CO-ORDINATION COMPOUNDS

Co-ordination Compounds

Transition metals form a large no. complex compounds in which the metal atoms are bound to a number of anions or neutral molecule by sharing of $e^{\ominus}$. such compound are known as co-ordination compounds.

Difference b/w Double Salt and Co-ordination Compound

Double Salt	Co-ordination Compounds.
→ They usually contain two simple salts in equimolar proportion	→ The simple salts from which they are formed may or may not be in equimolar prop.
→ They are ionic compound and do not contain any co-ordinate bond	→ They may or may not be ionic but the complex part always contain co-ordinate bond
• The properties of the double salts are the same as those of its constituent compounds.	The properties of the co-ordination compounds are different from its constituent.
• In the double salt metal ions show their normal valency	• In a co-ordination compound the metal ion satisfy its two type of valencies called primary and secondary valency.
• A double salt loses its identity in the solution	• A co-ordination compounds retain its identity in its solution.
e.g $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$	e.g $K_4[Fe(CN)_6]$

→ Types of Co-ordination Compounds

Cationic Complex	Anionic Complex	Neutral Complex
complex ion carry +ve charge	complex ion carry −ve charge	complex doesn't carry any charge
$[Co(NH_3)_6]^{2+}$	e.g $[Fe(CN)_6]^{4-}$	e.g $[Ni(CO)_4]$

Ligands

The atoms, ions or molecules which can donate the lone pair of e^- to central metal atom by co-ordinate bond in co-ordination compounds are called ligands.

Denticity of ligands :-

The number of donor atoms present in the ligand is called its denticity. On the basis of denticity ligands are of different forms as: monodentate, bidentate, tridentate, tetradentate, polydentate hexadentate etc.

Monodentate ligands

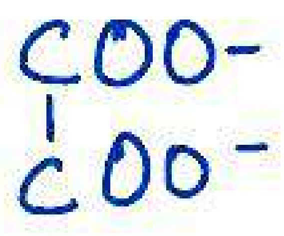
When a ligand is bound to a metal ion through a single donor atom

e.g Cl^-, Br^-, CN^-
$H_2\ddot{O}:$ $\ddot{N}H_3$, CO

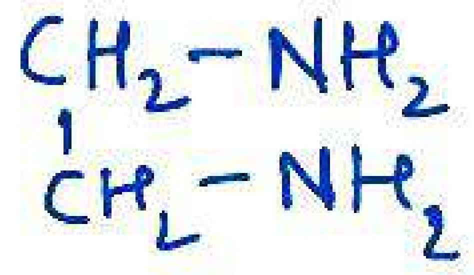
Bidentate ligands

When a ligand can bind through two donor atoms.

e.g oxalato , ethane-1,2 -diamine , Glycinato (Gly)



$$\begin{array}{l} COO^- \\ | \\ COO^- \end{array}$$



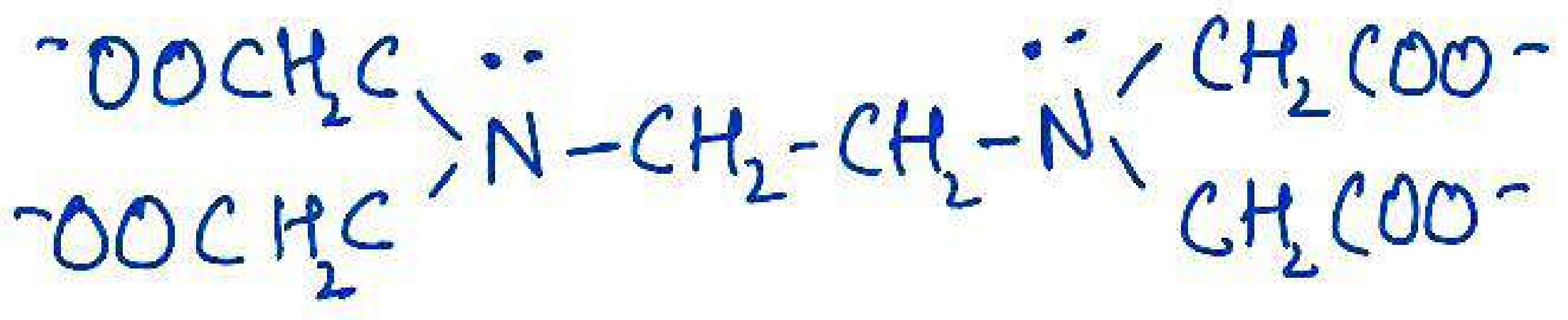
$$\begin{array}{l} CH_2-NH_2 \\ | \\ CH_2-NH_2 \end{array}$$

$H_2N-CH_2-COO^-$

Polydentate ligands

When a ligand have more than two donating sites.

e.g EDTA (Ethylene Diamine Tetra Acetate Ion)



$$\begin{array}{l} ^-OOCH_2C \\ ^-OOCH_2C \end{array}\!\!>\ddot{N}-CH_2-CH_2-\ddot{N}<\!\!\begin{array}{l} CH_2COO^- \\ CH_2COO^- \end{array}$$

Donor Atoms → 6

Hexadentate ligands.

Ambidentate ligands

Those ligands which have two donor atoms but use one atom to attach with a central metal atom. So these are monodentate ligands

e.g CN^- (Cyano) / NC^- (isocyano) } SCN^- (thiocyano) / NCS^- (isothiocyano)

Negative ligands which have negative charge

Symbol of ligands	Name of ligands	charge on ligands
CN^-	Cyanido	−1
Cl^-	Chlorido	−1
Br^-	Bromido	−1
I^-	iodido	−1
NO_2^-	Nitrito-N	−1
ONO^-	Nitrito-O	−1
OH^-	Hydroxo	−1
NO_3^-	Nitrato	−1
SCN^-	thiocyano	−1
NCS^-	isothiocyano	−1
CH_3COO^-	Acetato	−1
H^-	Hydrido	−1
O^{2-}	oxo	−2
O_2^{2-}	peroxo	−2
SO_3^{2-}	Sulphito	−2
SO_4^{2-}	Sulphato	−2
CO_3^{2-}	Carbonato	−2

Bidentate

gly	glycenato	−1
OX^{2-}	oxalato	−2

Neutral ligands

NH_3	ammine	0
$CH_3\text{-}NH_2$	Methylamine	0
H_2O	aqua	0
NO	Nitrosyl	0
CO	Carbonyl	0
CS	thio carbonyl	0
PH_3	Phosphine	0
	Triphenyl phosphine	0
H_2NCSNH_2	Thio urea	0
	Pyridine	0
CH_3	Methyl	0

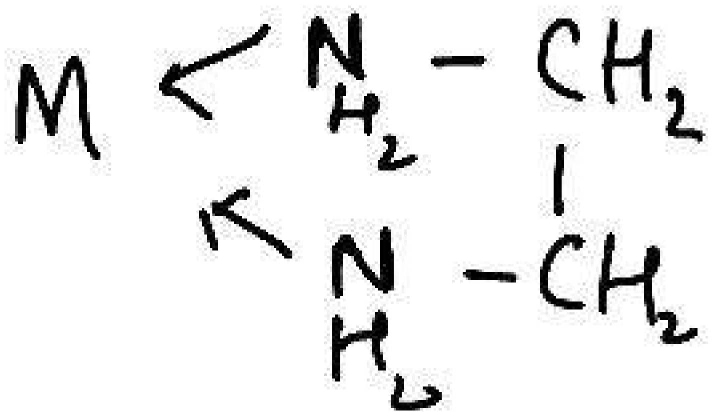
Bidentate

ethane-1,2-diamine	en	0

Chelating ligands :-

It is closed ring type compound formed by polydentate ligands (chelating ligand) on binding to central metal atom

e.g



Importance

- it forms more stable complex, called chelating effect

Use

- in softening of Hard water
- Detection of metal ion
- separation of f-block elements.

Co-ordination Entity

The central metal atom and the ligands which are directly attached to it are enclosed in square bracket and called co-ordination sphere or co-ordination entity

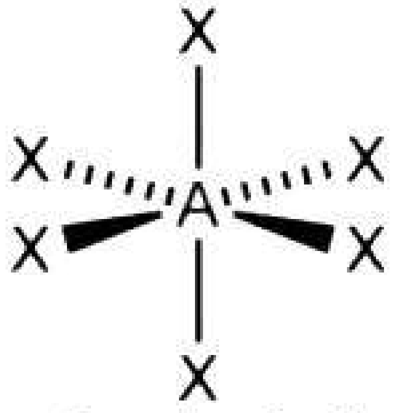
e.g $[Fe(CN)_6]^{4-}$ is called coordination sphere.

