [ ] as a right superscript with the number before the sign.
7. The charge of the cation(s) is balanced by the charge of the anion(s).

### ii) Naming of mononuclear coordination compounds :

1. The cation is named first in both positively and negatively charged coordination entities.
2. Ligands are named in alphabetical order before name of central atom/ion.
3. Name of anionic ligands - end in o  
 " " neutral, cationic ligands - same [Exception - H<sub>2</sub>O - Aqua, NH<sub>3</sub> - ammine, CO - carbonyl, NO - nitrosyl]
4. Prefix - mono, di, tri.... to indicate no. of individual ligands  
 Prefix - bis, tris, tetrakis to indicate ligands that have numerical prefix.

5. Oxi. state of metal is represented by roman numeral in parenthesis.

6. In cationic complex - metal is named same as the element.

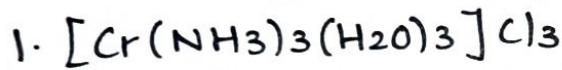
In anionic " - name of metal ends with suffix - ate.

[Exception - Fe - Ferrate  
Ag - Argentate]

7. name of counter ion.

- at first - anionic complex.
- at last - cationic complex.

### Examples:



→ complex is cationic.

→ Ligands - Ammine, Aqua  
(3) (3)

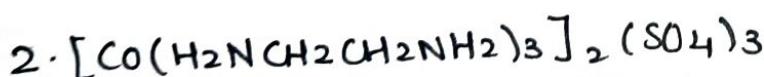
→ Calculate the oxi. state of Cr

$$x - 0 - 0 - 3 = 0$$

$$x = +3$$

So,

triammine-triaquachromium(III) chloride.



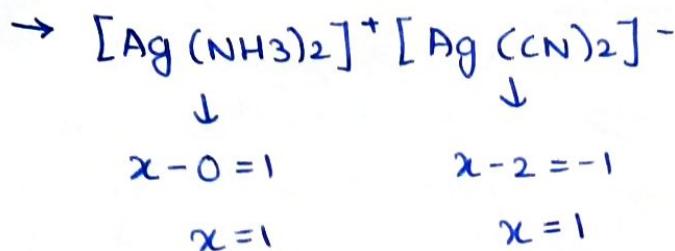
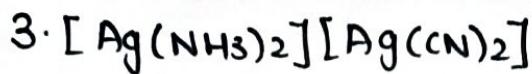
→ complex - cationic.

→ Ligands - en (3)

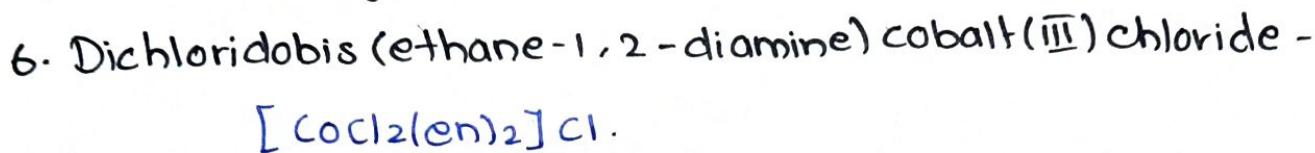
$$\rightarrow \text{oxi state } 2x - 0 - 6 = 0 \Rightarrow x = +3$$

So,

tris (ethane - 1, 2 - diamine) cobalt(III) sulphate.



diamminesilver (I) dicyanidoargentate (I)



## Bonding in Coordination Compounds

\* Nature of bonding in C.C

$\rightarrow$  VBT (Valence Bond Theory)  $\rightarrow$  LFT (Ligand field theory)

$\rightarrow$  CFT (Crystal Field " )  $\rightarrow$  MOT (Molecular Orbital theory).

### Valence bond theory

$\rightarrow$  metal atom/ion under the influence of ligands can use its  $(n-1)d$ ,  $ns$ ,  $np$  or  $ns$ ,  $np$ ,  $nd$  orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry.

$\rightarrow$  hybridised orbitals are allowed to overlap with ligand orbitals.

CN	Type of hybridisation	Distribution of hybrid orbitals
4	$sp^3$	tetrahedral
4	$dsp^2$	Square planar
5	$sp^3d$	Trigonal bipyramidal
6	$sp^3d^2$ (ooe)	Octahedral
6	$d^2sp^3$ (ioc)	Octahedral.

