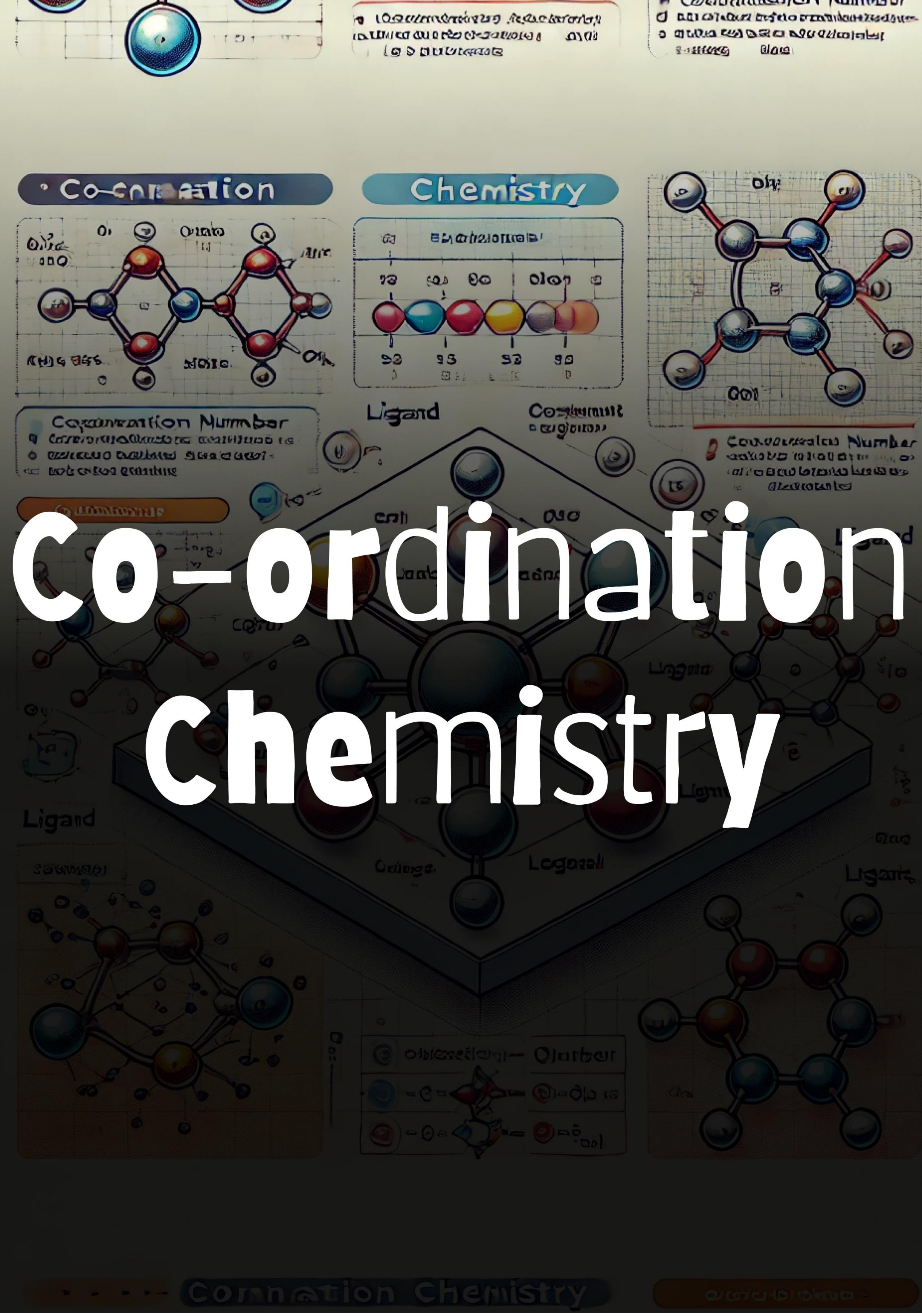


Co-ordination Chemistry

TYPES OF SALTS

simple, mixed, complex.

IMPORTANT TERMS IN CO-ORDINATION COMPOUND

Ligands – on the basis of charge
- on the basis of denticity
- Accepting or donating

Central atom

Co-ordination number

Co-ordination sphere

Ionisation sphere

NOMENCLATURE

BONDING IN CO-ORDINATION COMPOUNDS

Water theory

VBT

EAN Rule

CFST

ISOMERISM

Structural

Stereo isomers

SYNERGIC BONDING

APPLICATION OF CO-ORDINATION COMPOUNDS

-
-

Concept of co-ordination compound arises because of complex formation tendency of transition elements.

In complex compound, central atom is surrounded by cluster of ions or molecules.

The complex compound first formed as Prussian blue $Fe_4[Fe(CN)_6]_3$ by Diebach (Berlin colour maker).

T-Y-P-E-S O-F S-A-L-T-S

1. SIMPLE SALT

- which contains only a single type of cation and anion (eg:- NaCl)

2. MIXED SALT

- which containsmore than one type of cation or anion.

Eg Bleaching powder ($CaCl_2$) — Ca^{+2}, OCl^-, Cl^-

Microcosmic salt – ($NaNH_4HPO_4$) – Na^+, NH_4^+, HPO_4^{2}

3. DOUBLE SALT

- which are formed by more than on diffn simple states

These are stable in solid state and dissociate completly into respective ion in aq. soln from which they are formed.

Eg carnalite – $KCl \cdot MgCl_3 \cdot 6H_2O$

Alums – $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

4. COMPLEX SALT

- These salts are also formed by more than one single salt but its aquous solution do not have all ions in free form from which it is formed.

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6] \xrightarrow{aq} 4K^+ + [Fe(CN)_6]$$

$$2KI + HgI_2 \longrightarrow \underset{\text{nessler's Reagent}}{K_2[HgI_4]} \xrightarrow{aq} 2K^+ + [HgI_4]$$

Co-ordination compounds are examples of complex salts.

Complex salts are of 2 types.

PERFECT COMPLEX

Almost non-ionisable

E.g $2Cu^+ + H_2S \rightarrow Cu_2S \downarrow$

(Black ppt.)

$[Cu(CN)_4]^{3-} \xrightarrow{H_2S} X$

(no reax^n)

E.g $Fe^{+3} + 3SCN^- \rightarrow Fe(SCN)_3$

$[FeF_6]^{3-} \xrightarrow{SCN^-} XX$

IMPERFECT COMPLEX

Has tendency to dissociate feebly.

E.g. $Cd^{+2} + H_2S \rightarrow CdS \downarrow$

(Yellow ppt.)

$[Cd(CN)_4]^{2-} \xrightarrow{H_2S} CdS \downarrow$

(Yellow ppt.)

E.g. $Fe^{+3} + OH^- \rightarrow Fe(OH)_3$

(Reddish Brown)

$[FeF_6]^{3-} \xrightarrow{OH^-} Fe(OH)_3$

IMPORTANT TERMS USED IN CO-ORDINATION COMPOUNDS

Central atom - usually d-block elements containing vacant orbitals to accommodate e$^-$ density obtained from ligands.

Ligands - Neutral moleculs or ions surrounded to central atom. Ligands are attached with central atom with co-ordinate covalent or sigma e$^-$ donor bond.

Co-ordination number - Number of ligand atoms directly attached to central atom.

Generally, compounds of CN 4 or 6 are obtained.

Oxidation state of Central Atom

E.g. $K_4[Fe(CN)_6]$ → OS of Fe → +3

$K_4[Fe(H_2O)Cl_5]$ → O.S of Fe → +1

Co-ordination sphere

[- - - - -]

It is formed by central atom and ligands. It is non-ionisable in nature.

Ionisation sphere

Part outside the co-ordination sphere. It is ionisable in water.

$\underbrace{[Fe(H_2O)_6]}\underbrace{Cl_3}$ → ionisation sphere

O.S → +3

→ Co-o sphere

CN → 6

central atom - Fe

Ligand → H_2O

$[Fe(H_2O)_3(Cl)(NH_3)_2]Cl_2$

Ligand → H_2O, Cl, NH_3

CN → Fe

O.S → (+1)

$K_3[Fe(H_2O)(CN)_5]$

C.N → 6

ligands → H_2O, CN^-

TYPES OF LIGANDS

1. On the basis of charge

- Atomic
- Cation's
- Neutral

ⓐ ANIONIC LIGANDS

Suffix → "O"

F → Flouride
Cl^- → chlorido
Br^- → Bronido
I → Iodido
NH_2^- → Amido
NH → Iinido
N^{3-} → Nitrido
N_3 → Azido

If an anionic ligand is derived from hydro-carbon, then its name is written as common name.

CH_3 → methyl
$C_2H_5^-$ → ethyl

ⓑ NEUTRAL LIGANDS

H_2O → Aqua
NO → Nitrosyl
S_8 → octa sulphur
NH_3 → Ammine
CS → Thiocarbonyl
NH_2NH_2 → hydrazine
CO → carbonyl
NH_2CONH_2 → urea

ⓒ CATIONIC LIGANDS

Suffix → "ium"

O_2^+ → Dioxygenium
H^+ → Hydrogenium
NH_4^+ → Ammonium
NO_2^+ → Nitronium

NO^+ → Nitrosonium/ Nitrosylium
$NH_2NH_3^+$ → hydrozinium

2. On the basis of Denticity

Denticity = no. of donor atoms present in a ligand

ⓘ MONODENTAL LIGAND (D=1)

OCN^- = cyanato
SCN^- = Thiocyanato
CN^- = cyanido
NC^- = isocyanido or N- cyanido

NCO^- = Isocyanato or N- cyanato
NCS^- = Isothio cyanato or N- thiocyanato

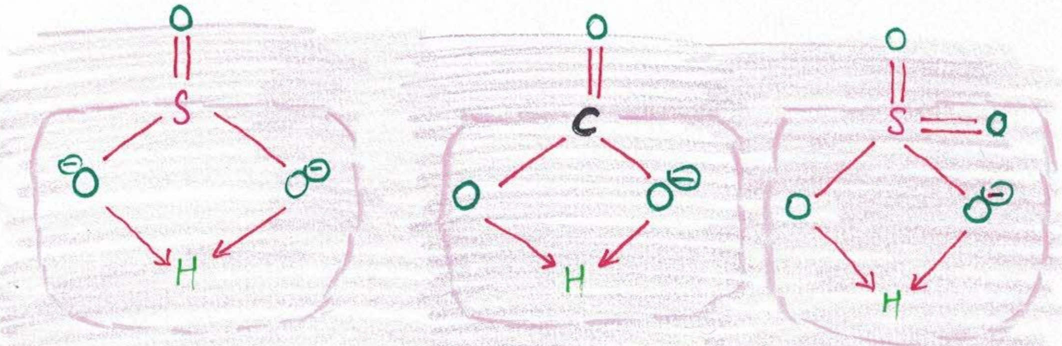
Cl^-, F^-, I^-, Br^-

SO_3^{-2} → Sulphito

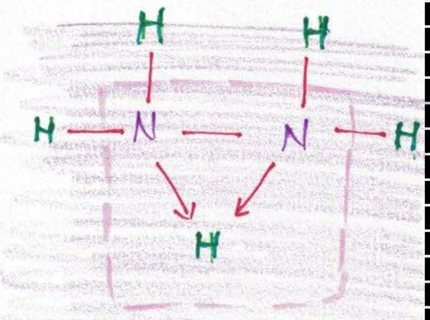
NH_2NH_2 → Hydrazine

SO_4^{-2} → Sulphato

CO_3^{-2} → Carbonato



4-membered rings (highly unstable)

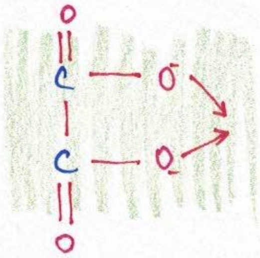


3M-ring

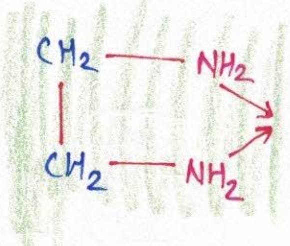
Hence, these Ligands will act as monodentate Ligands.