Counter Ion

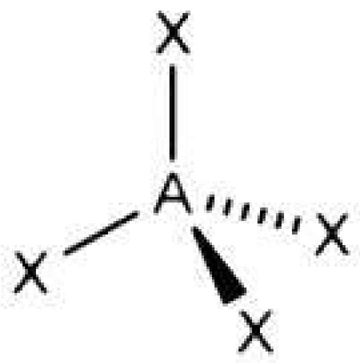
The ionisable groups written outside the square bracket and are called counter ions. eg $K_4[Fe(CN)_6]$ where K_4 ions are called counter ions

Co-ordination Polyhedron

The spatial arrangement of the ligands around the central metal atom is called co-ordination polyhedron e.g



Octahedral



Tetrahedral

Co-ordination Number

The total number of co-ordinate bond formed by ligands with central metal atom

$$\text{Co-ordination Number} = \sum(\text{Number of ligands} \times \text{Denticity})$$

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

$C.N = 6 \times 1 = 6$

$[CoCl_2(en)_2]^{1+}$

$C.N = 2 \times 1 + 2 \times 2 = 6$

Oxidation Number

The charge present on the central metal atom in a co-ordination compound is called oxidation number. It is always positive.

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

$$\downarrow$$

$$4(1) + x + 6(-1) = 0 \qquad \boxed{x = 2}$$

ON THE BASIS OF LIGANDS

Homoleptic in which only one type of ligands are present
e.g $K_4[Fe(CN)_6]$

Heteroleptic in which different type of ligands are present
e.g $[CoCl_2(en)_2]Cl$

Nomenclature of Co-ordination Compounds

e.g
- $K_4[Fe(CN)_6]$ → potassium hexacyanido ferrate (II)
- $[CrCl_2(H_2O)_4]NO_3$ → tetraaquadichlorido chromium (III) nitrate
- $[CoCl(NO_2)(NH_3)_4]NO_3$ → Tetraammine chlorido nitro-N-cobalt (III) nitrate
- $K_3[Fe(C_2O_4)_3]$ → potassium trioxalato ferrate (III)
- $K_3[Co(CN)_5(NO)]$ → potassium pentacyanido nitrosyl cobaltate (II)
- $[CoCl_2(en)_2]SO_4$ → dichlorido bis (ethane-1,2-diamine) cobalt (IV) sulphate
- $[CoCl(ONO)(en)_2]^+$ → chlorido bis (ethane-1,2-diamine) nitrito-O cobalt (III) ion
- $[Ni(CO)_4]$ → tetracarbonyl nickel (0)
- $Li[AlH_4]$ → lithium tetrahydrido aluminate (III)

Werner Theory

- Metals possess two types of valencies, called primary or ionisable valency (oxidation number and secondary or non-ionisable valency (Co-ordination Number)
- The primary valencies are non-directional.
- The complex compound do not show any property of the central metal atom and the ligands present in it.

Valence Bond Theory :

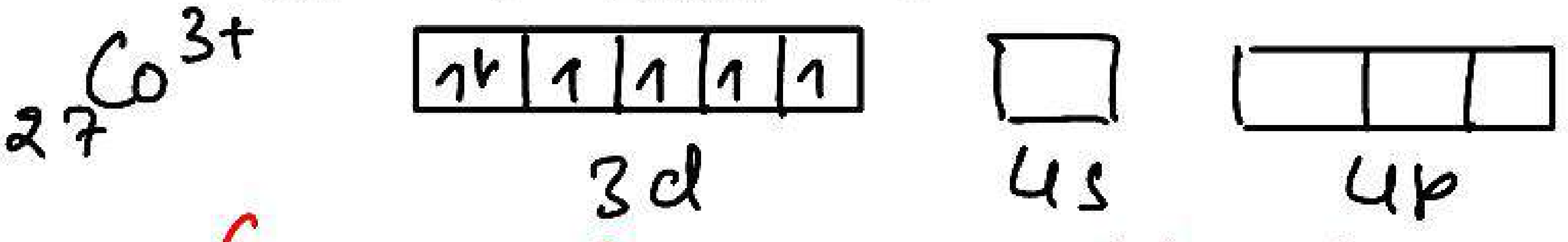
Acc. to this theory, metal-ligand bond arises due to the donation of electron pair from ligands to central metal atom

the metal atom or ion under the influence of ligands can use (n-1)d, ns, np, nd orbitals for hybridisation

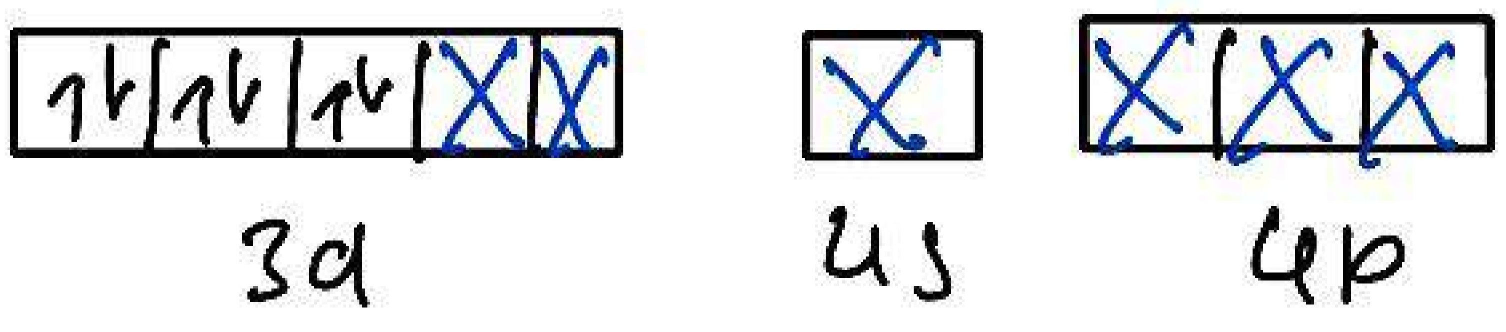
Hybridisation	C.N	Geometry	Example
sp	2	linear	$[Ag(CN)_2]^-$
sp^2	3	Trigonal planar	$[HgI_3]^-$
sp^3	4	Tetrahedral	$[Ni(CO)_4]$
dsp^2	4	Square planar	$[Ni(CN)_4]^{2-}$
dsp^3	5	Square pyramidal	$Fe(CO)_5$
d^2sp^3	6	Octahedral (inner)	$[Cr(NH_3)_6]^{3+}$
sp^3d^2	6	Octahedral (outer)	$[FeF_6]^{3-}$