## \* Magnetic behaviour

- Paramagnetic - unpaired  $e\theta$ .
- Diamagnetic - no unpaired  $e\theta$

## \* Hybridisation

- $d^2sp^3$  - inner orbital / low spin / spin paired complex.
- $sp^3d^2$  - outer orbital / high spin / spin free complex

\* Magnetic moment  $M = \sqrt{n(n+1)} BM$ .

## \* Magnetic properties:

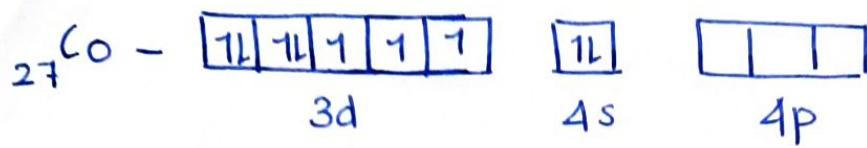
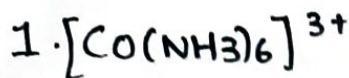
→ 3d series

- $Ti^{3+}(d^1)$ ,  $V^{3+}(d^2)$ ,  $Cr^{3+}(d^3)$  - 2 vacant d orbitals are available for octahedral hyb. with 4s & 4p.
- $d^4(Cr^{2+}, Mn^{3+})$ ,  $d^5(Mn^{2+}, Fe^{3+})$ ,  $d^6(Fe^{2+}, Co^{3+})$  cases, we get vacant d orbitals by pairing 3d  $e\theta$  leaving 2, 1, 0 unpaired  $e\theta$ .

→ Due to IOC & OOC.

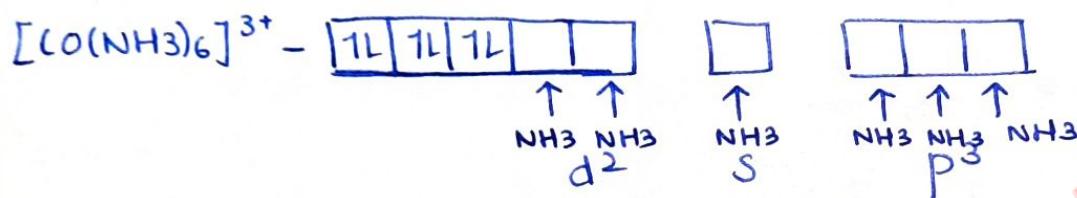
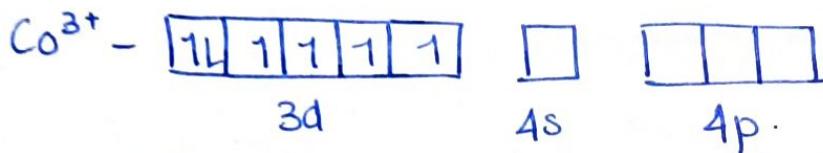
- $[Mn(CN)_6]^{3-}$  - 2 unpaired  $e\theta$  (IOC)
- $[MnCl_6]^{3-}$  - 4 " " (OOC)
- $[Fe(CN)_6]^{3-}$  - 1 " " (IOC)
- $[FeF_6]^{3-}$  - 5 " " (OOC)
- $[CoF_6]^{3-}$  - 4 " " (OOC)
- $[Co(C_2O_4)_3]^{3-}$  - 0 " " (IOC)

## Examples :



Oxi state of Co in  $[\text{Co}(\text{NH}_3)_6]^{3+}$

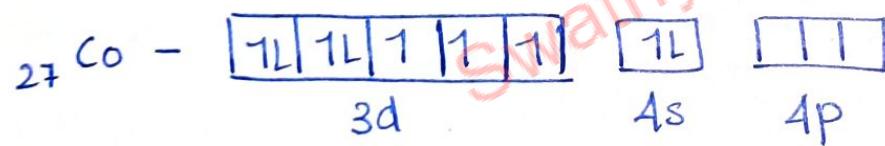
$$\chi - 0 = 3 \Rightarrow \chi = +3$$



Hyb : d<sup>2</sup>sp<sup>3</sup>  
(Ioc)