Ⓔ BIDENTAL LIGANDS (D=2)

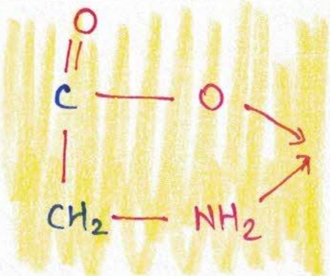
- oxalato (ox)
  symmetric ligand



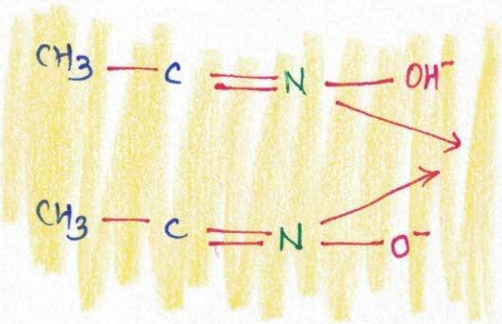
- Ethylenediamine (en)
  symmetric ligand



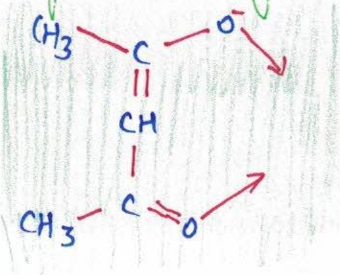
- Glycinato (gly)
  unsymmetric ligand



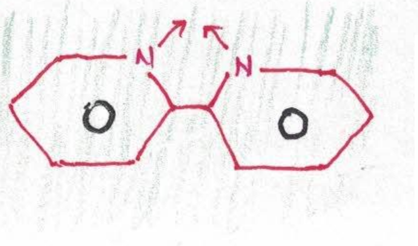
- Dimethyl glyoxime (DMG)
  unsymmetric ligand



- Acetyloacetato (acac)
  symmetric ligand



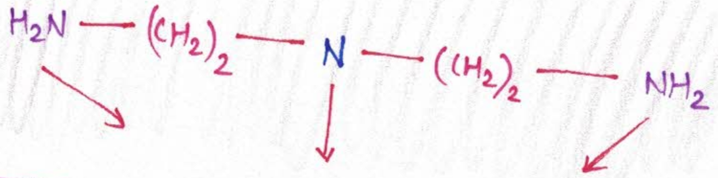
- 2-2' Dipyride



		ox	gly	DMG	ACAC
Donor atom	O - atom	2	1	0	2
	N - atom	0	1	2	0
	charge	-2	-1	-1	-1

(F) TRIDENTAL LIGANDS (D=3)

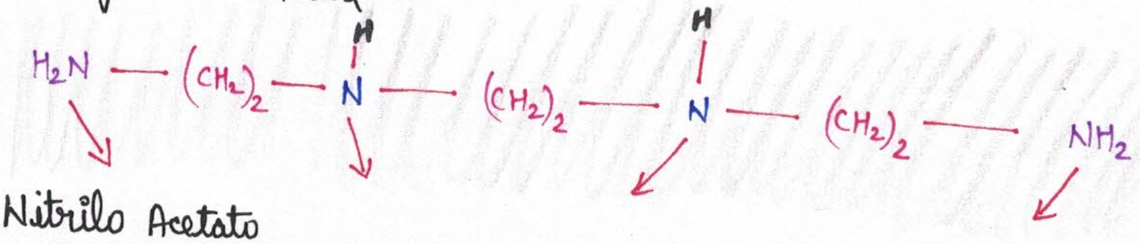
Diethylene triamine



$H_2N - (CH_2)_2 - N - (CH_2)_2 - NH_2$

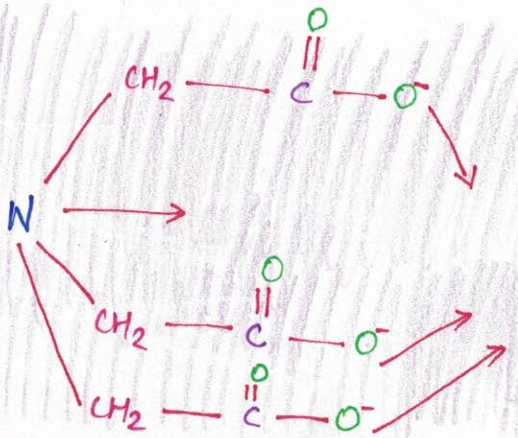
(G) TETRADENTAL LIGANDS (D=4)

Triethylene tetramine

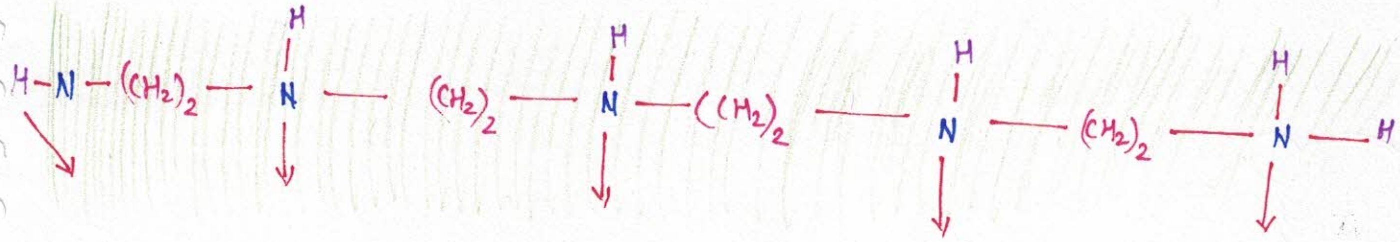


$H_2N - (CH_2)_2 - \overset{H}{\overset{|}{N}} - (CH_2)_2 - \overset{H}{\overset{|}{N}} - (CH_2)_2 - NH_2$

Nitrilo Acetato

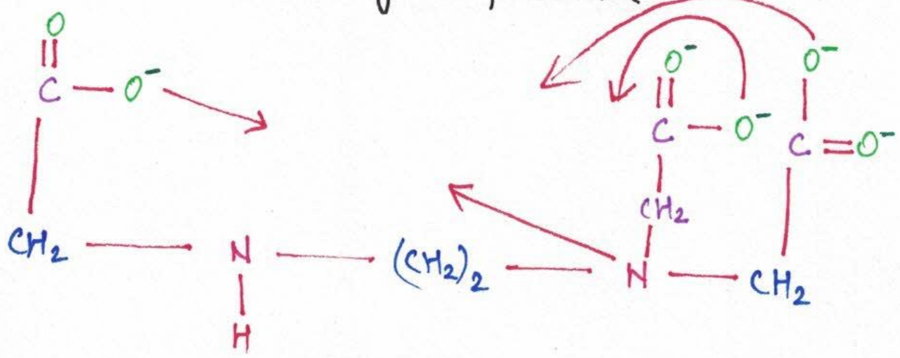


(H) PENTADENTATE LIGAND (D=5)



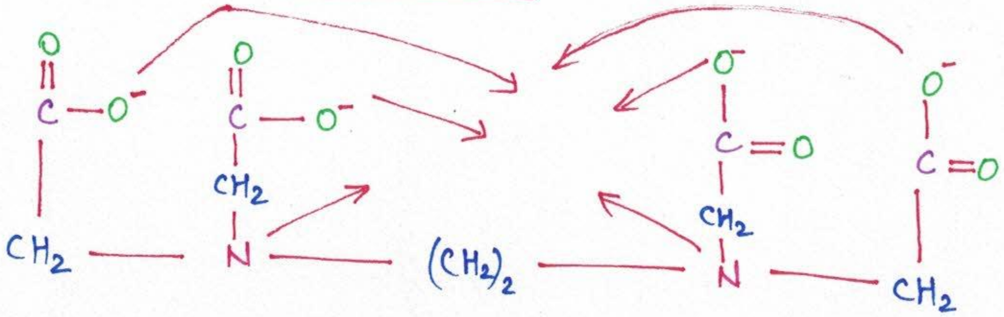
$H - N - (CH_2)_2 - \overset{H}{\overset{|}{N}} - (CH_2)_2 - \overset{H}{\overset{|}{N}} - ((CH_2)_2 - \overset{H}{\overset{|}{N}} - (CH_2)_2 - \overset{H}{\overset{|}{N}} - H$

Tetra ethylene pentamine



ethylene diamine triacetato

(I) HEXADENTAL LIGAND (D=6)



Ethylene diamine tetra Acetato ion

EDTA

Number of rings formed by each polydental Ligand = (D-1)

D = Denticity

No. of rings formed by

ⓐ $[Co(en)_3]^{+3} = 3$

ⓑ $[Co(ox)_2 en]^{-} = 3$

ⓒ $[Co(gly)(en)(H_2O)_2]^{2+} = 2$

(I) AMBIDENTATE LIGANDS

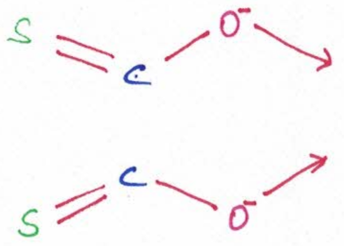
Ligands containing more than one donar atom. but at a time only one donar site will act.

Eg. ← OCN^- (cyanato), ← NCO^- (Isocyanato)

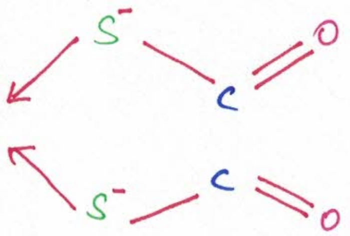
← SCN^- (Thiacyanato), ← NCS^- (Isothiacyanato)

← NO_2 (Nitrito)

NOTE - Ambidentate ligands are monodentate when their structure are linear but if central atom is sp^2 or sp^3 hybridised, then ambidentate ligand can be bidentate.



or



ⓚ FLEXIDENTATE LIGANDS

Ligands which have different denticity in different compounds.

E.g. $[Co(CH)_2SO_4]Cl$ and $[Co(en)_2SO_4Cl]$

↳ D=2 ↳ D=1

EDTA shows 6,5 or 4 denticity depending on pH of solution.

E.g. $[Co(EDTA)]^-$ and $[Co(EDTA)(H_2O)]^-$

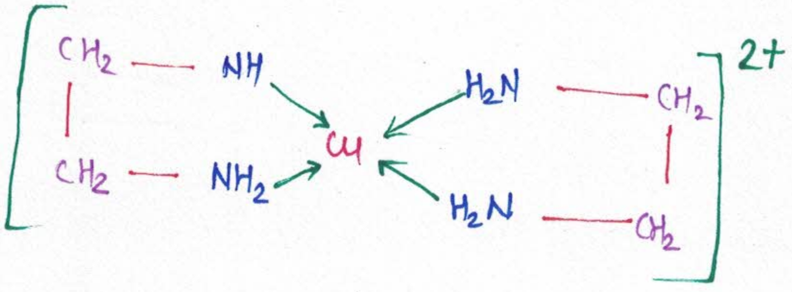
↳ D=6 ↳ D=5

ⓛ CHELATING LIGANDS

Polydentate Ligands which have tendency to form rings or chelate. usually 5 mambered or 6-membered rings are favourable.