e.g $[Co(NH_3)_6]^{3+}$

$Co^{3+} \rightarrow [Ar]^{18}\, 3d^6$



Co NH$_3$ is a strong ligand so pairing of $e^\ominus$ takes place



→ it is diamagnetic

hybridisation → d^2sp^3

Geometry → Octahedral

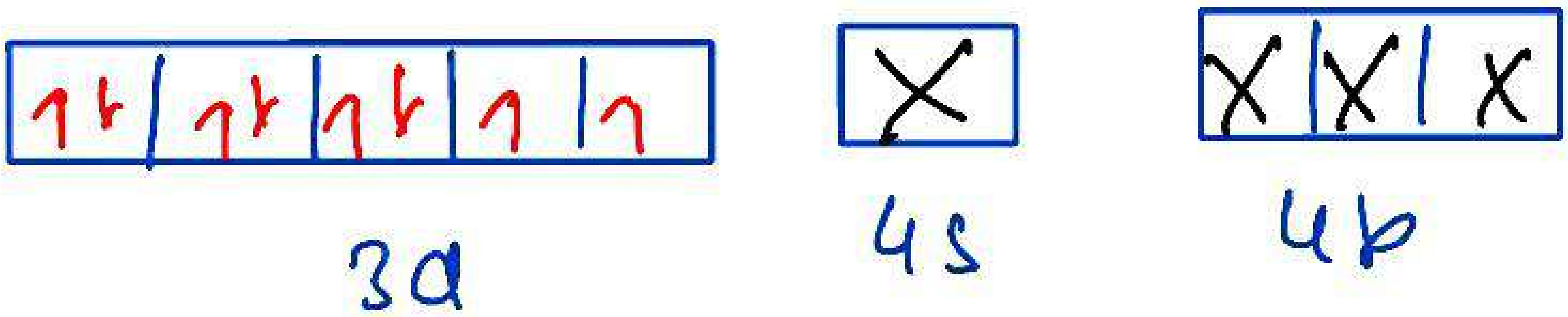
inner orbital complex

$\mu = \sqrt{n(n+2)}$

$= 0$ B.M

- $[NiCl_4]^{2-}$

${}_{28}Ni^{2+} \rightarrow [Ar]^{18}\ 3d^8\ 4s^0$



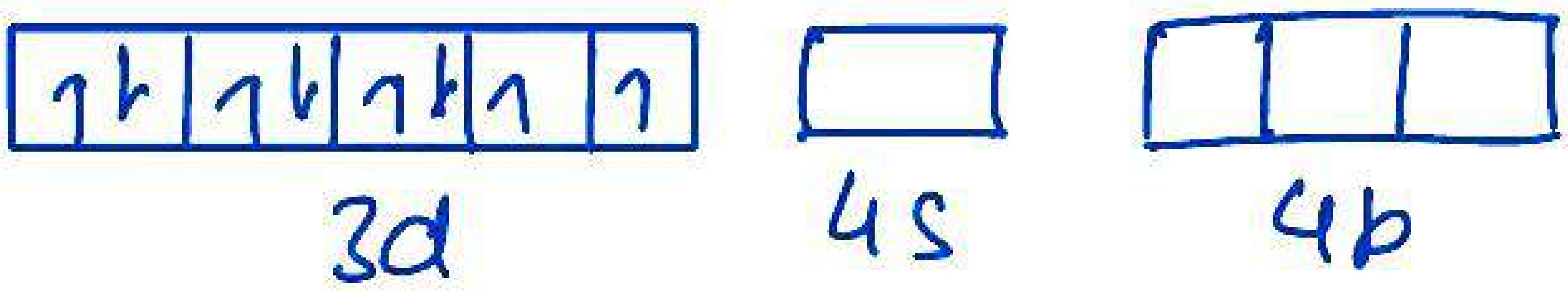
hybridisation → sp^3 Geometry → tetrahedral

It is paramagnetic in nature

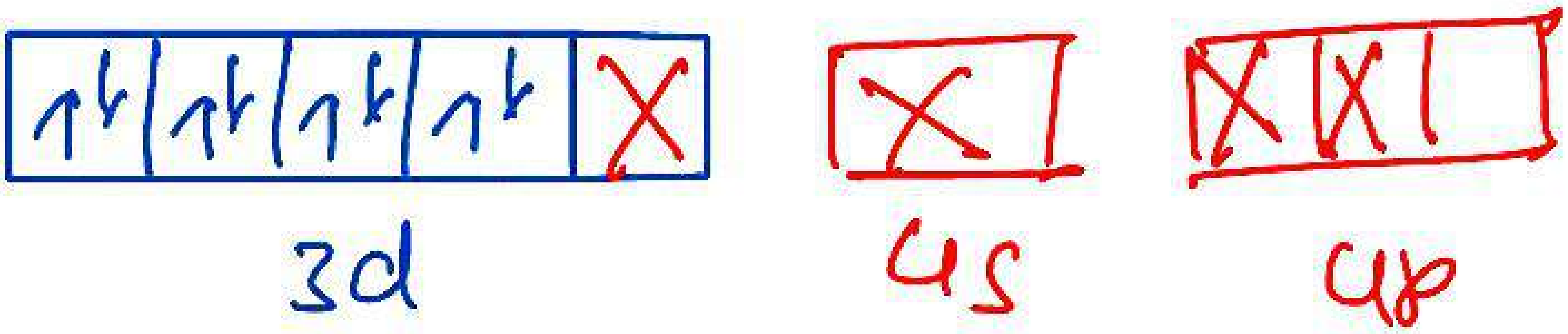
$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8}$ B.M

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

${}_{28}Ni^{2+} \rightarrow [Ar]^{18}\ 3d^8\ 4s^0$



CN is a strong ligand so pairing of $e^{\ominus}$ takes place



hybridisation → dsp^2

Geometry → Square planar

It is diamagnetic in nature.

CRYSTAL FIELD THEORY:

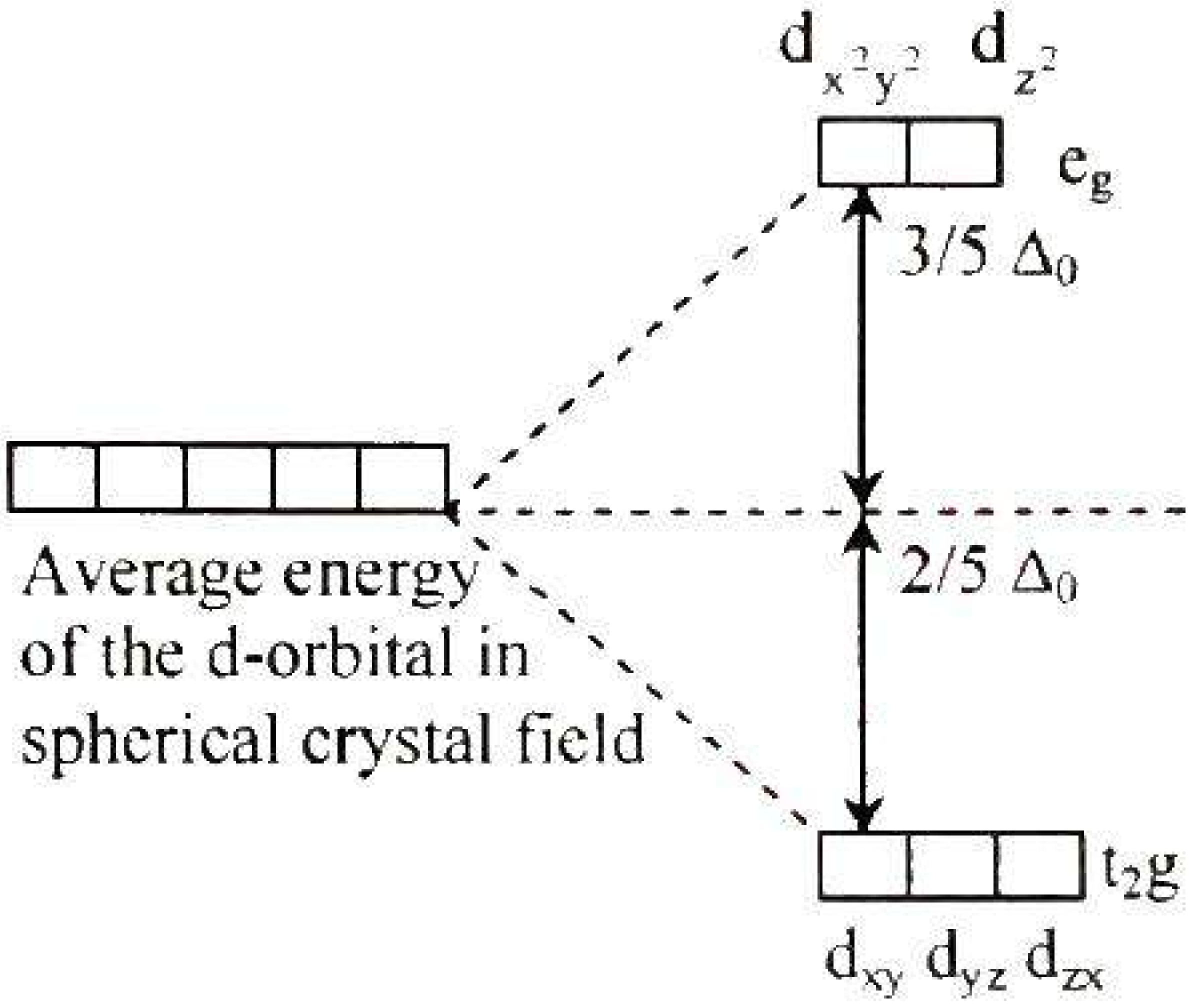
- Metal - ligand bond is ionic in nature. So, there is electrostatic force of attraction b/w metal and ligands
- The ligands are treated as negative centres and these negative centres are so arranged around central metal atom that there is minimum repulsion

b/w them.

