

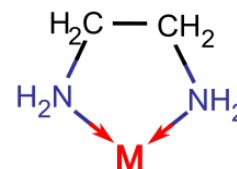
Revision Notes on Coordination Compounds

Ligands: an ion or molecule capable of donating a pair of electrons to the central atom via a donor atom.

- **Unidentate ligands:** Ligands with only one donor atom, e.g. NH_3 , Cl^- , F^- etc.
- **Bidentate ligands:** Ligands with two donor atoms, e.g. ethylenediamine, $\text{C}_2\text{O}_4^{2-}$ (oxalate ion) etc.
- **Tridentate ligands:** Ligands which have three donor atoms per ligand, e.g. (dien) diethyl triamine.
- **Hexadentate ligands:** Ligands which have six donor atoms per ligand, e.g. EDTA.

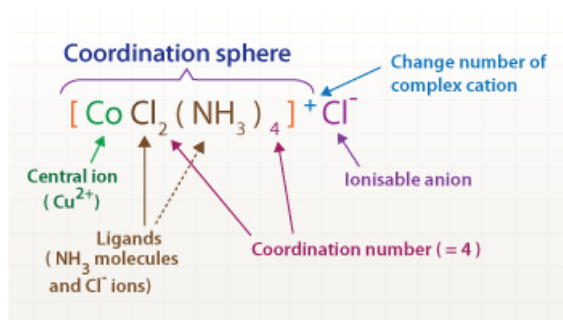
Chelating Ligands:

- Multidentate ligand simultaneously coordinating to a metal ion through more than one site is called chelating ligand. Example: Ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)
- These ligands produce a ring like structure called chelate.
- Chelation increases the stability of complex.

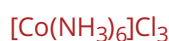


Werner's Theory:

- Metals possess two types of valencies i.e. primary (ionizable) valency and secondary (nonionizable) valency.
- Secondary valency of a metal is equal to the number of ligands attached to it i.e. coordination number.
- Primary valencies are satisfied by negative ions, while secondary valencies may be satisfied by neutral, negative or positive ions.



- Secondary valencies have a fixed orientation around the metal in space.



Primary Valencies = 3Cl^-

Secondary Valencies = 6NH_3

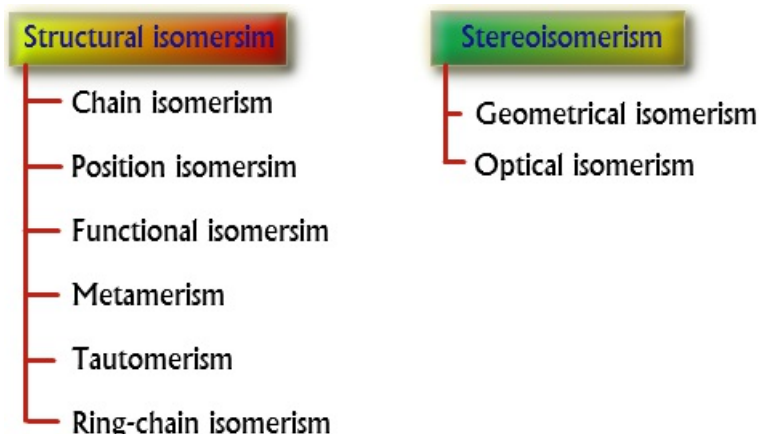
Coordination Sphere = $[\text{Co}(\text{NH}_3)_6]^{3-}$

Nomenclature of Complexes:

- Positive ion is named first followed by negative ion.
- Negative ligands are named by adding suffix - o.
- Positive ligands are named by adding prefix - ium.
- Neutral ligands are named as such without adding any suffix or prefix.
- Ligands are named in alphabetical order.
- Name of the ligands is written first followed by name of metal with its oxidation number mentioned in roman numbers in simple parenthesis.
- Number of the polysyllabic ligands i.e. ligands which have numbers in their name, is indicated by prefixes bis, tris etc,
- Number and name of solvent of crystallization if any, present in the complex is written in the end of the name of complex.
- When both cation and anion are complex ions, the metal in negative complex is named by adding suffix-ate.
- In case of bridging ligands:
 $[\text{Name of the groups to the left of bridging ligand (Oxidation state)}] - \mu - [\text{Name of the groups to the right of bridging ligand (Oxidation state)}] - [\text{Name of negative ion}]$

