2

# Co-ordination Chemistry.

addition cpd
(or) மூலக்கூறு கூட்டுச் சேர்மம்
Molecular cpd

double Salts
Ex: Mohr's Salt
FAS

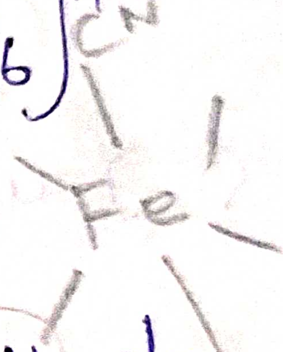
Co-ordn. cpds,
$K_4[Fe(CN)_6]$

$K^+ [Fe(CN)$

Complex Ion → $[Fe(CN)_6]^{4-}$ $-1$ $-6$ $+2$

Central Metal Ion → $[\underline{Fe}(CN)_6]^{4-}$

Ligand → $[Fe(\underline{CN})_6]^{4-}$



Ligand → $e^-$ donor $C\underline{N}$ → N-donor atom

Metal Ion → $e^-$ acceptor.

C.N < 4 - $Zn^{2+}$, $Ca^{2+}$, $Pt^{2+}$, $Cd^{2+}$, $Ni^{2+}$
6 - $Fe^{3+}$, $Fe^{2+}$, $Co^{3+}$, $Pt^{3+}$, $Cr^{3+}$

## IUPAC Nomenclature

1. +ve Ion ; -ve Ion
2. Ligand → -ve, Neutral, +ve.
3. ide → 'o'
4. ate → 'o'

4. Neutral ligand - $H_2O$ , $NH_3$
Spl Name - aquo Ammine

5. +ve Ligands (ium)
Ex. $H_2N-NH_3^+$ Hydrazium.

6. If the cpx Ion is +ve the central atom is called their usual name.

But -ve Ion is named as the end of the word is ate

7. oxidn no., is given in ( ) in Roman letter.

8. The complecated ligands are named as - Bis, tris, tetrakis

+ve cpx.

$[Pt(NH_3)_3Cl_3]Cl$

$[Ag(NH_3)_2]Cl_2$

Neutral ~~Ligand~~ cpx

$[Pt(NH_3)_2Cl_2]$

$[Co(NH_3)_2Cl_2]$

-ve cpx.

$K_2[Ni(CN)_4]$ , $K_4[Fe(CN)]$

# Werner's theory. (1893)

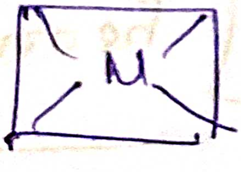
1. Central Metal Ion
2. Ligands are surrounded by co-ordination Bond.
3. C.N
4. Primary Valency — Metal having 2 valencies
   Secondary Valency

1° ⇒ equal to oxidn no., of the Metal.

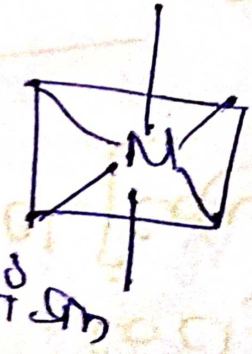
2° ⇒ equal to C.N

⑤ The gp of Metal, Ligands are called co-ordination Sphere.