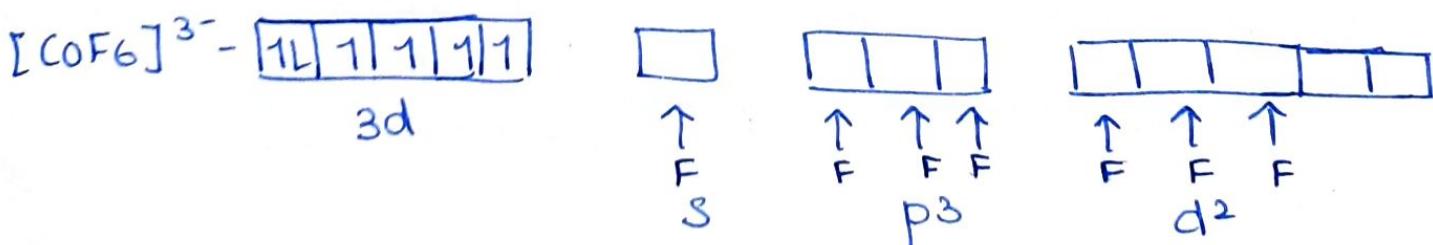
Geometry : Octahedral

Magnetic : Diamagnetic



Oxi state of Co in  $[\text{CoF}_6]^{3-}$

$$\chi - 6 = -3 \quad \chi = +3$$



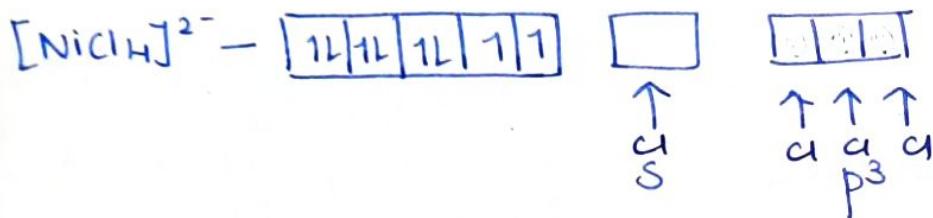
sp<sup>3</sup>d<sup>2</sup> (OOC) , Octahedral , Paramagnetic

$$\mu = \sqrt{4 \times 5} = \sqrt{20}$$

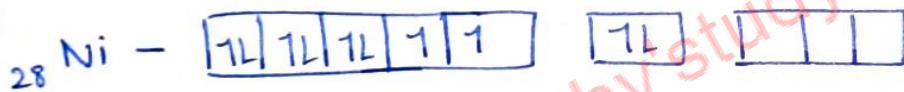


Oxi-state of Ni in  $[\text{NiCl}_4]^{2-}$

$$x - 4 = -2 \Rightarrow x = 2$$

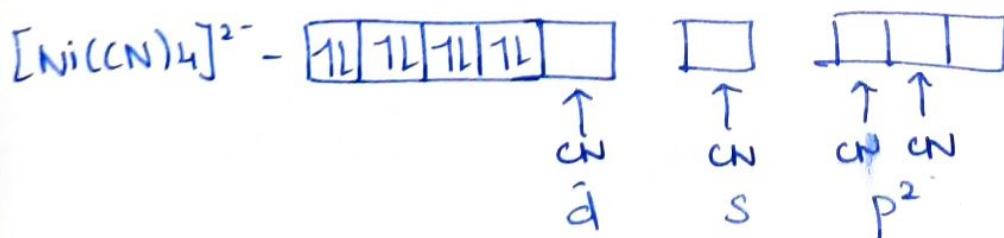
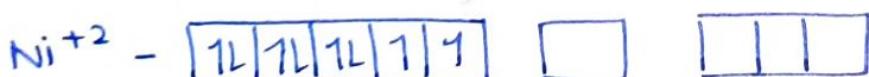


$\text{sp}^3$ , Tetrahedral, Paramagnetic,  $\mu = \sqrt{2 \times 3} = \sqrt{6}$ , high spin complex.



