

COMPLEX COMPOUNDS

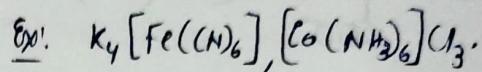
→ Double salt

- ① addⁿ of compounds, lose their properties in aq. medium.
- ② Fully hydrolysis.
- ③ Constituent ions are similar with properties (aq).
- ④ due to metallic bond

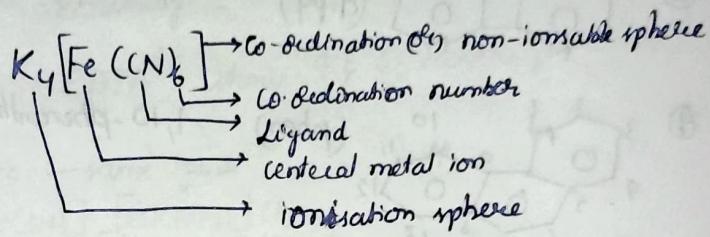
Ex: $KCl \cdot MgCl_2 \cdot 6H_2O$, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Complex salt

- ① addⁿ compounds, doesn't lose identity in aq. medium.
- ② Partial hydrolysis.
- ③ Constituent ion properties are different in (aq).
- ④ due to dative bond.



Complex compound:



Ligand: e^- pair donor atom or ion. Ex: (N^-) , (Cl^-) , (Br^-) , etc.

→ Denticity: ability to donate e^- pairs.

Mono -1
 bi -2
 poly -> 2

① Mono dentate — forms 1 dative bond

Ex: ve: ends with: 'O' (or) 'ido'

-ve ligand
+ve ligand
neutral ligand

F^- - fluorido

CH_3COO^- - acetato

Cl^- - chlorido

O^2- - oxo

Br^- - bromido

O_2^- - peroxo

I^- - iodido

OH^- - hydroxido

H^- - hydrido

NO_2^- - nitro & N sp²

N^{3-} - nitrido

ONO^- - nitrito-O

N_3^- - azido

CN^- - cyanide

NH_2^- - amido

SCN^- - thiocyanide

NCS^- - isothiocyanide

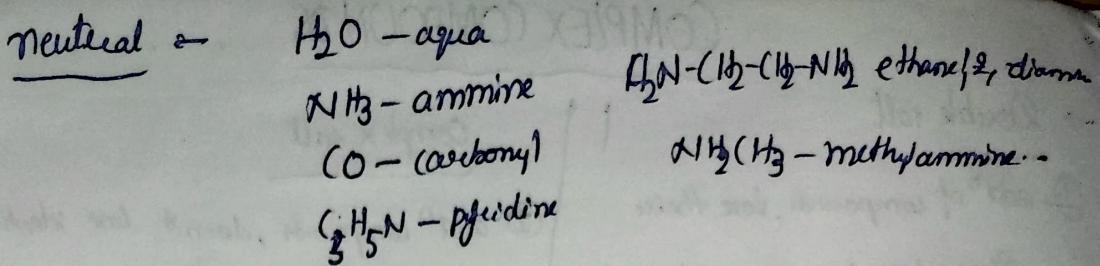
amide
-2 donor atoms
contain both
-ve & +ve

+ve :

NO^+ - nitronium

NO_2^+ - nitronium - sp

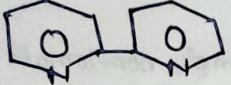
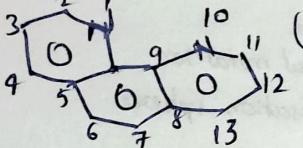
$NH_2NH_2^+$ - hydrazinium



I Bidentate ligands:

Abbreviation

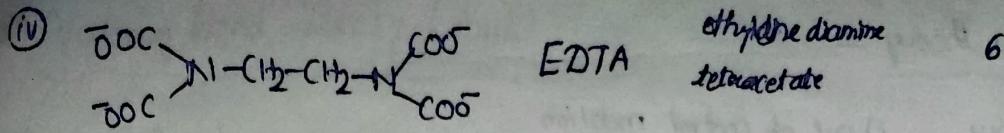
Charge

①	$CH_2-\ddot{N}H_2$ \downarrow $CH_2-\ddot{N}H_2$	(en)	ethylene diamine	0
②	COO^- \downarrow COO^-	(ox)	oxalate ion	-2
③		(dipy)	1,2-dipyridine	0
④		(phen)	1,10-phenanthroline	0
⑤	$CH_2-\ddot{N}H_2$ \downarrow COO^-	(gly)	glycerato ion	-1
⑥	$CH_3-\overset{\delta}{C}-CH=CH-COO^-$	(acac)	acetylacetato	-1
⑦	$CH_3-C=N-OH$ \downarrow $H_3C-C-N-O^-$	(dmg)	dimethyl glyoximate	-1

II Polydentate ligands

Identify

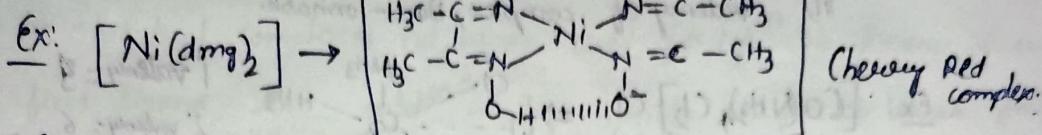
①	$CH_2-CH_2-\ddot{N}H_2$ \downarrow $CH_2-\ddot{N}H$ \uparrow $CH_2-CH_2-\ddot{N}H_2$	(dien)	diethylenetriamine	3
②	$NH-(CH_2)_2-\ddot{N}H_2$ \downarrow $(CH_2)_3$ \downarrow $CH_2-(CH_2)_2-NH_2$	(teden)	triethylenetetraamine	4



→ Chelating ligands:

→ Ring formation by ligands mostly bidentate.

→ Rings ↑ stability ↑



→ Polydentate ligands:

Ligands show variable dentativity.

Ex: SO_4^{2-} - 1 & 2, EDTA $^{4-}$ show 4 & 6 dentativity.

Complex
Homoleptic - same ligands

Ex: $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

Heteroleptic - different ligands:

Ex: $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, $[\text{PtBrClF}]$, $[\text{Co}(\text{en})_3\text{Cl}_2]^+$.

→ Coordination polyhedron - spatial arrangement (3d space geometry)

→ Mononuclear - 1 metal ion - Ex: $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{PtCl}_4]^{2-}$

Polyatomic - 2 or more metal ions Ex: $(\text{O}_2\text{C})_8\text{Mn}_2(\text{CO})_{10}$.

⇒ IUPAC Nomenclature

① i) +ve ion + prefix + ligand + (·M·A(ate)+O·S(·)).

ii) prefix + ligand + C·M·A + O·S(·) + counterion

Ex: i) $\text{K}_4^{+}[\text{Fe}(\text{CN})_6]^{4-}$ - potassium hexa cyanoferrate(III).

ii) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ - hexa ammine cobalt(II) chloride

$[\text{Zn}(\text{OH})_4]^{2-}$ - tetrahydroxo zincate(II) ion.

② i) Ligands must be arranged acc to alphabetical order.

Ex: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$.

ii) for polydentate ligands, abbreviation should be considered.

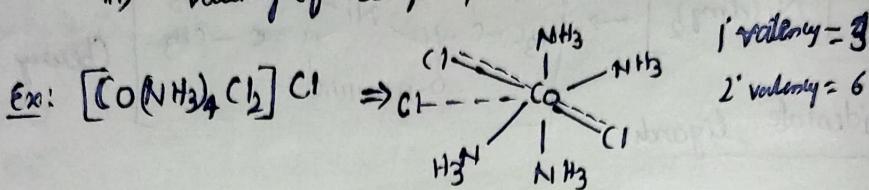
Ex: $[\text{O}(\text{NH}_3)_2\text{Br}(\text{l-en})]\text{Cl}$.

⇒ Werner theory -

- 1' Valency - i) O's of central metalion
 ii) $\leftarrow \rightarrow$ lines, only -ve ligands satisfy, ionic bond.
 iii) don't involve in geometry, ionisable.