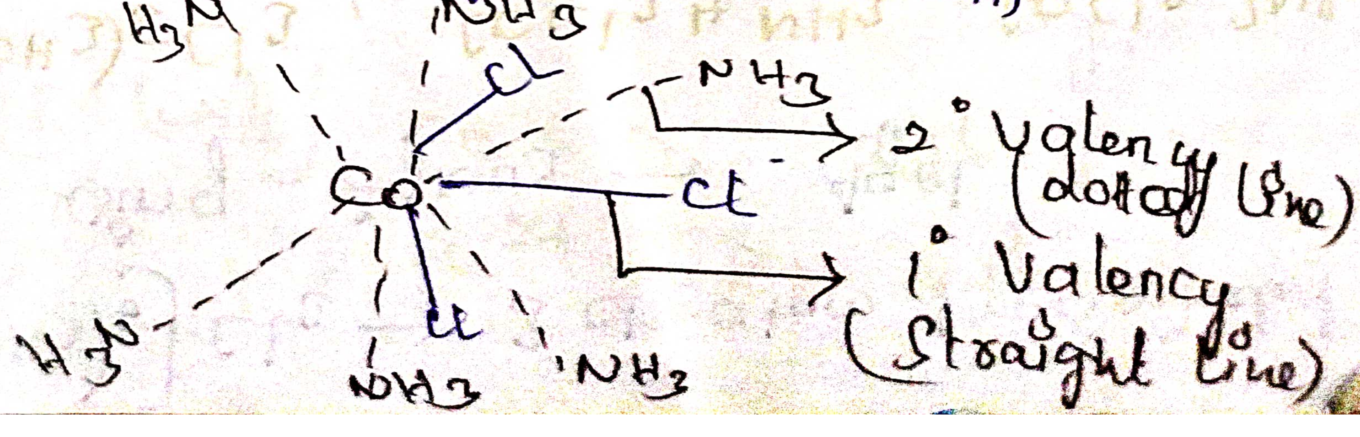
⑥ C.N - 4



C.N - 6 →



7. cpx having Isomerism



$[Co(NH_3)_6]Cl_3 \rightarrow$ 3 cl atom precipitated by using $AgNO_3 \longrightarrow AgCl$

$Co(NH_3)_5Cl_3$ , $CoCl_3 \, 4NH_3$ , $CoCl_3 \, 3NH_3$

$[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ $[Co(NH_3)_3Cl_3]$

———— x ————

Sidgwick's theory [EAN theory]

Pair of $e^-$ are ~~translated~~ transfamed

$$H^+ + :NH_3 \longrightarrow [H:NH_3] \text{ or } [NH_4]^+$$

EAN

EAN = $\boxed{\text{atomic No} - \text{loss of } e^- + \text{gain of } e^-}$

$K_4[Fe(CN)_6]$ $\underline{\uparrow\downarrow}$ Fe $\Longrightarrow$ 26 $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$

$Fe^{2+} \Longrightarrow$ Loss of $e^- = 2$

Gain of $e^- \Longrightarrow 6\,CN \Longrightarrow 6 \times 2 = 12$

$$26 - 2 + 12 = 36$$

~~Kr~~ 26 = Kr atomic No,

$26 - 2 + 12 = 36$

~~Kr~~ 26 = Kr atomic No,

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x

Pauling's theory [VBT]

Explain with $e^-$ Confi, Types of Bond, Shape & Mag. prop.,

1. Central metal atom is give the vacated s,p,d orbital equal to C.N
2. Vacanted orbitals are hybridised
3. Metal orbital overlap with Ligand orbitals to gu a strong bond.
4. 2° or Inner (n-1)d orbital ($d^2sp^3$) → low spin
   outer nd orbital ($sp^3d^2$) → High spin
5. Ligand gu. Pair of $e^-$ are given to metal atom
6. Unpaired $e^-$ → Para Mag.,
   Paired $e^-$ → Dia Mag.,

$K_4[Fe(CN)_6]$ Fe = 26 $3d^6$ $4s^2$

$Fe^{2+}$ = Ar $3d^6$

$3d^6\ 4s^2$ ↑↓ ↑ ↑ ↑ ↑ ↑↓

$3d^6$ ↑↓ ↑ ↑ ↑ ↑

$CN^-$ $\underbrace{\boxed{↑↓}\boxed{↑↓}\boxed{↑↓}\boxed{××}\boxed{××}\quad\boxed{××}\quad\boxed{××}\boxed{××}\boxed{××}}$

low spin cpx. $CN^-$ $d^2sp^3$. Dia mag.