Oxi state of Ni in  $[\text{Ni}(\text{CN})_4]^{2-}$

$$x - 4 = -2 \Rightarrow x = 2$$



- $\text{dsp}^2$  (Low spin complex)
- diamagnetic
- Square planar

## Limitations of VBT

- \* involves a no. of assumptions.
- \* doesn't give quantitative interpretation of magnetic data.
- \* doesn't explain colour of c.c.
- \* doesn't give quantitative interpretation of thermodynamic, Kinetic Stabilities of c.c.
- \* doesn't distinguish b/w weak & strong ligands.
- \* doesn't make exact predictions regarding tetrahedral & square planar str. of 4 - c.c.

## Crystal Field Theory

- \* considers metal-ligand bond to be ionic.
- \* ligands - point charges (anions)  
- point dipole (neutral)
- \* 5 d orbitals - degenerate
- \* When negative field surrounds M  $\rightarrow$  symmetrical  $\rightarrow$  degeneracy is maintained.
- \* When negative field is due to ligands  $\rightarrow$  asymmetrical  $\rightarrow$  degeneracy is lifted  $\rightarrow$  splitting of d orbitals.

### A) Crystal field splitting in octahedral coordination entities

- \* 6 ligands surround the metal atom/ion.
- \* Repulsion b/w  $e_g$  in d-orbitals and  $e_g$  in ligands.  
 $\rightarrow$  max when d orbital is directed towards ligand. So,  $d_{x^2-y^2}$ ,  $d_{z^2}$  experience more repulsion.
- $\rightarrow$  min when d orbital is away from the ligand. So,  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  experience less repulsion.
- \* This yields 3 orbitals of lower energy,  $t_{2g}$  set & 2 orbitals of higher energy  $e_g$  set.

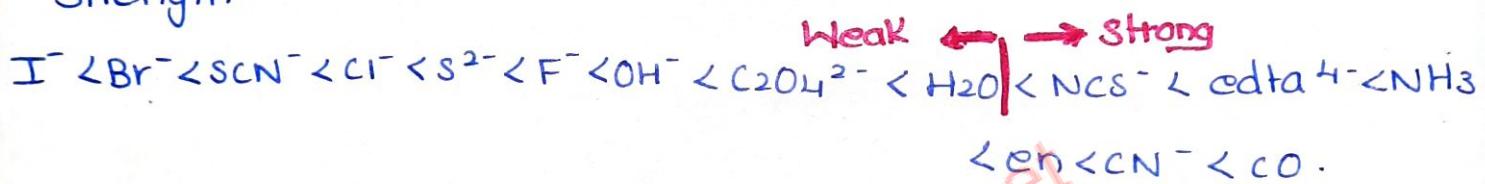
\* Splitting of degenerate levels due to the presence of ligands in a definite geometry  $\Rightarrow$  Crystal field splitting.

\* Energy of separation -  $\Delta_0$ .

\* Energy of 2 eg orbitals  $\uparrow$  by  $\frac{3}{5} \Delta_0$  & that of 3 t<sub>2g</sub> levels  $\downarrow$  by  $\frac{2}{5} \Delta_0$ .

\*  $\Delta_0$ . crystal field splitting depends on ligand & charge of metal.

\* Ligands can be arranged in series of increasing field strength:



### Spectrochemical Series

→ Single d e $\ominus$  occupy t<sub>2g</sub> orbitals. For d<sup>4</sup> ions:

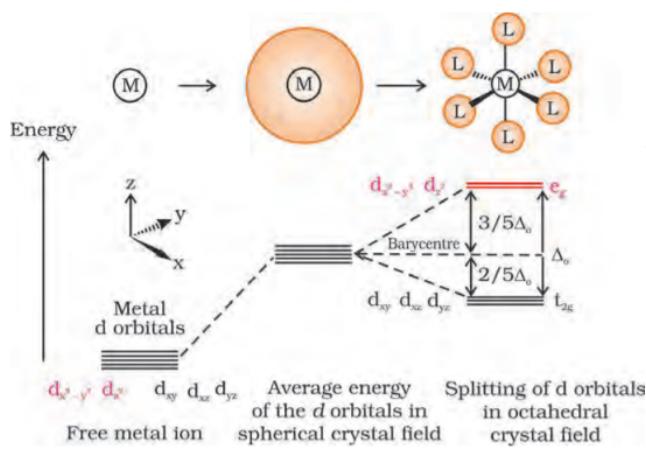
\* 4<sup>th</sup> e $\ominus$  could either enter t<sub>2g</sub> level & pair with an existing e $\ominus$ .