- 2' valency - i) no. of dative bonds

- ii) $\leftarrow \rightarrow$ line, -ve, neutral, ~~++-~~ satisfy through co-ordinate covalent bond.
 iii) valency of complex, non-ionisable



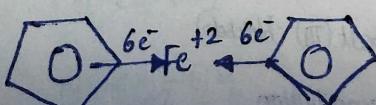
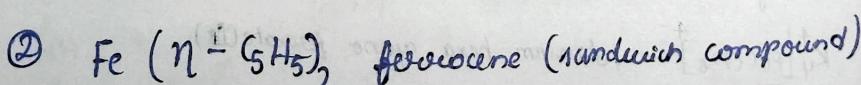
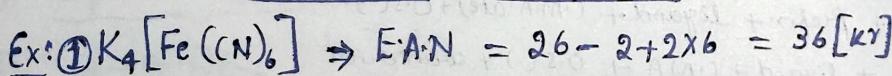
- Limitations - i) don't explain colour, magnetic & directional property of dative bonds.

- ii) Why elements forms complexes?

⇒ Sidgwick theory :

- i) 1' valency formed by e transfer, 2' valency of metal corresponds to no. of dative bonds.
 ii) central metal ion will continue accepting e from ligand to attain nearest noble gas config.
 iii) total no. of e's around C.M.A = E.A.No.

$$\text{E.A.N} = Z - O.S + 2 \times (\text{C.No})$$



- Limitations - i) don't explain colour, magnetic & stability of complexes.

- ii) Why complexes with less no. of e's than nearest noble gas are more stable?

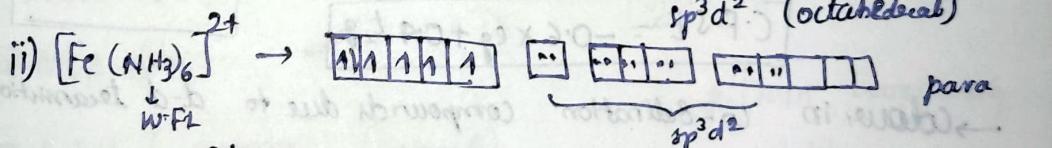
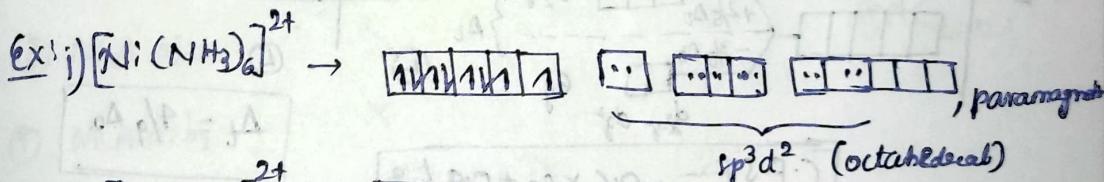
⇒ Valency Bond Theory (Pauli)

- C.M.A derives adequate e⁻s & form ion by creating vacant orbitals (O.s.)
- In octahedral complexes (n-1)d, ns, np used for hybⁿ in presence of strong field ligand d^2sp^3 - inner orbital (8) low spin (8) spin paired (8) strong field (8) covalent complexes (pairing against Hunds rule).
- In tetrahedral complexes nd, ns, np used for hybⁿ in presence of weak field ligand then sp^3d^2 - high spin (8) spin free (8) weak field (8) ionic complexes (acc. to Hunds rule)
- Incompletely filled orbitals give magnetic moment.

for d^4, d^5, d^6, d^7 - ligand strength applied.

$d^1, d^2, d^3, d^8, d^9, d^{10}$ - ligand strength is not applied

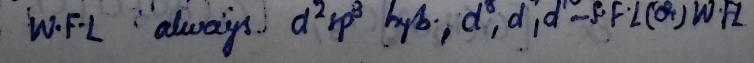
Limitations - i) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ excepted - tetrahedral sp^3 , actual - sq. planar (d_{sp^2}).
 ii) thermodynamic & kinetic stabilities of coordination compounds, magnetic data & colour properties not explained



→ sp^3 & dsp^2 complexes won't show isomerism

• Trick $d^5, d^6, d^7 - S.F.L$ (SF) $d^8, d^9, d^{10} - W.F.L$ (WF) d^2sp^3 hyb. d^4, d^5, d^6, d^7 [SF] (SF) d^2sp^3 to sp^3d^2 (SF) (SF)

always sp^3d^2 hyb.