——— × ———

## CFT

1\. ~~Central~~ +

Bethe & Van Vleck.

* Interaction of d orbital of the atom & the Ligand.

It produce CF effect.

1\. Central metal atom surrounded by by Ligands.

2\. The interaction b/w metal ion & Ligand is electrostatic (ionic)

3\. does not consider orbital overlap

4. Ligands -vely Charged.

Neutral Ligands polarised by the +ve Charge.

5. Interaction b/w $e^-$ & metal ion are repulsive. This force causing the splitting of the d orbital of the metal $t_{2g}$ & $e_g$. This is called CFT

**Spectrochemical Series.**

Strong Ligand $CN^-$ CO $\Delta_o$ is high

weak Ligand $I^-$, Br $\Delta_o$ is low

$I^- < Br^- < Cl^- \lesssim CN < F^- < OH^- < C_2O_2^{2-} \simeq H_2O < NH_3 < en < NO_2 < CN < CO$

weak Ligand → weak field (or) low spin

Strong " → " " (or) High spin

|  |  |  |  |  |
|---|---|---|---|---|
| d4 | 3 | 1 | - | -6 |
|  | 3 | 2 | - | -0 |
|  | 4 | 2 | - | 4 |
|  | 5 | 2 | - | -8 |
|  | 6 | 2 |  | -12 |
|  | 6 | 3 |  | -6 |
|  | 6 | 4 |  | -0 |

$-4(3)+6(1)$

$-12+6=-6$

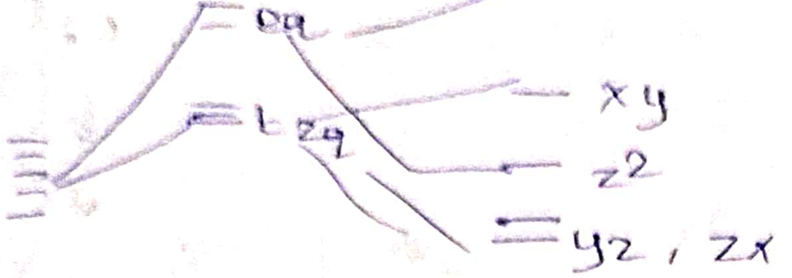
$-12+12=\underline{0}$

## low spin.

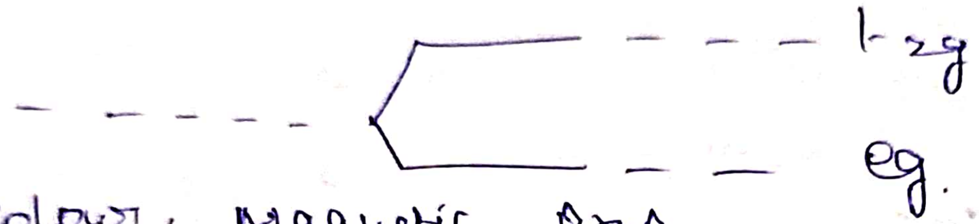
|  |  |  |  |  |
|---|---|---|---|---|
|  | 1 | 0 |  | -4 |
|  | 2 | 0 |  | -8 |
|  | 3 | 0 |  | -12 |
|  | 4 | 0 |  | -16 |
|  | 5 | 0 |  | -20 |
|  | 6 | 0 |  | -24 |
| d7 | 6 | 1 | ✓ | -18 |
| d8 | 6 | 2 |  | -12 |
| d9 | 6 | 3 |  | -6 |
| d10 | 6 | 4 |  | -0 |

$-4P+6E$

## Square planar



Td



colour, magnetic prop.

**Strong Ligand** → paired $e^-$ → **Low Spin cpx**

**weak Ligand** → Unpaired $e^-$ → **High Spin cpx**

**Mag., prop**

Unpaired $e^-$ ⟶ para

paired $e^-$ ⟶ Dia

**Colours**

d-d transition

$[Ti(H_2O)_6]^{3+}$