\* Occupies the eg level.

This depends on  $\Delta_0$  & P [energy required for e $\ominus$  pairing in single orbital (pairing energy)].

i)  $\Delta_0 < P$  - t<sub>2g</sub><sup>3</sup> eg<sup>1</sup> - weak field ligands - high spin complex.

ii)  $\Delta_0 > P$  - t<sub>2g</sub><sup>4</sup> eg<sup>0</sup> - strong .. " - low " "

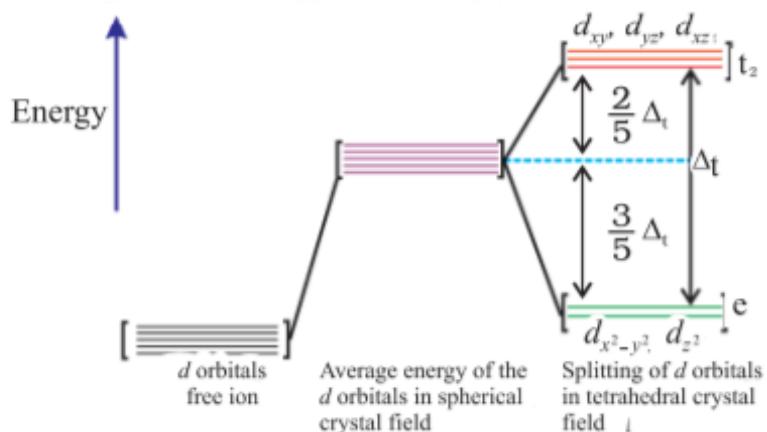


## B) Crystal field splitting in tetrahedral coordination entities

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$$*\Delta_t = \frac{4}{9} \Delta_o$$

- \* inverted & smaller as compared to octahedral field splitting.
- \*  $g \rightarrow$  for complexes with centre of sym. So, tetrahedral complexes lack symmetry.



### Colour in coordination compounds:

- \* colour of the complex is complementary to that which is absorbed.
- \*  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  → octahedral, violet in colour.  
 $\rightarrow \text{Ti}^{3+}(3d^1) - t_{2g}$

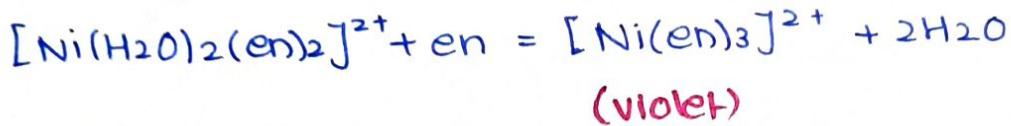
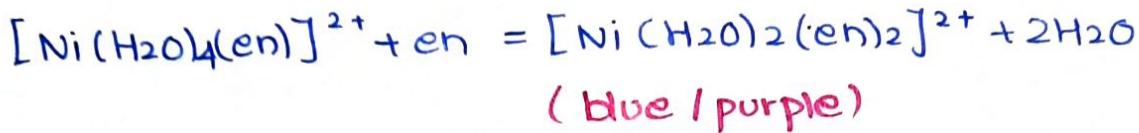
If it receives energy (blue green light) then the  $e^{\ominus}$  excites from  $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$ .

This attributes to its colour.

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{CN})_6]^{3-}$	310	Ultraviolet Not in visible region	Pale Yellow
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	498	Blue Green	Violet

- \* In the absence of ligands - no crystal field splitting - colourless
- \*  $[\text{Ti}(\text{H}_2\text{O})_6]\text{Cl}_3$  on heating - colourless.
- \*  $\text{CuSO}_4$  - colourless but  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow$  blue.
- \*  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + \text{en} = [\text{Ni}(\text{H}_2\text{O})_4(\text{en})]^{2+} + 2\text{H}_2\text{O}$

(green) (pale blue)

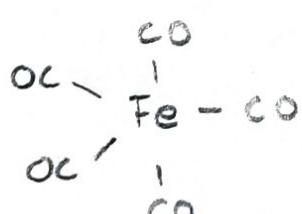
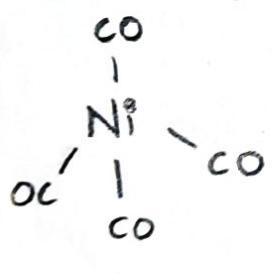