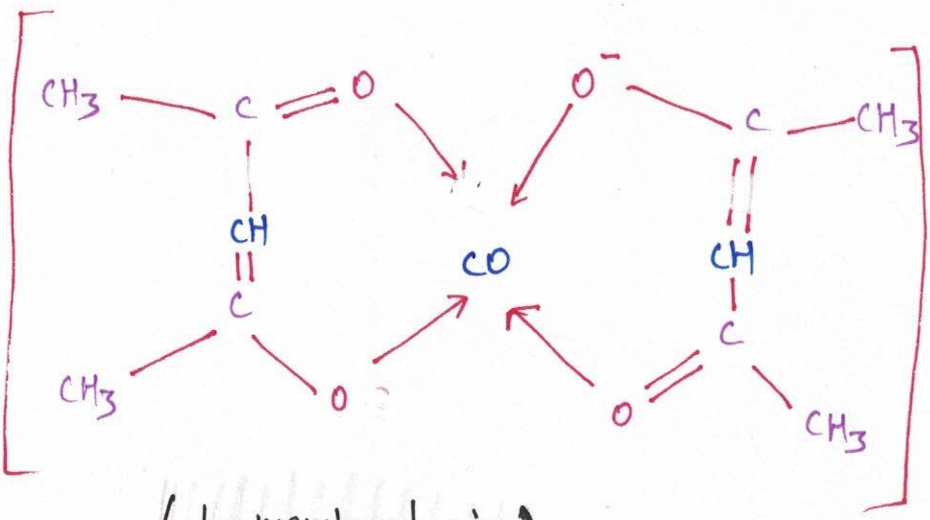
5-membered ring is stable in saturated ligands while 6-membered ring is stable in unsaturated ligands because of conjugation.

$[Cu(en)_2]^{2+}$ ⇒



5 member ring (saturated)

◎ Bonds are in conjugation (unsaturation) (6-membered ring)



(6-membered ring)

◎ Stability of chilating ligand complex are higher than monodentate ligand complex. Because of high value of formation const. (or equilibilium const. of formation of complex).

- $N^{+2} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$ $K_f = 10^8$
- $N^{+2} + 3en \rightleftharpoons [Ni(en)_3]^{2+}$ $K_f = 10^{18}$

$[Ni(en)_3]^{+2}$ will be thermodynamically more stable.

K_f high, ΔG more -ve

$$\boxed{\Delta G = -RT \ln K_f}$$

Q. a. $Co^{+3} + 4CH_3COO^- + 2NH_3 \rightleftharpoons [Co(OAC)_4(NH_3)_2]^-$ K_1
(OA)

b. $Co^{+3} + 4OAc^- + en \rightleftharpoons [Co[OAc)_4(en)]^-$ K_2

c. $Co^{+3} + 2OX^{-2} + en \rightleftharpoons [Co(OX)_2(en)]^-$ K_3

d. $Co^{+3} + EDTA^{4-} \rightleftharpoons [Co(EDTA)]^-$ K_4

If bond enthalpies in all above complex are equal then, what is the correct order of formation constants?

Ans - K_4 K_3 K_2 K_1

{More chelating complexes in ring will be more stable}

3. On Basis of Accepting or Donating Native

Classical Ligands

Ligands which do not have vacant d- orbital or π^* orbital $(M \xleftarrow{\sigma} L)$

E.g OH^-, NH_3, F^-

Non- classical Ligands

Ligands containing vacant d or π^* orbital

Type I

$M \underset{\sigma}{\overset{\pi}{\rightleftarrows}} L$

Eg CO, NO, NO^+, CN^-

Type II

$M \underset{\pi}{\overset{\pi}{\rightleftarrows}} L$

Eg C_6H_6.

$CH_2{=}CH_2$

NOMENCLATURE OF CO-ORDINATION COMPOUND

Naming of cation is done first followed by anion.

Naming of co-ordination sphere -

a. Naming of Ligands is done in alphabetical order.

b. For same type of Ligands, prefix - di, tri, tetra - - - are used.

c. If di, tri tetra etc are present in the name of ligand chelating ligand Prefix - bis, tris tetrakis etc.

d. After the naming of Ligand, name of central atom will be written based on charge present on co-ordination sphere.

METAL	CO-ORDINATION SPHERE + ve charge or neutral	 -ve charge
Fe	Iron	Ferrate
Cu	Copper	cupperate
Zn	Zinc	Zincate
Ag	Silver	Argnentate
Au	Gold	Aurrate
W	Tungsten	Tungstate/wolfram
Pb	Lead	Plumbate
Sn	Tin	stannate
Mn	Manganese	Manganate

O.s of central atom written in Roman form

NAMING OF IONISATION SPHERE

Name of ion will be written as per as its name without using prefix - di, tri, tetra etc

$[Fe(H_2O)_6]Cl_3$ → Hexa aqua Iron (III) chloride

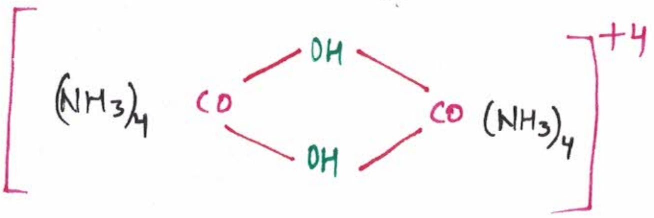
$[Co(H_2O)(NH_3)_5]Cl_3$ → Tetra ammine aqua cobalt (III) chloride

$[Co(NH_3)_2(en)_2]Cl_2$ → Diammine bis-(ethylen diamine) cobalt (III) chloride

NAMING OF BRIDGING LIGANDS COMPOUNDS

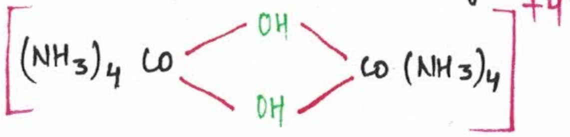
Bridge ligand is the ligand which is connected by more than one central atom.

E.g. $[(H_2O)_5Cr - OH - Cr(H_2O)_5]^{+5}$



Name of bridge element ligand is written by using μ prefix.

Name of eq. 2.



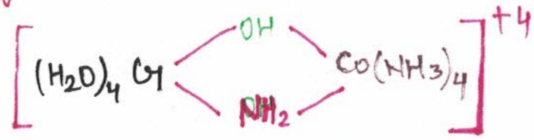
$$\left[(NH_3)_4Co\begin{matrix}OH\\ \\OH\end{matrix}Co(NH_3)_4\right]^{+4}$$

Tetraammine cobalt (III) - di - μ - hydroxatitraammine cobalt ion (III)

or → Di-(μ-hydroxo octaammine di-cobalt (III) ion)

or → Di-(μ-hydroxo bis (tetraammine cobalt (III)) ion)

or → Bis-(μ-hydroxo - tetraammine cobalt (III)) ion



$$\left[(H_2O)_4Cr\begin{matrix}OH\\ \\NH_2\end{matrix}Co(NH_3)_4\right]^{+4}$$

Tetraaqua cromium (III) - μ - amido - μ - hydroxo - Tetraaqua cobalt (III) ion

Q. Write the IUPAC name of following -

ⓐ $[Pt(NH_3)_2(H_2O)(Cl)(Br)(I)]I$

Diammine aqua bromido chlorido iodido platinum (IV) iodide.

ⓑ $[Co(gly)_3]$

Triglycinato cobalt (III)

ⓒ $[Co(gly)_2\cdot(NH_3)_2]Cl$

Diamminebis (glycinato) cobalt (III) chloride

ⓓ $Na_3[Au(CN)_4]$

Sodium tetracyanido aurite (I)

(i) $[Fe(CN)_6]^{4-}$

Hexacyanido ferrate (II) ion

ⓔ $Na[Ag(CN)_2]$

Sodium dicyanido augentate (I)

ⓕ $[Co(en)_3][Cr(CN)_6]$

tris-(ethylenediamine) cobalt (III) triajanido cromate (III)

ⓖ $[Ni(H_2O)_6][Ni(CN)_6]$

Hexa aqua nickel (III) hexacyanido nicklate (III)

ⓗ $[Pt(NH_3)_6][PtCl_6]$

Hexaammine platinum (II) Hexachlorido platinate (IV)

BONDING IN COORDINATION COMPOUND

1. Warner Theory
2. EAN Theory (Sidgwick)
3. VBT (Valence Bond Theory)
4. CFST (crystal Field Splitting Theory)

WARNOR THEORY

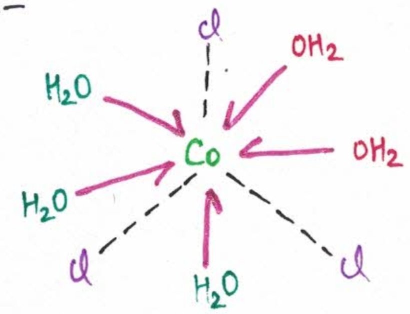
1893

By ALFRED WUNER - FATHER OF CO-ORDINATION CHEMISTRY

According to it there are 2 types of valencies in co-ordination compounds Primary & secondary

PRIMARY VALENCY	SECONDARY VALENCY
It is satisfied by anions only.	satisfied by neutral species or sometimes by anion also.
It decides the O.S of central atom.	It decides the co-ordination no. of central atom.
Variable in nature	invariable in nature
Denated by datted line (------)	Denated by Dark line (⟶)
Non - dirctional	Dirctional (decides str.)
ionisable in nature	non - ionisable in nature

on the basis of above postulates, werner decided the str. of $CoCl_3 \cdot 6H_2O$ and $CuSO_4 \cdot 4H_2O$ as:-

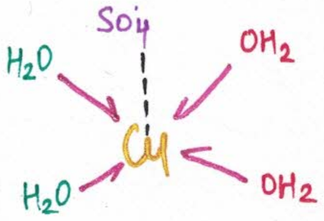


$[Co(H_2O)_6]Cl_3$

PV = 3 S.V = 6

C.N = 6 O.S = 3 C.V. = 0

(octahedral) (common valency)



$[Cu(OH_2)_4]SO_4$

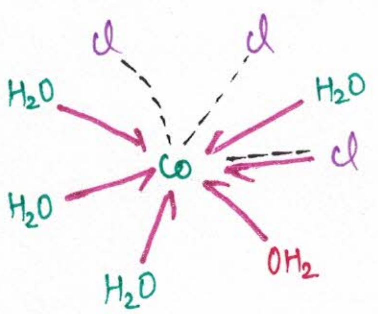
P.V = 1 S.V = 4

C.V = 0 O.S = 2

C.N = 4

Q. Draw the structure of following by using werner concept.

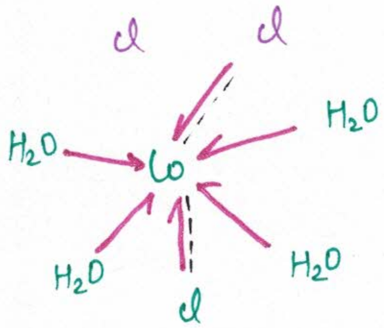
ⓐ $CoCl_3 \cdot 5H_2O$ ⓑ $CoCl_3 \cdot 4H_2O$ ⓒ $CoCl_3 \cdot 3H_2O$