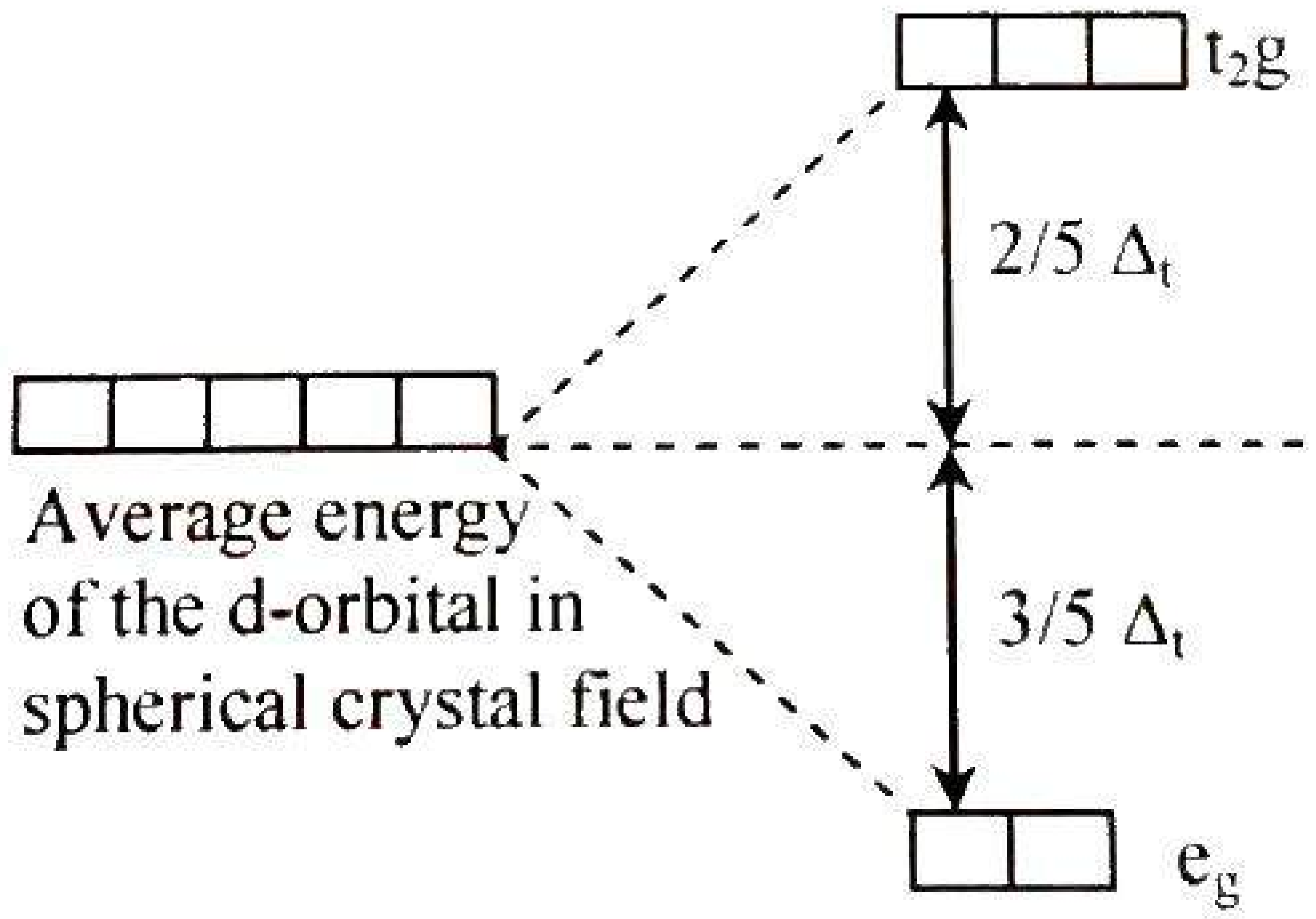
- In a free transition metal ion, all the five d-orbitals have equal energies (degenerate orbitals) but when it takes part in complex formation these d-orbitals split in two parts.

it is called d-d transition or crystal field splitting.

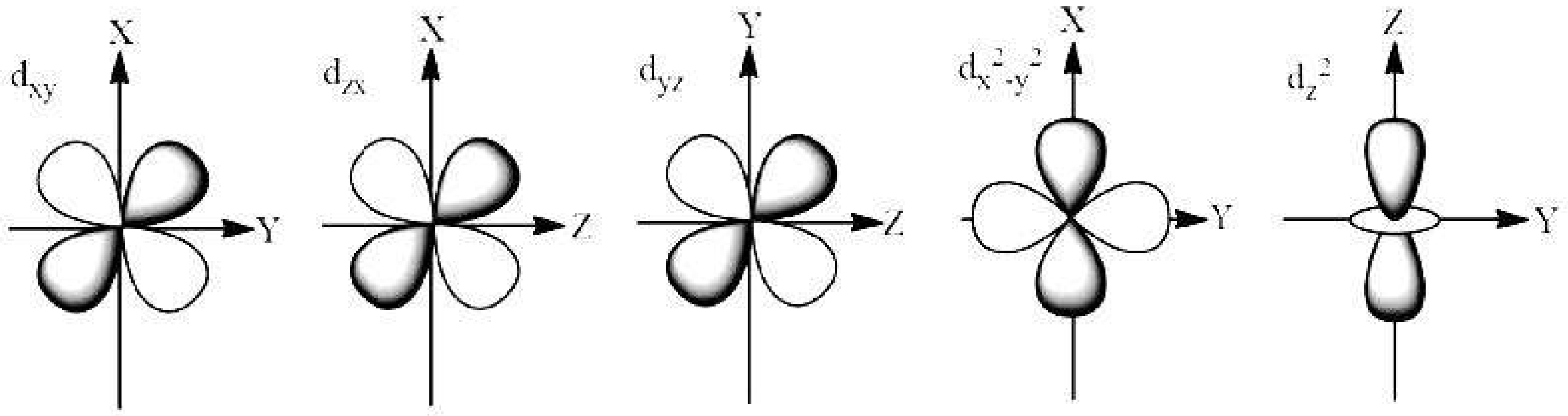
For Octahedral Complex



For Tetrahedral Complex



Shape of d-orbitals



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

Spectrochemical Series :

arrangement of all ligands in order of increasing CFSE value is called spectrochemical series. The ligands with small value of CFSE are called weak ligands and the ligands with higher value of CFSE are called strong ligand

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < OX$

$< H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$

ISOMERISM

Two or more co-ordination compounds which have same molecular formula but have different ways of attachment of their ligands to the central metal atom and have different properties. These are called isomers. The phenomenon is known as isomerism.

ISOMERISM

Structural Isomers

arises due to the difference in the str. of co-ordination compounds

- Ionisation
- Hydrate
- Co-ordination
- Linkage

Stereo Isomers

arises due to the different spatial arrangement of ligands around the metal ion

- Geometrical isomerism
- Optical isomerism

1.) IONISATION ISOMERISM

This isomerism arises due to exchange of ionisable anion with anionic ligands. e.g

e.g $[CoBr(H_2O)_5]^+Cl^-$ and $[CoCl(H_2O)_5]^+Br^-$

$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

2.) HYDRATE ISOMERISM OR SOLVATE ISOMERISM

In this isomerism, water is taken as solvent. It has different no. of water molecule in the co-ordination sphere and outside it e.g

$[Co(H_2O)_6]Cl_3$, $[Co(H_2O)_4Cl_2]Cl.2H_2O$,

$[Co(H_2O)_3Cl_3].3H_2O$

CO·ORDINATION ISOMERISM

This type of isomerism occurs when there is interchange of ligands b/w cationic and anionic complexes of different metal ion present in a complex.

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

LINKAGE ISOMESISM

This type of isomerism is shown by the coordination compounds having ambidentate ligands

e.g $[Co(NH_3)_5(NO_2)]Cl$ and $[Co(NH_3)_5(ONO)]Cl$

STEREO ISOMERISM

Geometrical Isomerism

This isomerism is common in complexes with C.N 4 & 6.