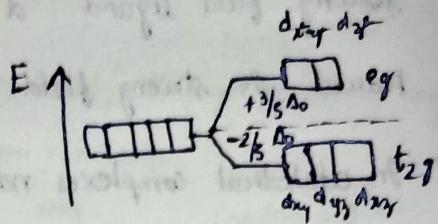
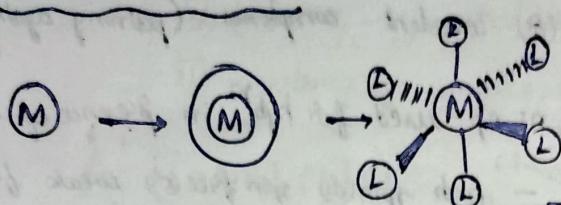




→ Crystal field theory

- Acc. to metal-ligand bond \approx ionic (due to electrostatic bonding)
- Ligands are point charges, anionic ligands are dipoles
- When ligand approaches C.M. ion d-orbital split into 2 sets

Octahedral complex



$$C.F.S.E = -0.4 \times t_{2g} + 0.6 \times e_g$$

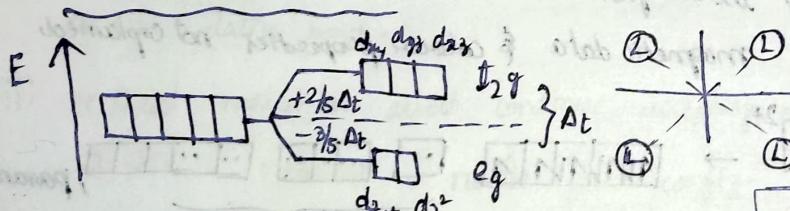
Spectrochemical series — $I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O^-$

$NCS^- < edta^{4-} < Py, NH_3 < en < NO_2^- < CN^- < CO.$

→ If $\Delta_0 < p$ 4^{th} e $^-$ $\rightarrow t_{2g}^3 e_g^1$.

$\Delta_0 > p$ 4^{th} e $^-$ $\rightarrow t_{2g}^4 e_g^0$ (energetically wrong, not logically).

Tetrahedral complex



$$C.F.S.E = -0.6 \times e_g + 0.4 \times t_{2g}$$

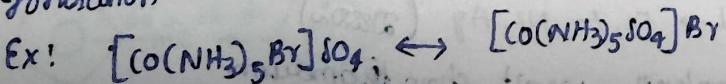
$$\Delta_t = 4/9 \Delta_0$$

→ colour in co-ordination compounds due to d-d transition of e $^-$

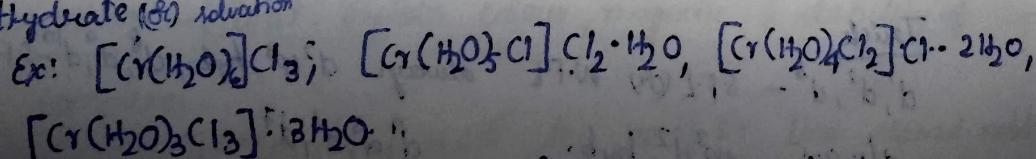
→ Iron(II) ions

→ Structural

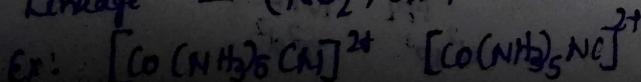
i) Ionisation



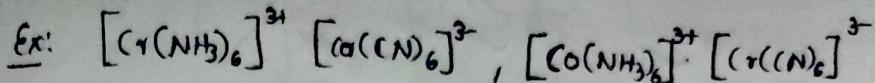
ii) Hydrate (8) solvation



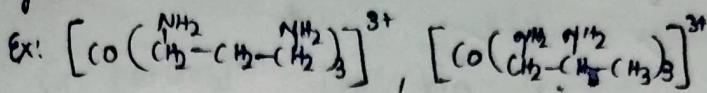
iii) Linkage — (NO₂, SCN, CN)