$[Co(H_2O)_5Cl]Cl_2$

P.V = 3 S.V = 6

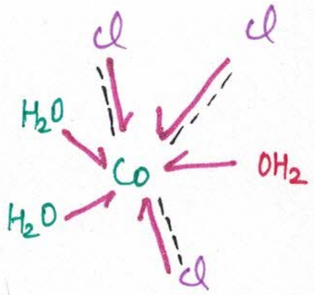
C.V = 1 O.S = +3



$[Co(H_2O)_4Cl_2]Cl$

P.V = 3 S.V = 6

C.V = 2 O.S = +3



$[Co(H_2O)_3(Cl)_3]$

P.V = 3 S.V = 6

C.V = 3

If H_2O is ligand in a complex, then CN = 6 [JEE 2010]

Werner used other following methods for calculation of confi. of co-ordination compound

Conductivity Method

Conductivity depends on -

[i] no. of ion

[ii] Magnitude of charge

$[Co(NH_3)_5Cl]Cl_2$ Ⓘ

$\downarrow$

$[Co(NH_3)_5Cl]^{+2} + 2Cl^-$

3 ions

$[Co(NH_3)_5Cl]SO_4$ Ⓘ

$\downarrow$

$[Co(NH_3)_5Cl]^{+2} + SO_4^{-2}$

2 ions

Ⓘ > Ⓘ

$[Co(NH_3)_5Br]SO_4$ (I)

$$[Co(NH_3)_5Br]SO_4 \longrightarrow [\quad]^{+2} + SO_4^{-2}$$

no. of ions = 2

charge = 4

$[Co(NH_3)_5SO_4]Br$ (II)

$$[Co(NH_3)_5SO_4]Br \longrightarrow [\quad]^{+} + Br^{-}$$

no. of ions = 2

charge = 2

(I) > (II)

Chemical Reaction Method

$Ag^+ + Cl^- \longrightarrow AgCl\downarrow$ (white)

$Ag^+ + Br \longrightarrow AgBr\downarrow$ (Pale yellow)

$Ag^+ + I^- \longrightarrow AgI\downarrow$ (Yellow)

$Ba^{+2} + SO_4^{-2} \longrightarrow BaSO_4\downarrow$ (white ppt.)

$$[Cr(NH_3)_4ClI]Br \xrightarrow{AgNO_3} AgBr\downarrow \text{ (Yellow)}$$

$$[Cr(NH_3)_4IBr]Cl \xrightarrow{AgNO_3} AgCl\downarrow \text{ (white)}$$

$CoCl_3 \cdot 6NH_3 + AgNO_3$ (excess) $\longrightarrow$ 3 mole $AgCl$

$[Co(NH_3)_6]Cl_3$

$CoCl_3 \cdot 5NH_3 + AgNO_3$ (excess) $\longrightarrow$ 2 mole $AgCl$

$[Co(NH_3)_5Cl]Cl_2$

$CoCl_3 \cdot 4NH_3 + AgNO_3$ (excess) $\longrightarrow$ 1 mole $AgCl$

$[Co(NH_3)_4Cl_2]Cl$

Colligative Properties Method

Q. 0.01 M of a compound containing $CoCl_3$ and NH_3 (1:4 molar ratio) has depression in freezing pt. 0.372. Calculate configuration of the compound. ($K_{f(H_2O)} = 1.86$).

Solution:- $\Delta T_f = i k_f m \Rightarrow 0.0372 = i(1.86)(0.01)$

$i = 2$

no. of ions = 2

$[Co(Cl)_2(NH_3)_4]Cl$

Reaction with conc. H_2SO_4

Conc. H_2SO_4 acts as a dehydrating agent.

On reaxn with concn H_2SO_4 decrease in weight shows that H_2O is present in ionisation sphere.

E.g $[Co(H_2O)_5Cl]SO_4 \xrightarrow[H_2SO_4]{conc} \text{no} \downarrow\downarrow \text{in wt}$

$[Co(H_2O)_4SO_4].H_2O \xrightarrow[H_2SO_4]{conc^n} \downarrow\downarrow \text{in wt}$

EAN (Effective Atomic Number)

by SIDGWICK

EAN = Atomic no (of central atom) − oxidation state + {no. of e^- obtained by Ligand in C.A.
or
2 × C.N.}

According to sidgwick if EAN value of central atom is equal to atomic no. of next nearest noble gas, then compound will be more stable.

Later on this concept was only fulfilled for stability of metal carbonyl compound.

Q. Calculate EAN of following:-

a. $[Fe(H_2O)_6]Cl_2$ EAN = $26 - 2 + 12 \Rightarrow 23 + 13 = 36$ [Kr]

b. $[Zn(H_2O)_4]^{+2}$ EAN = $30 - 2 + 8 \Rightarrow 36$ [Kr]

c. $[Cr(H_2O)_6]Cl_3$ EAN = $24 - 3 + 12 \Rightarrow 33$

d. $[Fe(CO_5)]$ EAN = $26 + 10 \Rightarrow 36$ [Kr]

APPLICATION OF EAN RULE

1. To decide the co-ordination number.

Zn^{+2} = $EAN = 30 + 2 + 2 \times C{\cdot}N$

$36 = 28 + 2 + C{\cdot}N$

$CN = 4$

Fe^{+2} = $EAN = 26 - 2 + 2 \times C{\cdot}N$

$36 = 24 + 2 \times C{\cdot}N$

$CN = 6$

Cu^{+} = $EAN = 36 = 29 - 1 + 2CN$

$8 = 2CN$

$CN = 4$

$[Fe(CO)_x] = 36 = 26 - 0 + 2x$

$\Rightarrow x = 5$

$[Co(CO)_x] = 36 - 27 = 2x$

$\Rightarrow 9/2 = x = 4.5$

2. To decide oxidising and reducing nature

$[Mn(CO)_6] \longrightarrow [Mn(CO)_6]^{+} + 6e^{-}$

will act as Reducing agent

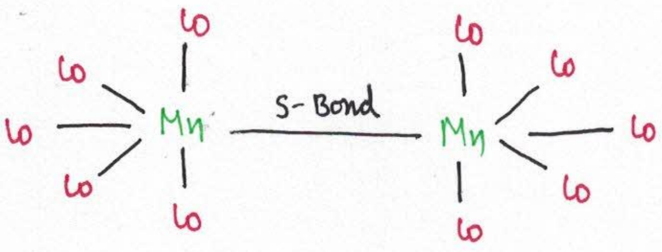
$EAN - 25 - 1 + 12$

$= 36\ [Kr]$

$[V(CO)_6] \xrightarrow{e^-} [V(CO)_6]^{-}$

$EAN = 23 + 12 = 35$ $EAN = 36$

oxidising agent



3. To decide which molecules dimerise or trimerise.

$$2Mn(CO)_5 \longrightarrow Mn_2(CO)_{10}$$

EAN $= 25 + 10 + ①$

$= 35$ ①

$= 36$ [Kr]

VBT (Valence Bond Theory)

POSTULATES

According to it, central atom provides no. of vacant orbitals which will depend on co-ordination number, to accomodate electron density obtained from ligands.

These vacant orbitals combine and form hybrid orbitals. These hybrid orbitals overlap. with field orbitals. of Ligand and form co-ordinate covalent bond.

If central metal provide $(n-1)d$ orbital, then inner orbital complex will be formed and if $(n)d$ orbital is used, then outer orbital complex will be formed.

In the presentof strong field ligand (SFL), pairing of unpaired e^- will occur.

If pairing of e^- will occur then type of complex will be low spin complex. otherwise complex will be high spin complex.

If unpaired e^- present in central atom or in any ligand of complex, then it will be paramagnetic else diamagnetic.

No. of unpaired e^- can be calculated by using property of magnetic moment.

$$\text{magnetic moment} = \sqrt{n(n+2)} \text{ B.M}$$

Depending on co-ordination no., following hybridisation are possible.

Co-ordination no.	Hybridisation	Orbitals used
2	sp ds {Linear}	$s + p_z$ $s + d_{z^2}$
3	sp^2 d^2s {Trigonal Planar}	$s + p_x + p_y$ $s + d_{xy} + d_{x^2y^2}$

4. sp^3, d^3s {Tetrahedral} — s px py pz / dxy dyz dzx s

dsp^2 {Square Law} — s px py dx^2y2

5 sp^3d, d^4s {Trigonal bi Pyramidal} — s px py pz dz^2 / dxy dyz dzx^2 s dx^2y2

dsp^3 {Square arganide} — dx^2 y^2 s px^2 py pz

6 sp^3d {octaheded} — s px py Pz dx^2y dz^2

d^2sp^3

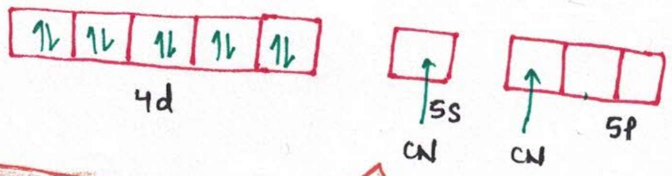
7 sp^3d {Pentagonal biyamidal}

8 sp^3d^4 {Square Anti primatic}

1. CO-ORDINATION NO. = 2

Component of CN = 2 are very rare.

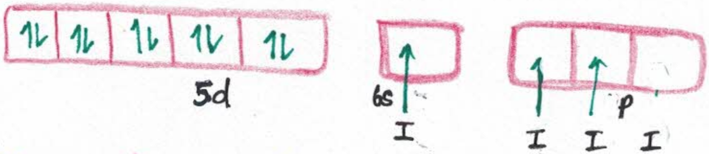
$[Ag(CN)_2]^-$ $Ag^+ = 4d^{10}\ 5s^0$



Hybri = sp Diamagnate

2. CO-ORDINATION NO. = 3

$[HgI_3]^-$ $Hg^{+2} = 5d^{10}\ 6s^0$

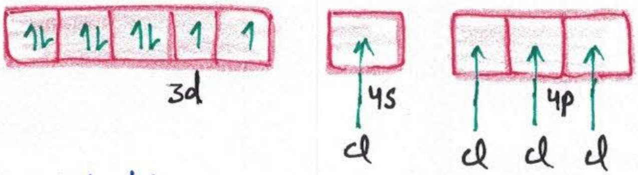


Hybridisation = sp^2 diamagnite trigonal planay

3. CO-ORDINATION NO. = 4

a. $[NiCl_4]^{2-}$

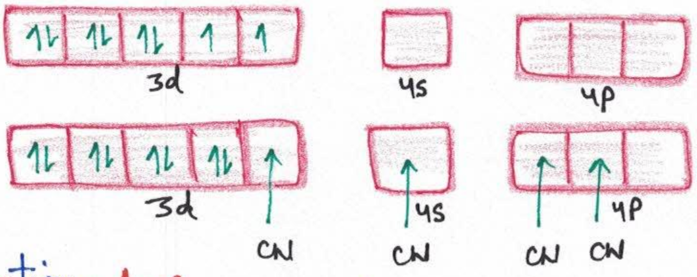
$Ni^{+2} = 3d^8\ 4s^0$



hybridisation = sp^3, tetrahedral, high spin, Paramagnetic

b. $[Ni(CN)_4]^{2-}$

$Ni^{+2} = 3d^8\ 4s^0$

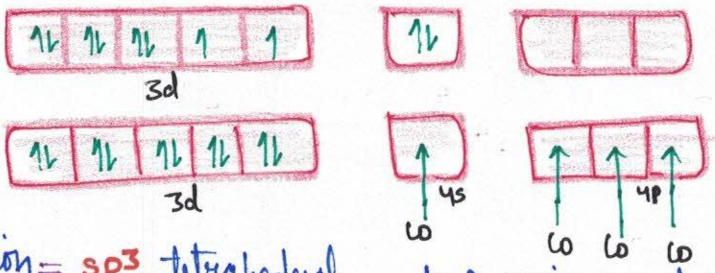


CN^- is SFL, pairing of e^- will occurs.