Geometrical isomers are of two type

Cis

⇒ same ligands are present at adjacent position

Trans

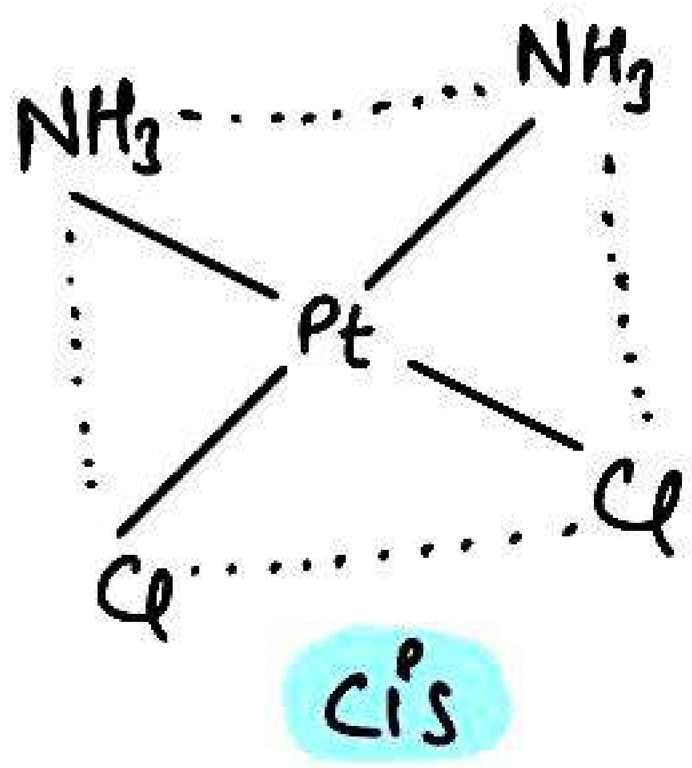
⇒ same ligands are present at opposite position

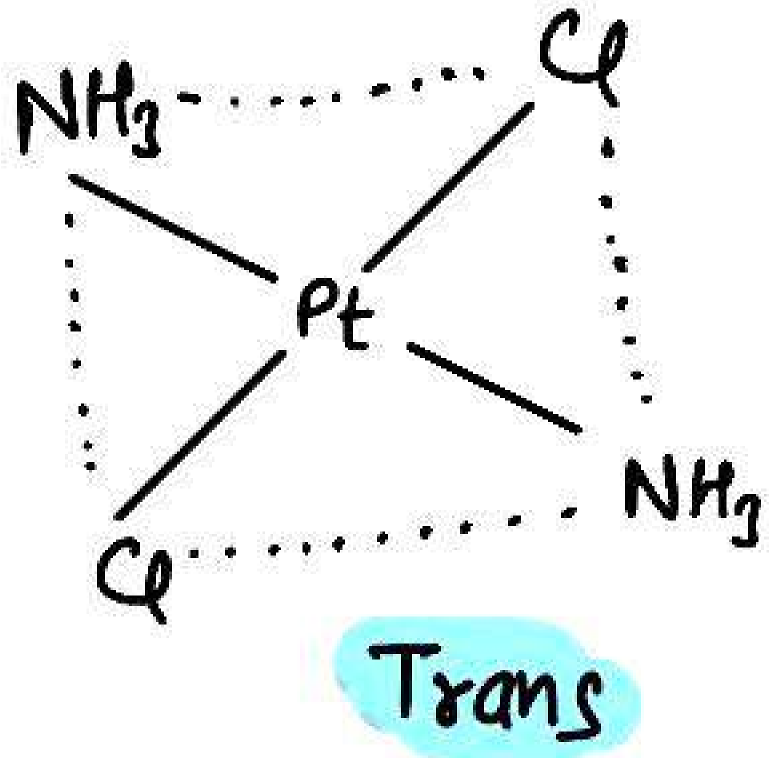
Optical Isomerism

These are the complexes which have chiral str. The pair of stereisomers are the mirror images of each other but may not be superimposed On the stereoisomers. These mirror images are called enantiomers. The enantiomers which rotate the plane polarised light in a clockwise direction is called dextrorotatory (d) or (+) and the enantiomer which rotate the plane polarised light in anti clockwise direction is laevorotatory (l) or (-)

- Tetrahedral complexes do not show Geometrical isomerism

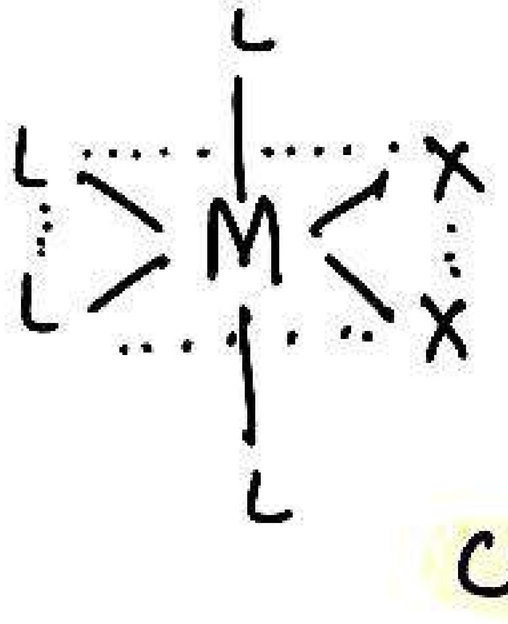
- Square planar complexes of formula $[MX_2L_2]$ (X and L are unidentate ligands) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis-isomer or opposite to each other in a trans isomer