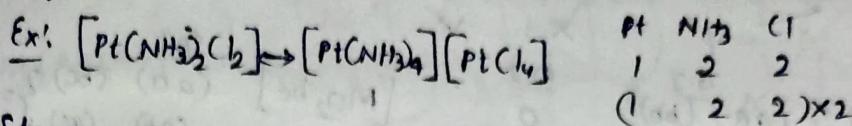
iv) Coordination isomerism



v) Ligand isomerism



vi) Polymerisation isomerism



⇒ Stereoisomerism

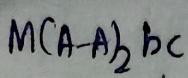
Square planar complex (C.N.O-4)

	G.I	O.I	T.I
① Ma_4	X	X	0
② Ma_3b	X	X	0
③ Ma_2b_2	✓	X	2
④ Mabcd	✓	X	$3 = \frac{6}{2} + 1$
⑤ M(A-A)_2	X	X	0
⑥ M(A-B)_2	✓	X	2
⑦ $\text{M(A-A)}\text{b}_2$	X	X	0
⑧ $\text{M(A-A)}\text{bc}$	X	X	0
⑨ $\text{M(A-B)}\text{b}_2$	X	X	0
⑩ $\text{M(A-B)}\text{bc}$	X	X	2

Octahedral complex (C.N.O-6)

* trans-isomer is stable

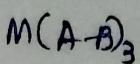
① Ma_6	X	X	0
② Ma_5b	X	X	0
③ Ma_4b_2	✓	X	2
④ Ma_3b_3	✓	X	2
⑤ $\text{Ma}_2\text{b}_2\text{c}_2$	✓	✓	$5+1=6$
⑥ $\text{Ma}\text{bcd}\text{ef}$	✓	✓	$15+15=30$
⑦ $\text{M(A-A)}_3\text{b}_2$	X	✓	2 → only O.T
⑧ $\text{M(A-A)}_2\text{b}_2$	✓	✓	$\frac{5+3}{2} = 3$



G.I

O.I

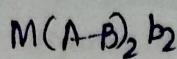
7-1
3



✓

✓

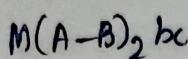
4



✓

✓

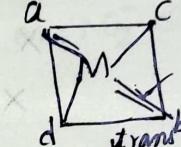
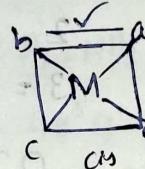
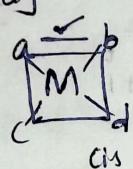
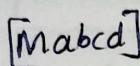
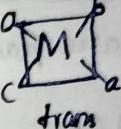
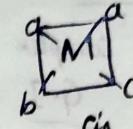
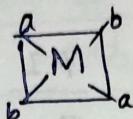
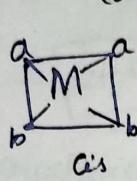
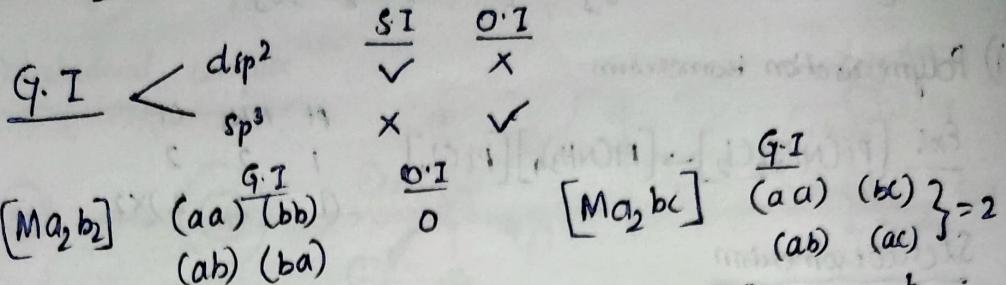
4