### Limitations of CFT

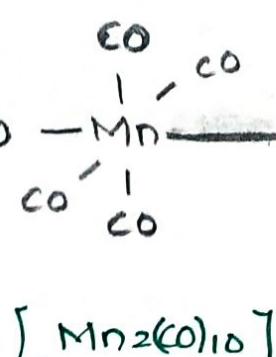
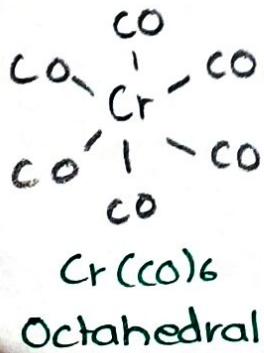
- from the assumptions that ligands are point charges, it follows that anionic ligands should exert greatest splitting effect. But it is at the low end of the spectrochemical series.
- doesn't account the covalent character of bonding.

### Bonding in metal carbonyls

- \* homoleptic carbonyls have simple well defined str.



$\text{Cr}(\text{CO})_6$   
Octahedral



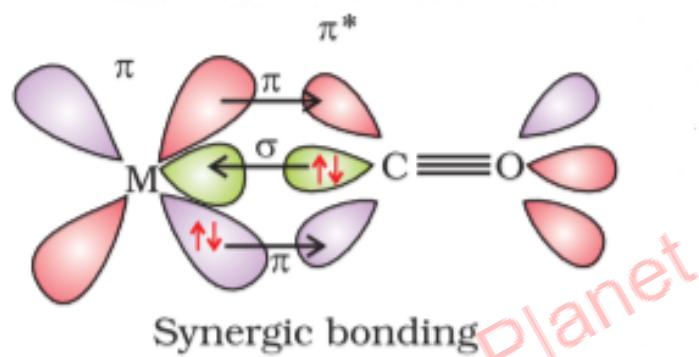
- Mn - Mn bond
- 2 sq. pyramidal str.

\* metal - carbon bond in metal carbonyls possess both  $\sigma$  &  $\pi$  character.

\* M-C  $\pi$  bond - donation of lp of  $\text{C}\equiv\text{O}$  on carbonyl carbon into vacant orbital of metal.

M-C  $\pi$  bond - donation of pair of  $e\ominus$  from a filled d orbital of metal into vacant antibonding  $\pi^*$  orbital of  $\text{C}\equiv\text{O}$

\* this bonding creates a synergic effect which strengthens the bond b/w CO & metal.

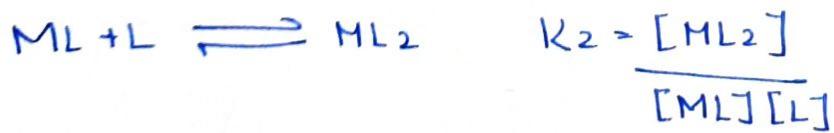


### Stability of coordination compounds

\* refers to degree of association b/w the 2 species involved in the state of equilibrium.

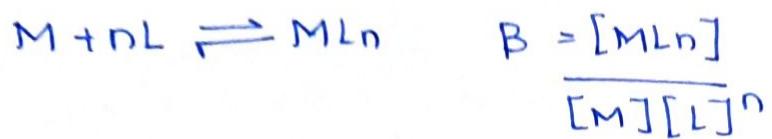


larger the stability const., higher prop. of  $\text{ML}_4$  exists in sol.



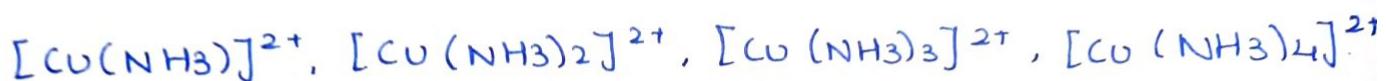
Here  $K_1, K_2, \dots, K_n$  are stepwise stability constants.

The overall stability const ( $\beta$ ) of the formation of species  $ML_n$  from  $M$ :



$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots \times K_n$$

Ex:



If  $K_1, K_2, K_3, K_4$  are stability const. of the successive reactions respectively then  $\beta_4$  would be:

$$\beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

\* The instability const. or dissociation const is the reciprocal of formation const.