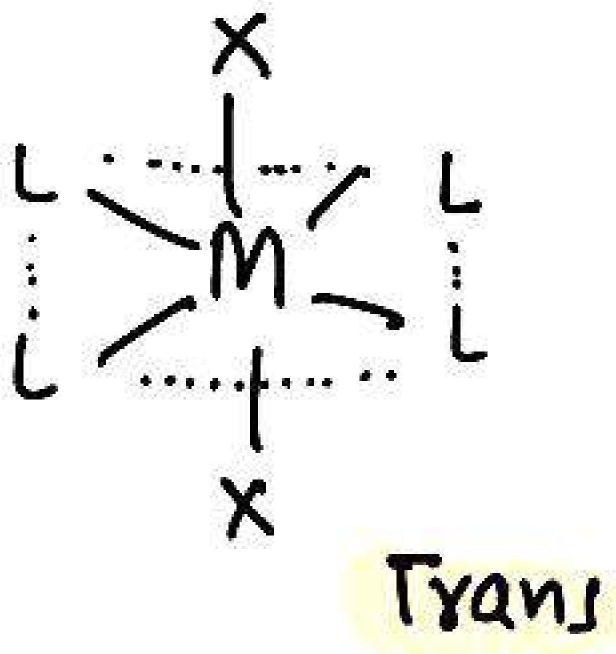




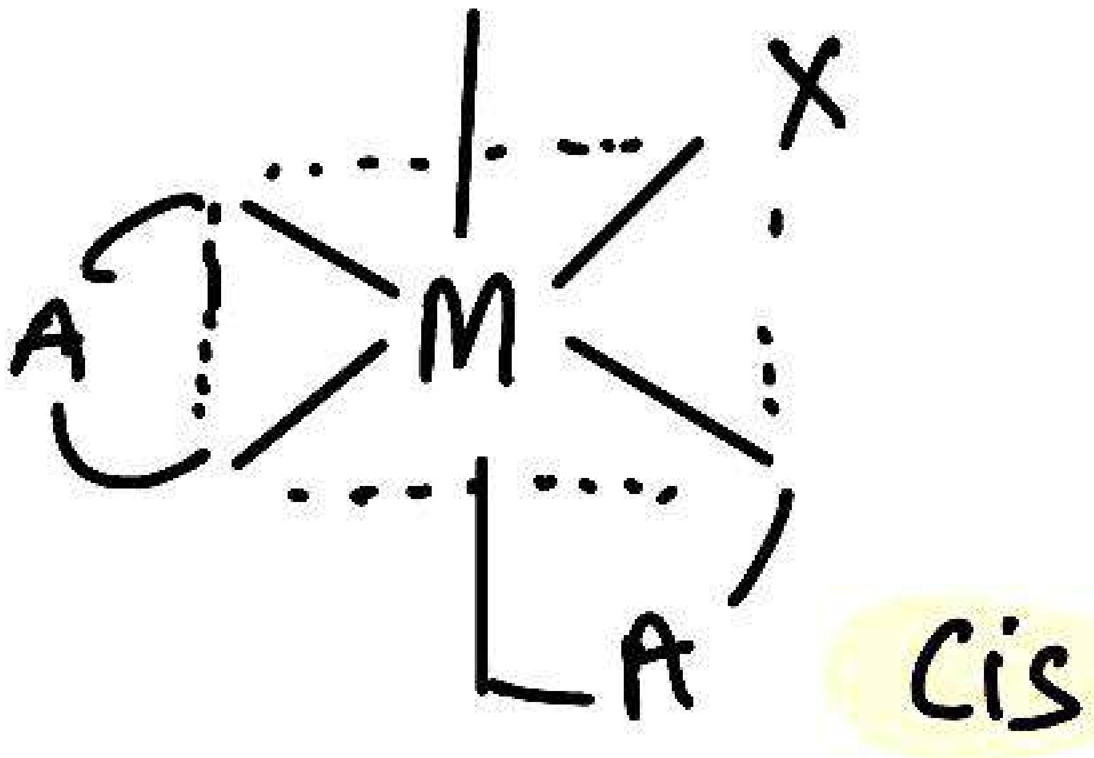
Octahedral complexes with C.N-6

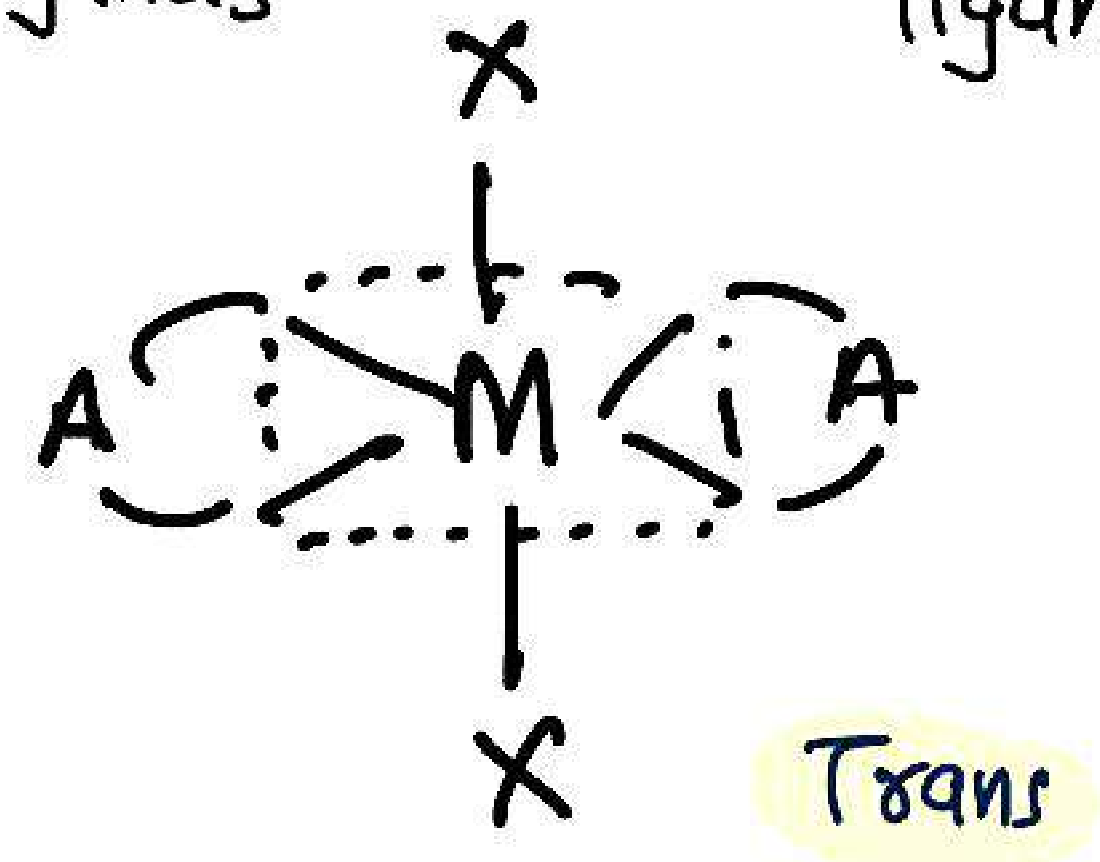
Type - MX_2L_4 e.g $[Co(NH_3)_4Cl_2]$



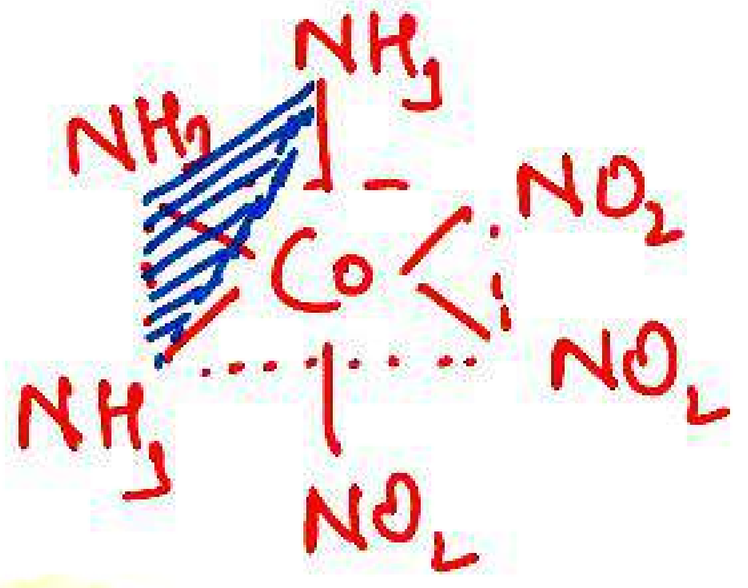


Type - MX_2A_2 (X- unidentate ligands A- Bidentate ligands)



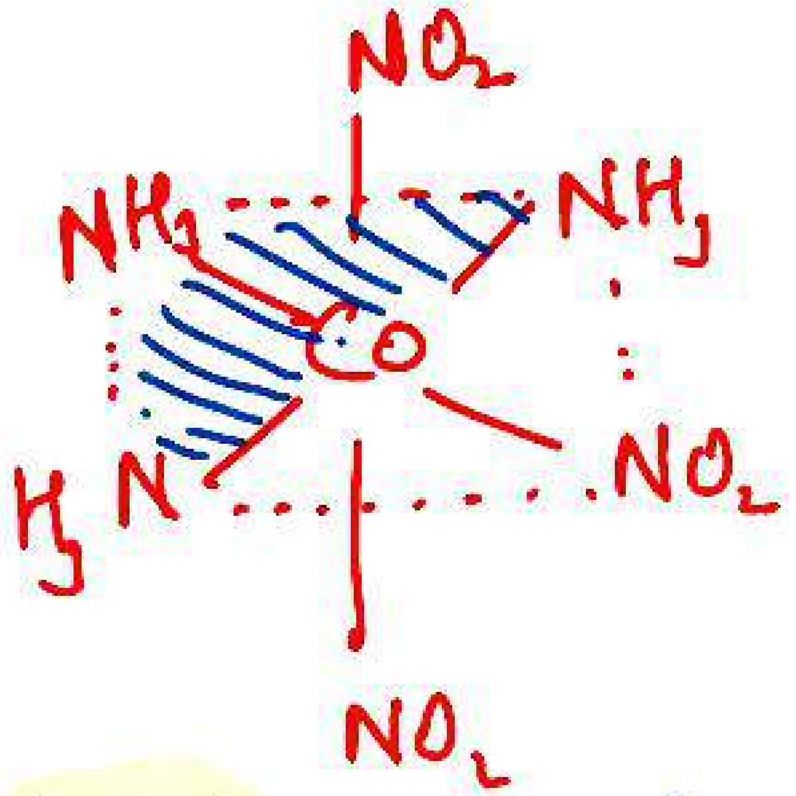


- In Octahedral complexes of the formula $[MA_3X_3]$
  eg $[Co(NH_3)_3(NO_2)_3]$



fac - facial

same ligands occupy one face of an octahedron



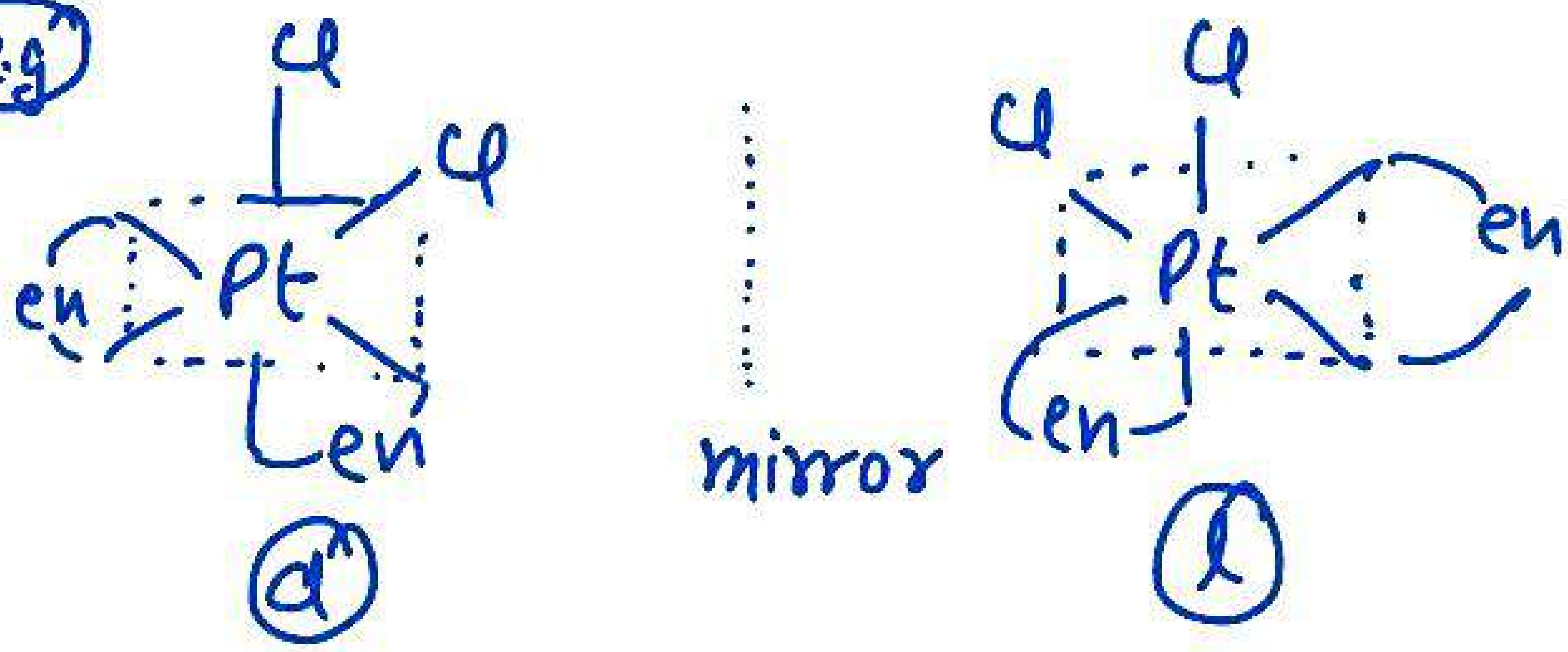
mer - meridional.