✓

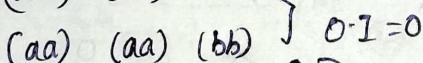
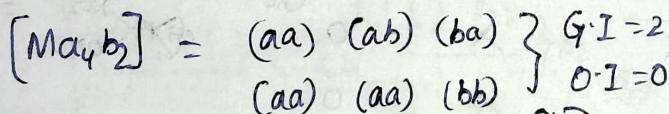
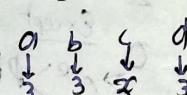
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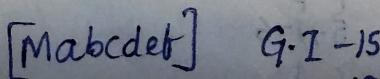
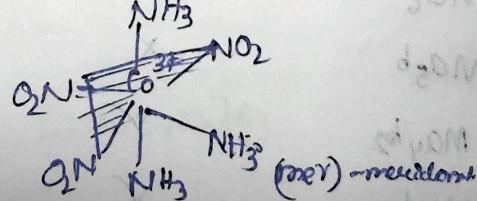
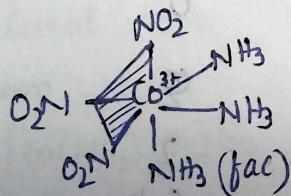
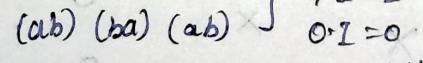
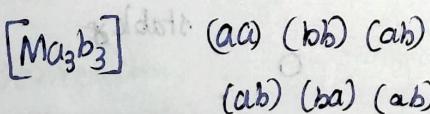
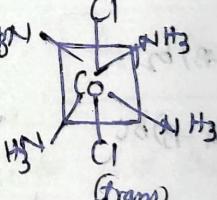
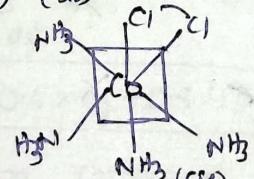


Ex: $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{Br}]$ - No. of G.I = 3

total of I's = 12

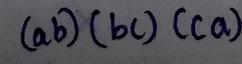
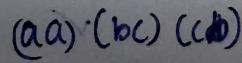
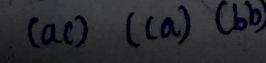
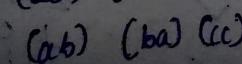
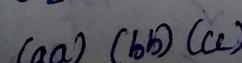
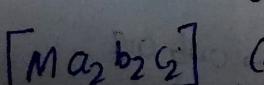


Ex: $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^{+1}$

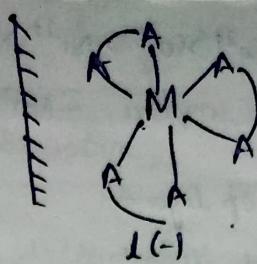
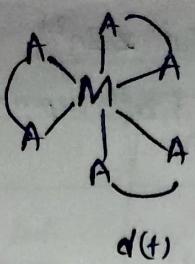
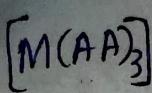


G.I - 15

O.I - 15

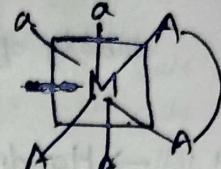
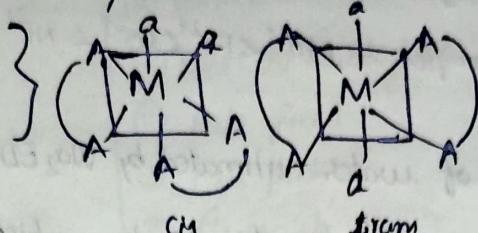
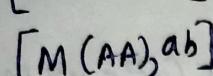
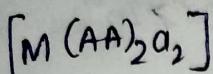
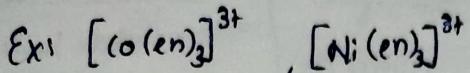


$\frac{9}{3} + \frac{9}{3} = 6$



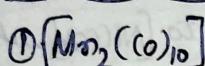
$O \cdot I - 2$

$G \cdot I - O$

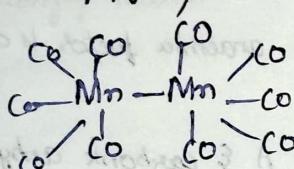


[cis-bidentate ligand
O.I.]