hybridisation = dsp^2, square planar, Low spin complex, diamagnetic

c. $[Ni^2(CO)_4]$

$Ni = 3d^8\ 4s^2$

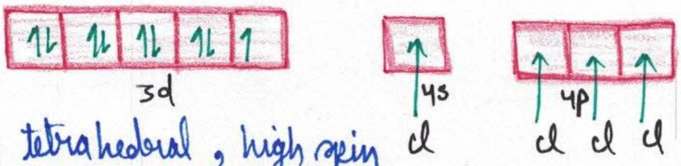


CO is SFL.

hybridisation = sp^3 tetrahedral, Low spin complex, diamagnetic

d. $[CuCl_4]^{2-}$

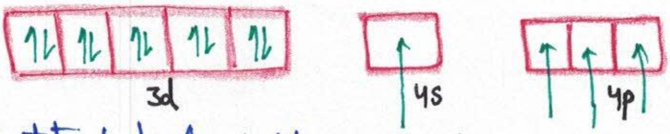
$Cu^{+2} = 3d^9\ 4s^0$



sp^3, tetrahedral, high spin

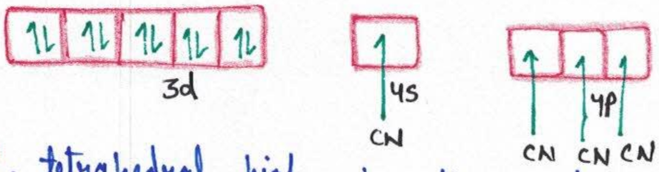
e. $[Cu(CN)_4]^{3-}$

$Cu^{+} = 3d^{10}\ 4s^0$



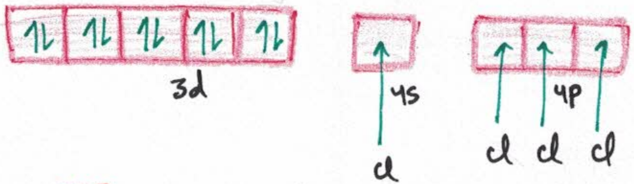
sp^3, tetrahedral, high spin, diamagnetic

f. $[Zn(CN)_4]^{2-}$



sp^3, tetrahedral, high spin, diamagnetic

g. $[ZnCl_4]^{2-}$ $Zn^{+3} = 3d^{10}, 4s^0$



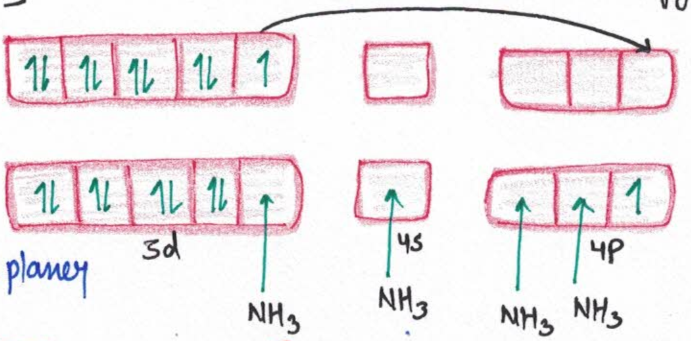
sp^3, Tetrahedral, high spin, diamagnetic

EXCEPTION OF VBT

CN=4, $3d^9$, SFL

one d-e⁻ is transferred in higher energy orbital

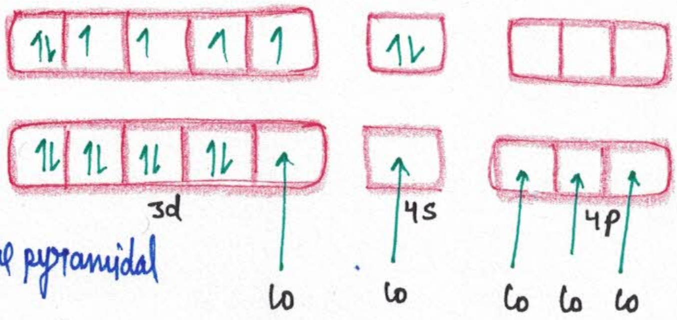
E.g. $[Cu(NH_3)_4]^{2+}$ $Cu^{+2} = 3d^9 4s^0$



dsp^2, square planer

CO-ORDINATION NO.= 5

$Fe(CO)_5$ $Fe = 3d^6 4s^2$

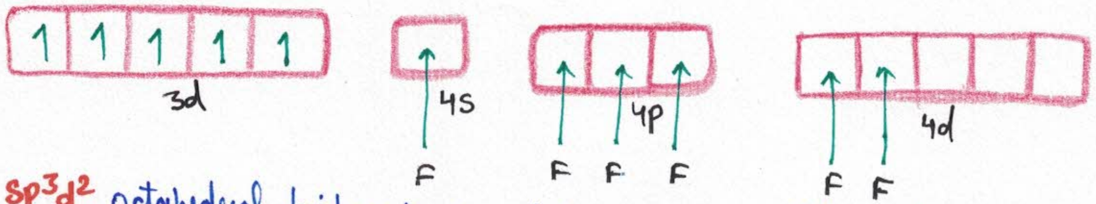


dsp^3, square pyramidal

$[Ni(CN)_5]^{3-}$

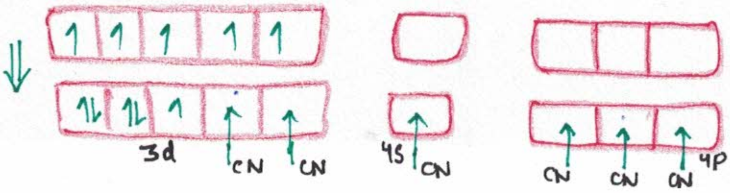
CO-ORDINATION No. = 6

a. $[FeF_6]^{-3}$ $Fe^{+3} = 3d^5 4s^0$



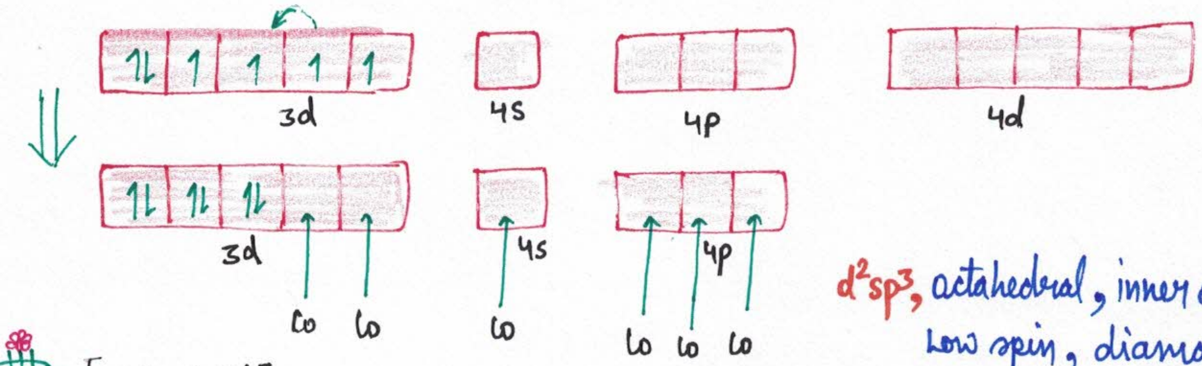
sp^3d^2, octahedral, high spin, complex, paramagnetic, outer orbital complex

b. $[Fe(CN)_6]^{3-}$



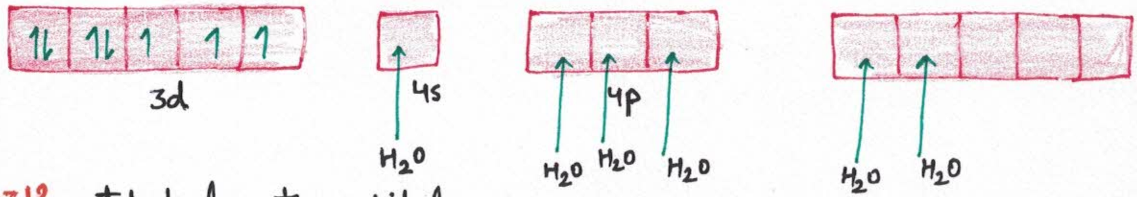
d^2sp^3, octahedral, inner orbital complex. Low spin paramagnetic.

c. $[Co(CO)_6]^{+3}$ $Co^{+3} = 3d^6 4s^0$



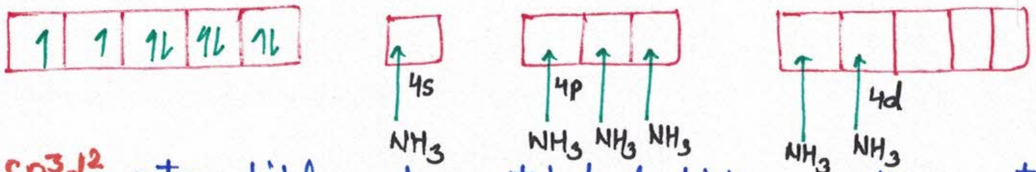
d^2sp^3, octahedral, inner orbital complex, low spin, diamagnetic

d. $[Ni(H_2O)_6]^{+3}$ $Ni^{+3} = 3d^7 4s^0$



sp^3d^2, octahedral, outer orbital complex, high spin, paramagnetic

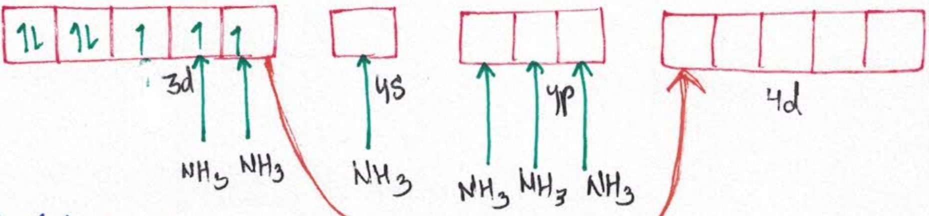
e. $[Zn(NH_3)_4]^{+2}$ $Zn^{+2} = 3d^{10} 4s^0$



sp^3d^2, outer orbital complex, octahedral, high spin, diamagnetic

EXCEPTION OF VBT

{CN = 6 + cl ^{7} + SFL} $[Co(NH_3)_6]^{+2}$ $Co^{+2} = 3d^7 4s^0$



$d^2s^2p^3$, octahedral low spin complex, paramagnetic, inner orbital complex.

- H_2O and $C_2O_4^{2-}$ (ox) are acting as SFL with Co^{+3}.
- NH_3 act as WFL with Fe^{+2} and Mn^{+2}.
- F^- act as SFL with Ni^{+4}

CFST (Crystal Field Spliting Theory) CFST

According to it, bond b/w central atom and ligand was considered as purely electrostatic in which central atom acts as +ve point charge while ligands acts as -ve point charge.