same ligands are in one plane

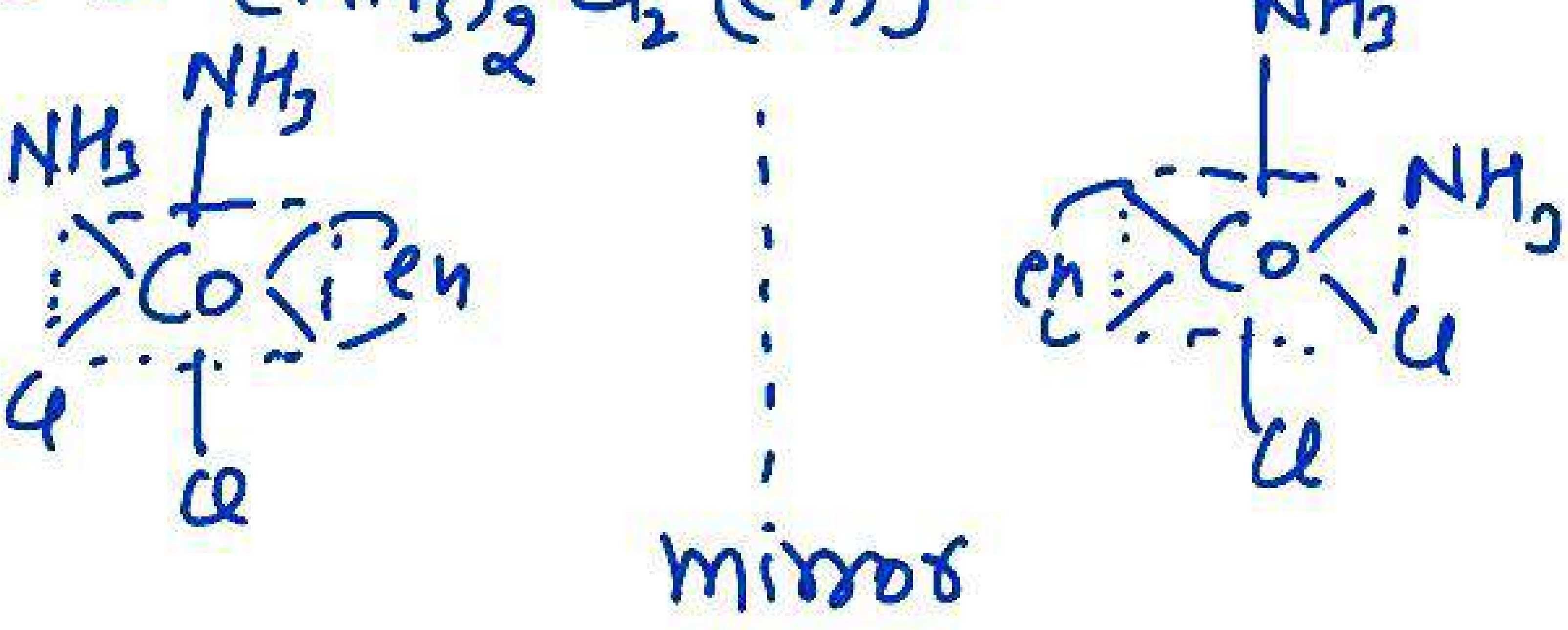
OPTICAL ISOMERS

- optical isomerism is common in Octahedral complexes involving bidentate ligands
- The equimolar mixture of 'd' and 'l' isomer is termed as the racemic mixture
- Trans isomer can't show optical isomers

(e.g)

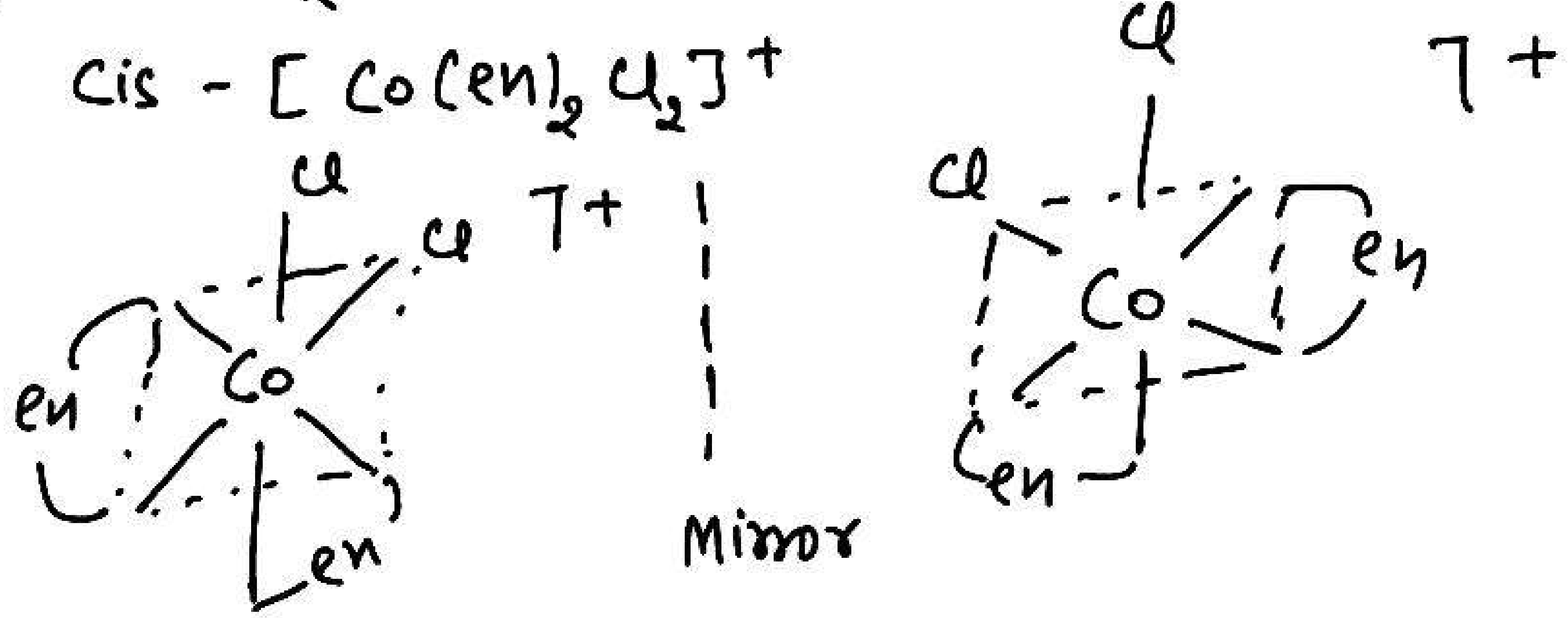


(eg) $[Co(NH_3)_2Cl_2(en)]^+$



eg $[M(AA)_2 X_2]^{n+}$

Cis - $[Co(en)_2Cl_2]^+$

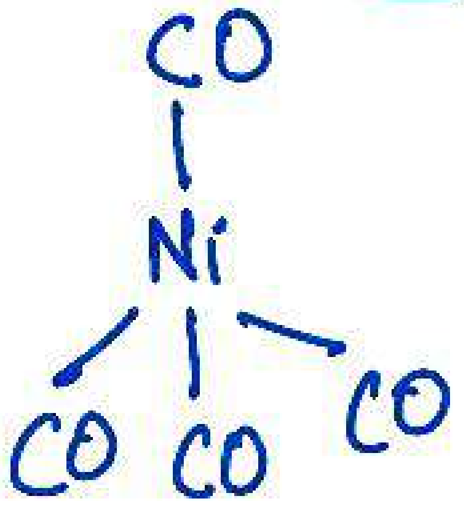


METAL CARBONYLS

Complex compounds that contain carbonyl ligands only are termed as metal carbonyl