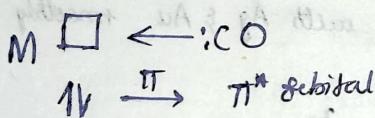
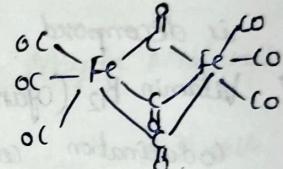
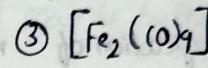
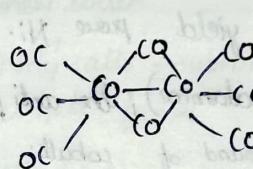
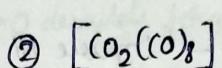
Metal carbonyls (Synergic effect)



2-1g, Pd^2 , Mn-Mn bond



acc to MO theory
 $(\text{CO} - \sigma 1s^2 \otimes 1s^2 \otimes 2p_z^2 \otimes 2s^2 \otimes 2p_y^2 \otimes 2p_x^2 = 10 2p_y^2, \text{Ti}^* 2p_x^0 = 10 2p_y^0)$



} both σ & π bonds

synergic effect ↑ when

$M-C \Rightarrow B \cdot O \uparrow B \cdot E \uparrow$ stability ↑ $\downarrow \uparrow B \cdot L \uparrow$

$C-O \Rightarrow B \cdot O \uparrow B \cdot E \uparrow$ stability ↑ $\downarrow \uparrow B \cdot L \uparrow$

Metal to few O's

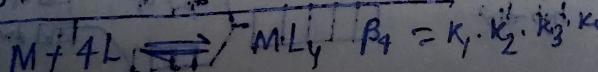
→ Bulky groups form

less stable complexes

as complex charge -ve ↑ back bonding ↑ then $B \cdot O \uparrow$

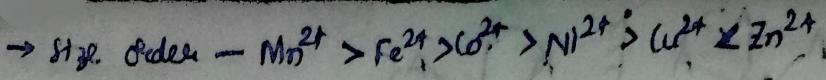
as complex charge +ve ↑ back bonding ↑ then $B \cdot O \uparrow$

Step wise stability const. & overall stability const.



$$\log_{10} \beta_4 = \log_{10} K_1 + \log_{10} K_2 + \log_{10} K_3 + \log_{10} K_4 = x$$

$$\frac{1}{\beta^2} = 10^{-2}$$



① Stability of high spin complexes - Mn^{2+} & Zn^{2+} depends on size of ion

\rightarrow size & charge of ligand

\rightarrow basic nature of ligand

\rightarrow chelating effect

Stability of complex - $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$

Uses : \rightarrow Hardness of water estimated by Na_2EDTA . (Ca^{2+} & Mg^{2+} form complexes)

\rightarrow Ag, Au make use in formation of complex which combines with CN^- in presence of O_2 & H_2O to form co-ordination entity $[\text{Au}(\text{CN})_2]$ in aqua soln.

Au can be separated in metallic form from this soln. by addition of Zn.

\rightarrow Purification of metals - impure Ni is converted to $[\text{Ni}(\text{CO})_4]$ which is decomposed to yield pure Ni.

\rightarrow Vitamin B_{12} (cyanocobalamin), the anti pernicious anaemia factor is a coordination compound of cobalt.

\rightarrow Enzymes of Co are carbonylpeptidase A & carbonic antitydease.

\rightarrow Wilkinson catalyst - $[(\text{Ph}_3\text{P})_3\text{RhCl}]$

Articides can be electrodeplated with Ag & Au smoothly $[\text{Ag}(\text{CN})_2]^-$ & $[\text{Au}(\text{CN})_2]$.

\rightarrow photography $\text{AgBr} \rightarrow [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

Cu & Fe are removed from body by D-penicillamine & deferoxamine B.

\rightarrow EDTA for lead poisoning. Pt complexes for curing tumors.

cu $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ for cancer.

\rightarrow Ruby is Al_2O_3 about 0.5-1% Cr^{3+} ions and randomly occupied by Al^{3+} .
Emerald Cr^{3+} occupies octahedral sites in beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$)

$[\text{Ni}(\text{dmso})_2]$