In free metal ion, energy of all 5 d-orbitals are equal i-e; orbitals are in degenerated form.

When a ligand approaches to central atom, repulsion will generate between lone pair of ligand and electron present in metal orbital, due to which energy of some orbitals will increase while energy of some other orbitals will decrease.

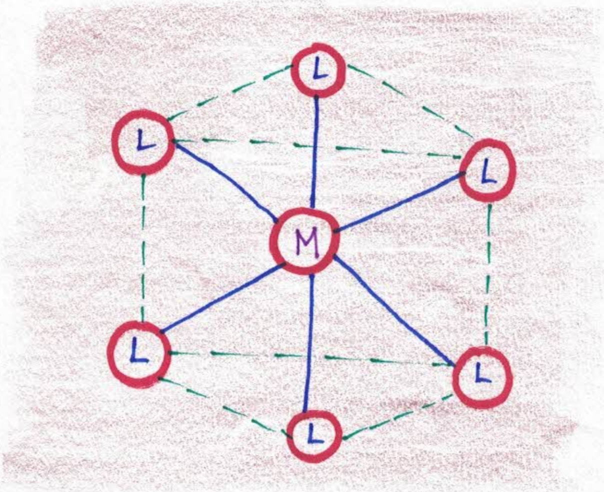
There are 5-orbitals

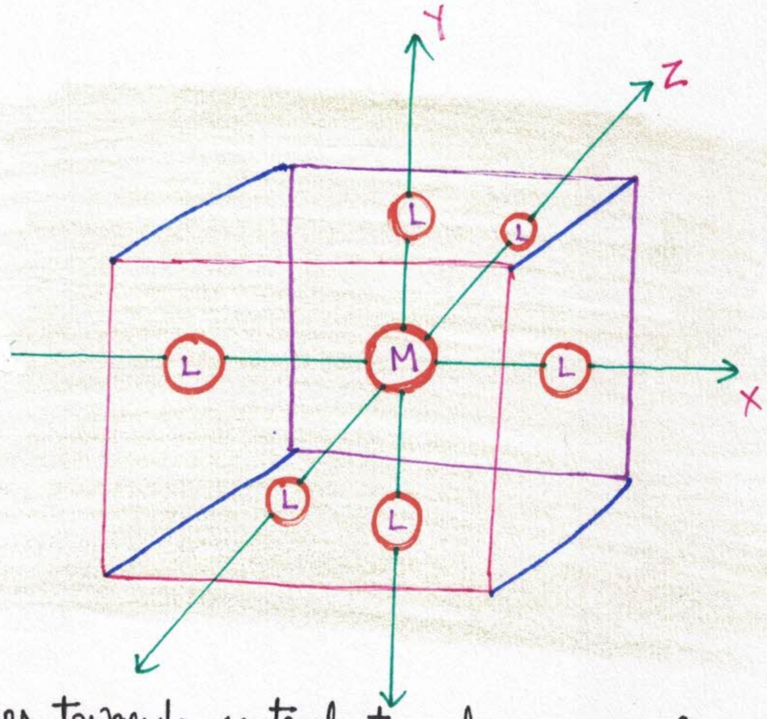
$$\underbrace{d_{xy} \quad d_{yz} \quad d_{zx}}_{(t_{2g})} \qquad\qquad \underbrace{d_{x^2y^2} \quad d_{z^2}}_{(e_g)}$$

non-axial   axial

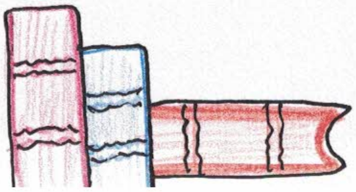
ORBITAL SPRITTING IN CN=6

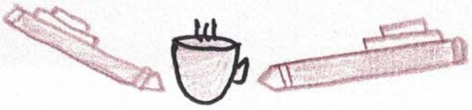
Shape – octahedral

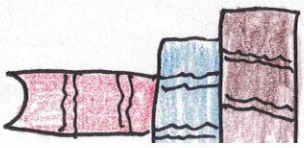


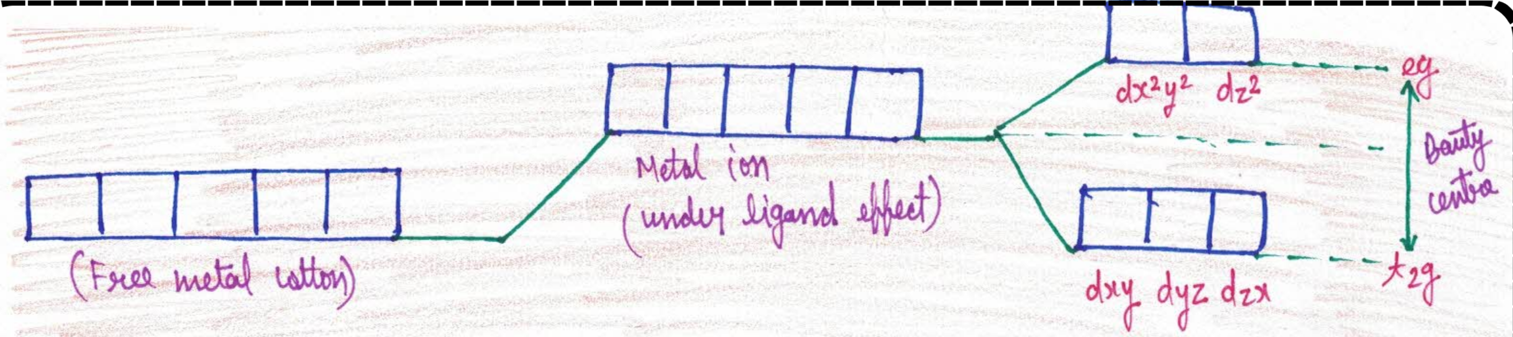


In this arrangement, ligand approaches towards central atom along the axis due to which repulsion will increase in orbitals which are of axial type.









Δ_c - splitting energy gap (in octahedral)
($\Delta_o = 10\,Dq$)

CFSE (crystal Field) = $[-0.4\,n_{t_{2g}} + 0.6\,n_{e_g}]\,\Delta_o$
(splitting energy)

Total CFSE value = $[-0.4\,n_{t_{2g}} + 0.6\,n_{e_g}]\,\Delta_o + xP$

x = no. of paired e⁻

P = pairing energy (c/m)

{1 KJ/mol = 83.6 CM^{-1} , 1 KCal/mol = 350 CM^{-1}}

$n_{t_{2g}}$, n_{e_g} = no. of e⁻ in t_{2g}, eg level respectively.

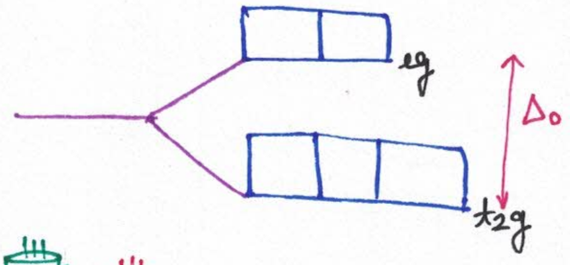
$$\Delta E = \frac{hc}{\lambda} = hc(\bar{\nu}) \qquad \frac{1}{\lambda} \rightarrow CM^{-1}$$

$\Delta E = hc \times \left(\frac{1}{\lambda}\right)$ and get the value of E in particular unit.

CALCULATION OF CFSE IN DIFFERENT CONFIGURATION

1. d^1

Config = $t_{2g}^{1,0,0}\ e_g^{0,0}$
CFSE = $0.4\,\Delta_o$



2. d^2

Config = $t_{2g}^{1,1,0}\ e_g^{0,0}$
CFSE = $-0.8\,\Delta_o$

3. d^3

Config = $t_{2g}^{1,1,1}\ e_g^{0,0}$
CFSE = $-1.2\,\Delta_o$

4. d^4

ⓐ $\Delta_o > P$

Confi = $t_{2g}^{2,1,1}\ e_g^{0,0}$
CFSE = $-1.6\,\Delta_o$

ⓑ $\Delta_o < P$

Confi = $t_{2g}^{1,1,1}\ e_g^{1,0}$
CFSE = $-1.2\,\Delta_o + 0.6\,\Delta_o = -0.6\,\Delta_o$

5. d^5

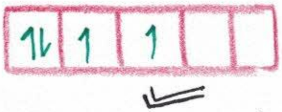
(a) $\Delta_o > P$ config $= t_{2g}^{2,2,1}\ eg^{0,0}$

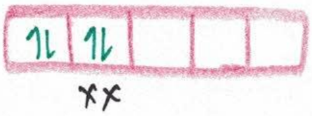
(b) $\Delta_o < P$ config $= t_{2g}^{2,1,1}\ eg^{1,1}$

What is the no. of unpaired e⁻ in $[Cr(NH_3)_6]^{+2}$

Cr^{+2} $3d^4 4s^0$

∵ NH_3 is a SFL pairing of e⁻ will occur





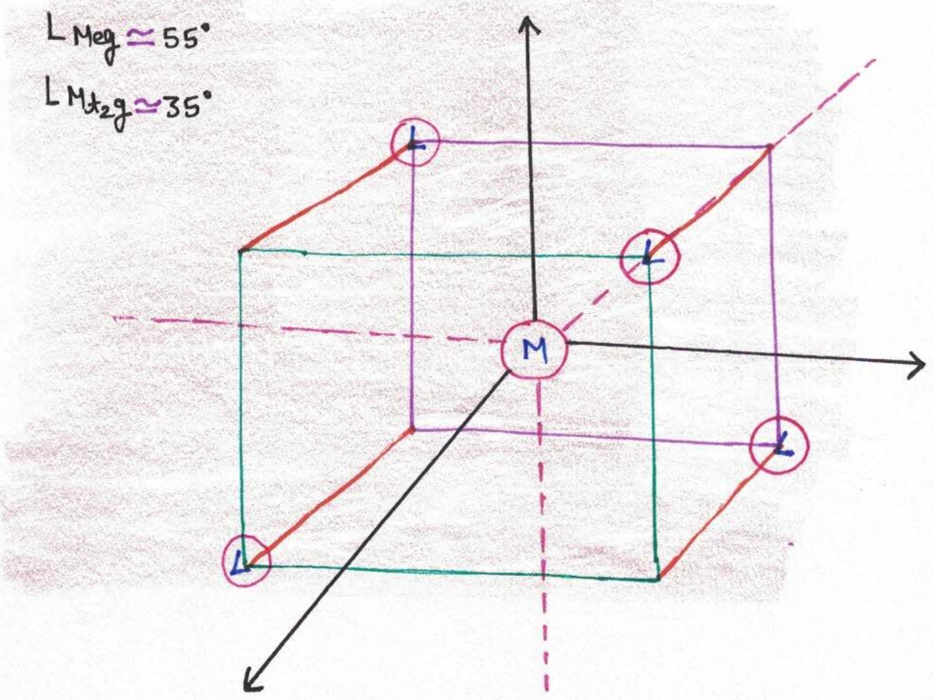
no. of unpaired e⁻ = 2

ORBITAL SPLITTING IN (CN = 4)