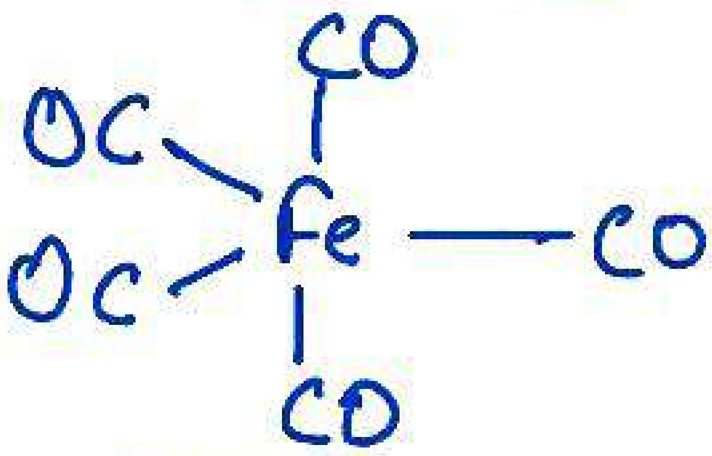
eg

$Ni(CO)_4$



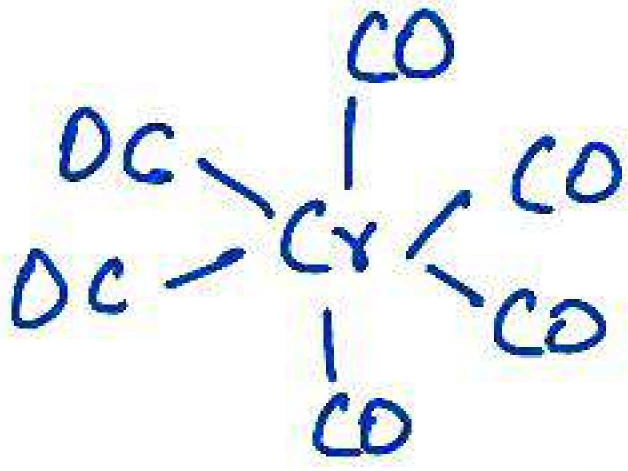
Tetrahedral

$Fe(CO)_5$



Trigonal Bipyramidal

$Cr(CO)_6$



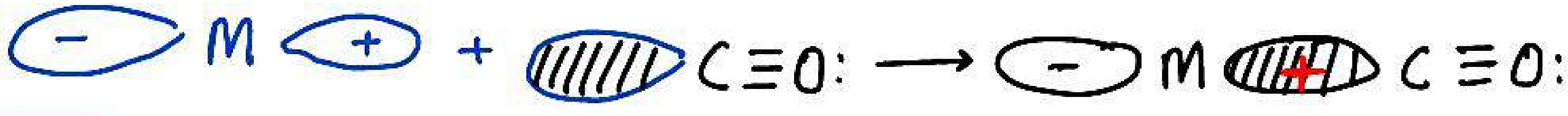
Octahedral

BONDING IN METAL CARBONYLS

- In metal carbonyls, the metal-carbon bond has both s- and p-character, CO ligand attach itself to metal atom from the carbon atom to form metal-carbon bond It is a weak donor

M-C σ bond is formed by the donation of lone pair of e^- on the carbonyl carbon to the vacant orbital of metal

- M-C π bond is formed by the donation of a pair of e^- from the filled d-orbital of the metal to vacant antibonding π* orbital of CO. This property of back bonding which stabilise the metal - ligand bond is termed as Synergic effect

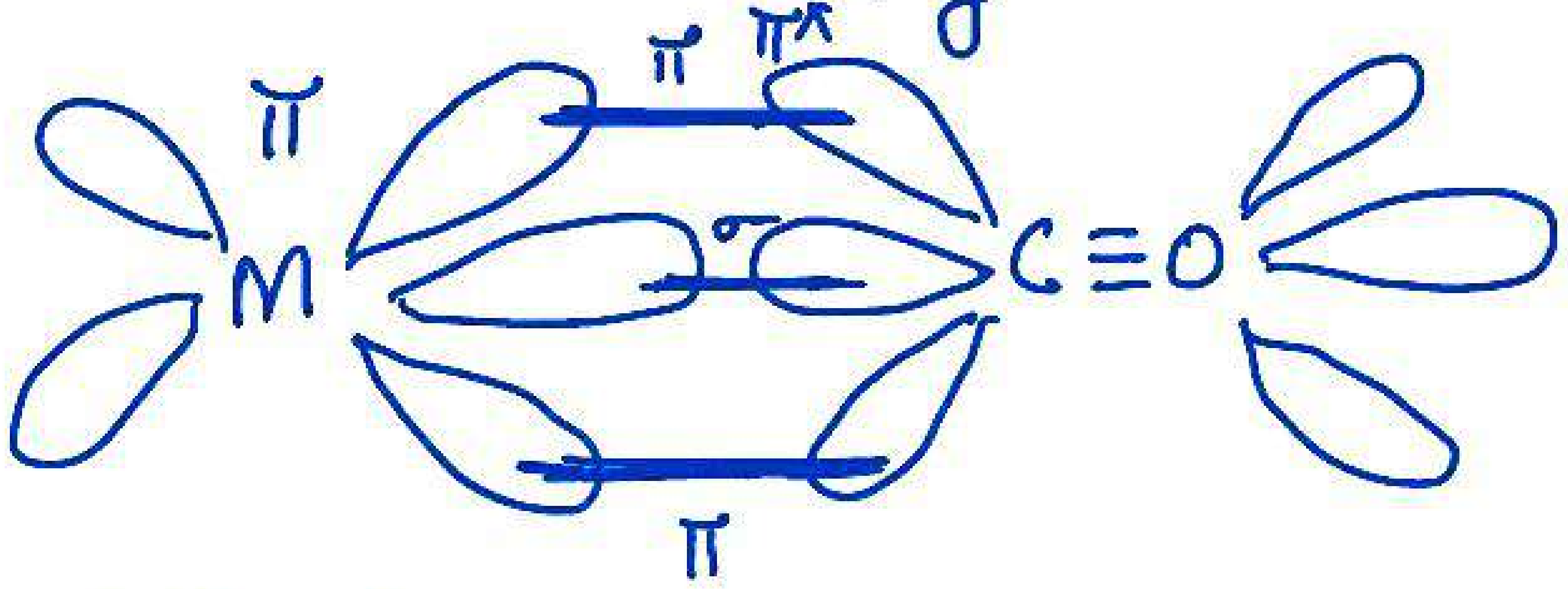


σ-overlap

Donation of lone pair of $e^{\ominus}$ from carbon atom into a vacant orbital of the metal.

π-overlap

Donation of $e^{\ominus}$ from a filled metal d-orbital into a vacant antibonding π-orbital of CO.



Factors Affecting Stability of a Complex

- **Charge on central metal atom** → as charge on central metal atom increases, stability of complex increases
- **Nature of metal ion** – stability order is 3d<4d<5d series
- **Nature of ligands** – strong field ligands form more stable complex
- **Presence of chelate Ring**: More the chelation, More is stability
- **Effect of Multidentate ligands**: If the ligands are multidentate, the stability of complex increases

→ Significance of Co-ordination Compounds

- ↳ In Biological System
- ↳ In Medicinal Chemistry
- ↳ In Analytical chemistry
- ↳ In the extraction / Metallurgy of metals
- ↳ Estimation of Hardness of water
- ↳ In Catalysis ↳ In Photography

In Medicines

- Vitamin B_{12} is used to prevent anaemia
- A complex of Ca^{2+} with EDTA is used for the treatment of lead poisoning.
- A complex of platinum i.e cis-platin is used in the treatment of cancer in chemotherapy.

In Biological Importance

Many biological important natural compounds are co-ordination complexes e.g.

Chlorophyll : a complex of Mg^{2+}
Haemoglobin : a complex of Fe^{2+}
Vitamin B_{12} : a complex of Co^{3+}