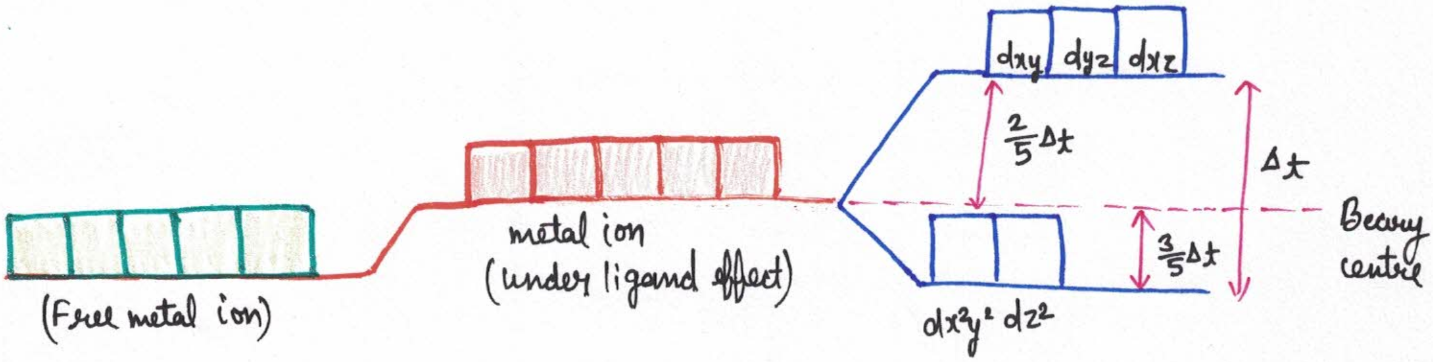
CN = 4

Tetrahedral

Square planar



In this arrangement ligand approaches to central atom along in between the axis due to which repulsion will generate in orbitals of non-axial type.



$$\Delta_t = \frac{4}{9}\Delta_o = \left(\frac{2}{3}\right)\times\left(\frac{2}{3}\right)\times\Delta_o$$

no. of ligands are 2/3 of that in octahedral

In this arrangement, ligands are not exactly approaching along the axis.

COLOUR IN CO-ORDINATION COMPOUNDS

The colour in co-ordination compound arises because of following 3 reasons :-

ⓐ d-d transition ⓑ Polarisation ⓒ charge transfer

ⓐ d-d TRANSITION

Transition of e⁻ from lower energy d-orbital to higher energy d-orbital is k/as d-d transition.

a. Metal should be attached with ligand.

b. d-orbital should be partially filled, i.e. d^1-d^9 configuration.

- when light of certain energy is absorbed e⁻ from lower energy d-orbital excite to higher energy d-orbital and during returning to lower energy d-orbital, energy released in the form of electromagnetic radiation. If corresponding wave-length lies in visible range (3800 - 7000 Å) then colour appears.

©. CHARGE TRANSFER

LIGAND TO METAL - Temporary transfer of charge from ligand orbital to metal orbital. In this condition, migration of e⁻ taking place from lignd to central metal.

E.g. (MnO_4^-) Pink (MnO_4^{2-}) Green ($Cr_2O_7^{2-}$) Orange (CrO_4^{2-}) Yellow

METAL TO LIGAND - Temporary transfer of charge from metal orbital to ligand orbital.

E.g. CO, NO, CN^-, etc.

METAL TO METAL - Temporary transfer of charge from one metal (lower O.S) to other metal (high O.S).

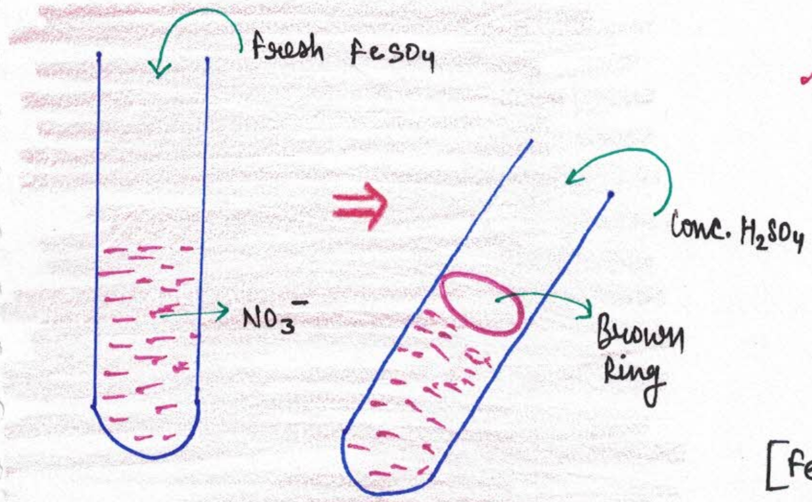
Both metal should not be present in same co-ordination spere.

Prussian blue - $\underset{III}{Fe_4}[\underset{II}{Fe}(CN)_6]_3$ **Turm bull blue** - $\underset{II}{Fe_3}[\underset{III}{Fe}(CN)_6]_2$

Other important examples of lignd to metal charge transfer.

A. .... BROWN RING COMPLEX ....

$[Fe(H_2O)_5NO]SO_4$



$$NO_3^- + Fe^{+2} \longrightarrow NO + Fe^{+3}$$

$$Fe^{+2} + NO + H_2O + SO_4^{2-} \longrightarrow [Fe(H_2O)_5NO]SO$$

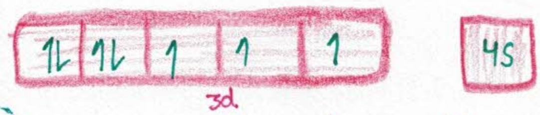
(Brown ring)

Experimentally, magnetic moment = $\sqrt{15}$ B.

no. of unpaired e⁻ = 3

$[Fe(H_2O)_5NO]SO_4$

$Fe^+ = [Ar]\,3d^7 4s^0$



Fe^+ Ligand = NO^+ O.S of Fe is +1.

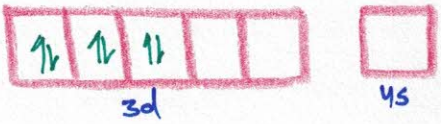
B. .... SODIUM NITROPRUSSIDE ....

$Na_2[Fe(CN)_5NO]$

experimental magnetic moment = 0

$Fe^{+2} = [Ar]^{3}d^{6}4s^{0}$

Fe^{+2}, NO^{+}



Intensity of colour due to charge transfer is higher than from d-d transfer because in charge transfer, Laprate's rule is not required.

ISOMERISM

STRUCTURAL ISOMORISM

- Ionisation
- Hydrate
- Linkage
- Co-ordination position
- Polymerisation

STEREOISOMORISM

- G.I
- D.I

Monodental ligand – a, b, c, d

bidental ligand – AA, BB, CC ..... (symmetric)
AB, BC, CD ...... (unsymmetric)

1. IONISATION ISOMERISM

different ions during ionisation or diff ion in ionisation sphere.

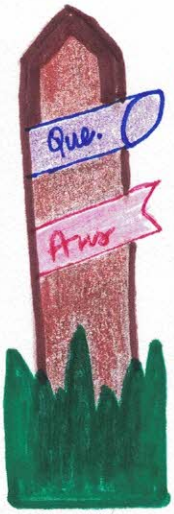
E.g $[Co(NH_3)_5Br]SO_4$

- $AgNO_3$ – ✗
- $BaCl_2$ – white ppt ($BaSO_4$)

$[Co(NH_3)_5SO_4]Br$

- $AgNO_3$ – yellow ppt ($AgBr$)
- $BaCl_2$ – ✗

These isomers can be differentiated by chemical test or molar conductivity.



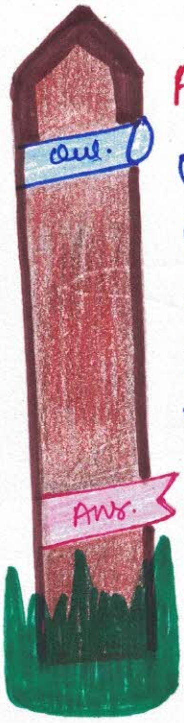
How many ionisation isomers are possible for following?

a. $[Fe(H_2O)_4ClBr]I$ = 3

b. $[Fe(H_2O)_5Cl]Br$ = 2

c. $[Fe(H_2O)_5Br]Br$ = 1

● During ionisation isomer formation, one anion is replaced by other anion, such that CN does not changes.



Among the following which does not follow ionisation isomerism?

a. $[Co(NH_3)_5Cl]Cl$

b. $Na_2[Fe(CN)_5NO]$

c. $[Fe(H_2O)_6]^{+9}$

d. $[Co(H_2O)_5Cl]SO_4$

e. $[Co(NH_3)_5Cl]Br$

f. $[Co(NH_3)_6]Cl_3$

g. $K_4[Fe(CN)_6]$

h. $[Fe(H_2O)_4SO_4]Cl$ → Bidentate

i. $[Co(NH_3)_6][CoCl_6]$ → anion is complex.

a, b, c, d, e, h, f

b. HYDRATE OR SOLVATED ISOMERISM

Ionic compounds in which H_2O molecules are in hydrated form are different in ionisation sphere.

E.g. $[Fe(H_2O)_6]Cl_3$, $[Fe(H_2O)_5Cl]Cl_2, H_2O$, $[Fe(H_2O)_4Cl_2]Cl\cdot 2H_2O$

If solvent is different from H_2O like ammonia, alcohol, diethyle ether, then this type of isomerism will be known as solvated isomerism.

c. LINKAGE ISOMERISM

Given by complex containing ambidentate ligands.

E.g. $[Fe(H_2O)_5NO_2]Cl_2$, $[Fe(H_2O)_5(ONO)]$

COORDINATION ISOMERISM

Ionic compounds in which both cation and anion are co-ordination sphere.

Isomers are formed by exchange of ligands between central atom.

E.g. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

How many co-ordination isomers are possible?

$[Cr(NH_3)_6][Fe(CN)_6]$

Cr^{+3} Fe^{+3}

$[Cr(NH_3)_3(CN)_3]^{-3}$ $[Fe(CN)_3(NH_3)_3]$

both are spheres are neutral, not a complex comp.

no. of co-ordination isomers = 6

Cr	Fe
$6NH_3$	$0NH_3$
$5NH_3$	$1NH_3$
$4NH_3$	$2NH_3$
$3NH_3$	$3NH_3$
$2NH_3$	$4NH_3$
$1NH_3$	$5NH_3$
$0NH_3$	$6NH_3$

STEREO ISOMERISM

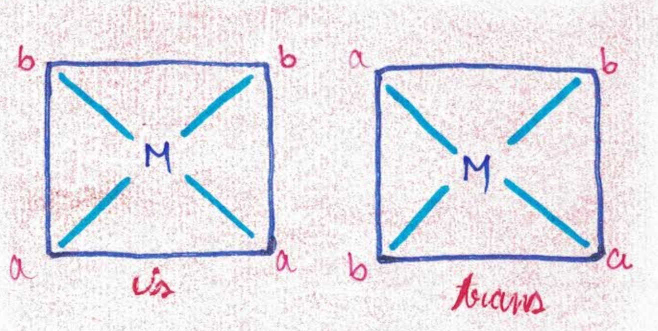
A GEOMETRICAL ISOMERISM

☞ CN – 4 → Tetrahedral (GI ××)

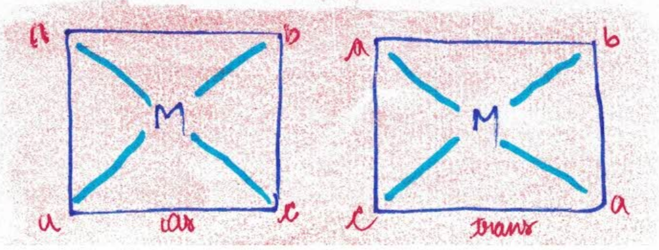
→ Square planar (GI ✓)

☞ Ma_4, Ma_3b, Mab_3 (GI ××)

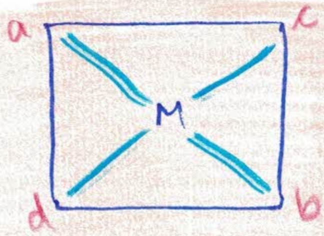
☞ Ma_2b_2 (GI ✓)

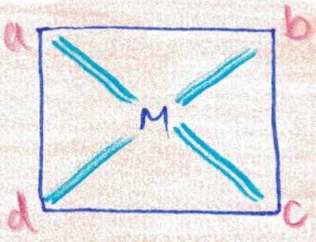


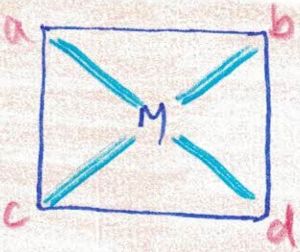
☞ Ma_2bc (GI ✓)



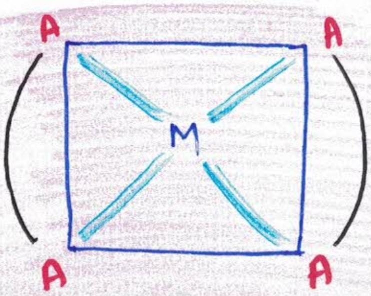
M (abcd)   3 GI

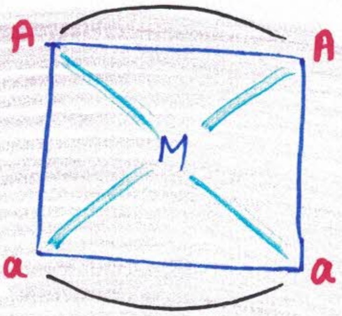






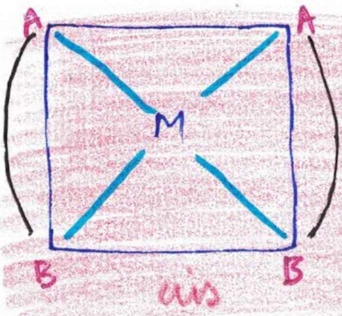
$M(AA)_2$ no GI $\Rightarrow$ $M(AA)a_2$, $M(AA)^{bc}$ no GI.

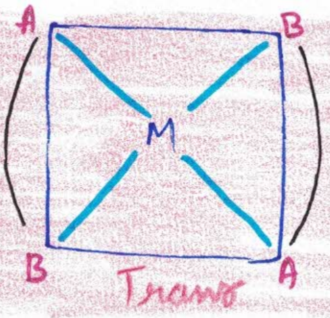


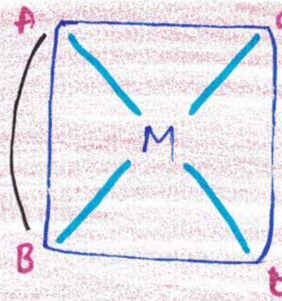


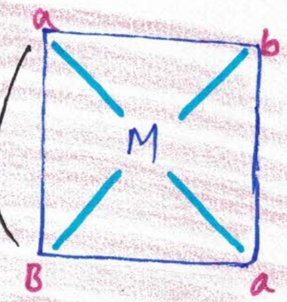
$M(AB)_2$

$\Rightarrow$ $M(AB)ab$









$M(AB)a_2$ (×× GI)
square planar

In CN=4 GI is possible in Ma_2b_2, Ma_2bc, M (abcd). $M(AB)_2$, $M(AB)ab$, M (AB) (CD).

Que. Among the following, which will give GI?

a. $[Zn(NH_3)_4]Cl_2$ b. $[Rb(Ph_3)_3Cl]Cl_2$

c. $[Pt(en)_2]^{+2}$ d. $[Pt(gly)_2]$

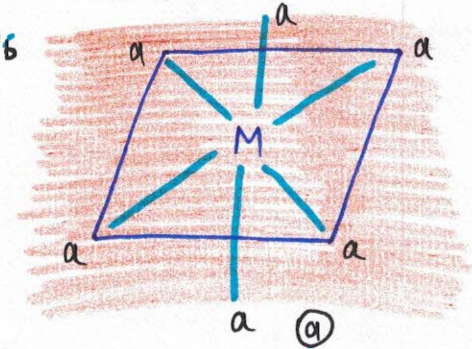
Ans.

a Tetrahedral   b square planar but Ma_3b

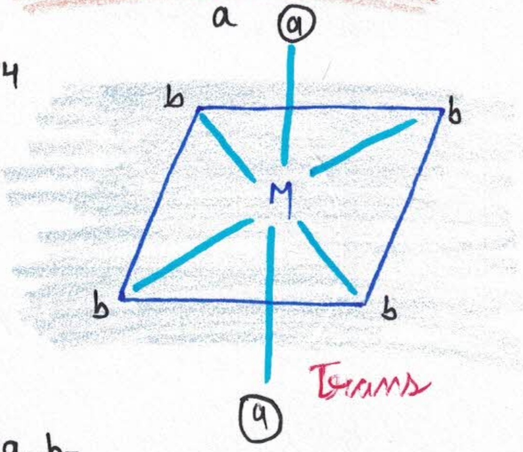
c Sq. planar but $M(AA)_2$ d. Sq. planar $M(AB)_2$

CN = 6 → octahedral

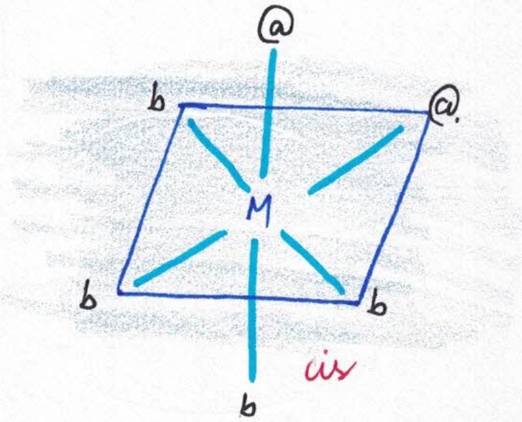
- Ma_6 $\quad$ Ma_5b , Mb_5a (no GI)



- Ma_2b_4

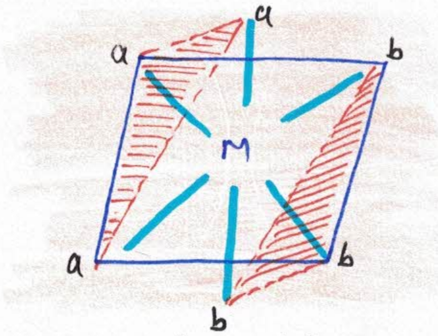


Trans

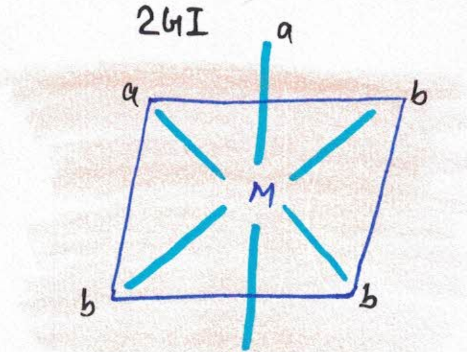


cis

- Ma_3b_3 $\quad$ 2GI



Fac (Facial form cis form)



Mer (Meridional form transform)

- $Ma_3b_2c = 3$
- $Ma_3bcd = 4$
- $Ma_2b_2d_2 = 5$
- $Ma_2b_2cd = 6$
- $M(a_2bcde) = 9$
- $M(abcdef) = 15$

M (abcdef)

a → b
a → c
a → d
a → e
a → f
⑤

b → c
b → d
b → e
b → f
④

c → d
c → e
c → f
③

d → e
d → f
②

c → f
①

$\boxed{\text{Total} = 15}$

$M(AA)_3$ ✗✗ $\quad$ $M(AA)_2a_2$ ✓

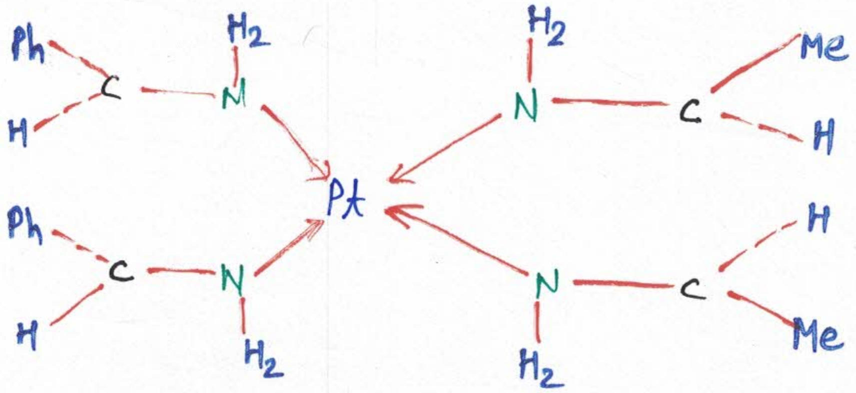
OPTICAL ISOMERISM

CONDITION

Molecule / complex sh contain chiral centre and molecule should be assymetric.

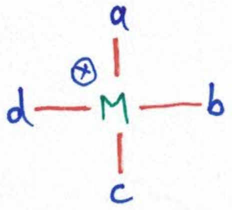
CN = 4 ⇒ square planar / O.I ×× concept in chiral ligand having chiral centre.

E.g

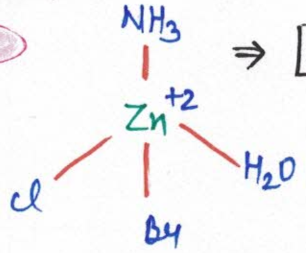


Tetrahedral (OI ✓✓)

- when all monodental ligands are different.



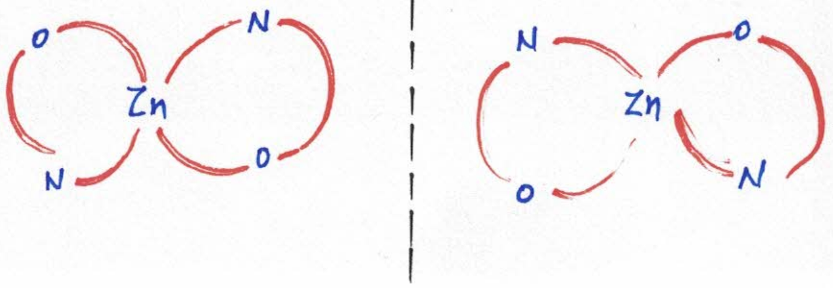
E.g



⇒ $[Zn(Cl)(Br)(H_2O)(NH_3)]$.

- bidental unsymmetric ligands

E.g $Zn(gly)_2$



CN = 6 Octahedral

Forms	GI	OI	Stereoisomers
Ma_6	0	0	0
Ma_5b	0	0	0
Ma_4b_2	2	0	2
Ma_3b_3	2	0	2
Ma_3b_2c	3	0	3
Ma_3bcd	4	1	5
$Ma_2b_2c_2$	5	1	6
Ma_2b_2cd	6	2	8
Ma_2bcde	9	6	15
$M(abcdef)$	15	15	30