Ligands	Name
Negative	
CH_3COO^-	Acetato
CN^-	Cyano
Br^-	Bromo
Cl^-	Chloro
F^-	Fluoro
OH^-	Hydrido
N^{3-}	Nitrido
$\text{C}_2\text{O}_4^{2-}$	Oxalato
SO_3^{2-}	Sulfito
O_2^-	Superoxo
O_2^{2-}	Peroxo
O^{2-}	Oxo
NH^{2-}	Imido
SO_4^{2-}	Sulphato
$\text{S}_2\text{O}_3^{2-}$	Thiosulfato
HS^-	Mercapto
Positive	
NO^+	Nitrosonium
NH_2NH_3^+	Hydrazinium
Neutral	
H_2O	Aqua
NH_3	Ammine
CO	Carbonyl
CH_3NH_2	Methylamine
NO	Nitrosyl
$\text{C}_5\text{H}_5\text{N}$	Pyridine

Isomerism in coordination compounds

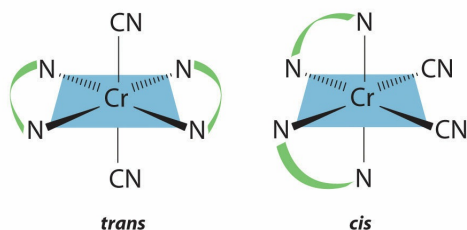


Structural Isomerism

- Ionization Isomerism:** Exchange of ligands between coordinate sphere and ionization sphere
 $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ & $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
- Hydrate Isomerism:** Exchange of water molecules between coordinate sphere and ionization sphere
 $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Br}_3$ & $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Br}]\text{Br}_2\text{H}_2\text{O}$
- Linkage Isomerism:** Ambient legend binds from the different binding sites to the metal atom.
 $\text{K}_2[\text{Cu}(\text{CNS})_4]$ & $\text{K}_2[\text{Cu}(\text{SCN})_4]$
- Coordination Isomerism:** Exchange of the metal atom between coordinate sphere and ionization sphere when both are complex ions.
 $[\text{Cr}(\text{NH}_3)_6][\text{CoF}_6]$ & $[\text{Co}(\text{NH}_3)_6][\text{CrF}_6]$.
- Ligand Isomerism:** Different isomers of the same ligands attached to the metal.
 $[\text{Co}(\text{pn})_2\text{Br}]\text{Cl}_2$ & $[\text{Co}(\text{tn})_2\text{Br}]\text{Cl}_2$ Where,
 pn = 1,2- Diaminopropane
 tn = 1,3- Diaminopropane.

Stereoisomerism:

a.Geometrical Isomerism: When two similar ligands are on adjacent position the isomer is called cis isomer while hen they are on opposite positions, the isomer is called trans isomer.



b.Optical Isomerism: In order to show optical isomerism, the complex should form a non superimposable mirror image which rotates the place of polarized light in opposite direction.

Valence Bond Theory:

Hybridization:

Find out the hybridization of central metal ion using following steps:

- Write down the electronic configuration of metal atom.
- Find out oxidation state of metal atom.
- Write down the electronic configuration of metal ion.
- Write down the configuration of complex to find out hybridization.
- Strong field ligands cause the pairing of electrons.
Strong Field Ligands: CO, CN⁻, NO₂⁻, en, py, NH₃.
Weak Filed Ligands: H₂O, OH⁻, F⁻, Cl⁻, Br⁻, I⁻

When the d orbital taking part in hybridization is inside the s and p orbital taking part in hybridization with respect to the nucleus, it is called an inner orbital complex. **Example:** d²sp³ hybridization of [Co(NH₃)₆]³⁺ involves 3d, 4s and 4p orbital, hence it is an inner orbital complex.

When the d orbital taking part in hybridization outside the s and p orbital taking part in hybridization with respect to the nucleus, it is called an outer orbital complex.

Example: sp³d² hybridization of [CoF₆]³⁻ involves 4d, 4s and 4p orbital, hence it is an inner orbital complex.

Geometry:

Coordination Number	Hybridization	Geometry
4	sp ³	Tetrahedral
	dsp ²	Square Planar
6	d ² sp ³ & sp ³ d ²	Oct

Magnetic Properties:

- Diamagnetic: All the electrons paired.
- Paramagnetic: Contains unpaired electrons.

Spin:

- Spin paired: All electrons paired.
- Spin free: Contains unpaired electrons.

Colour:

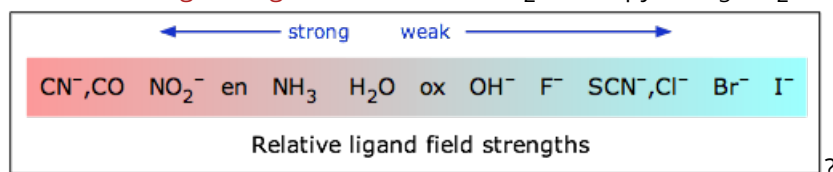
Compound must contain free electrons in order to show colour.

Crystal Field Theory:

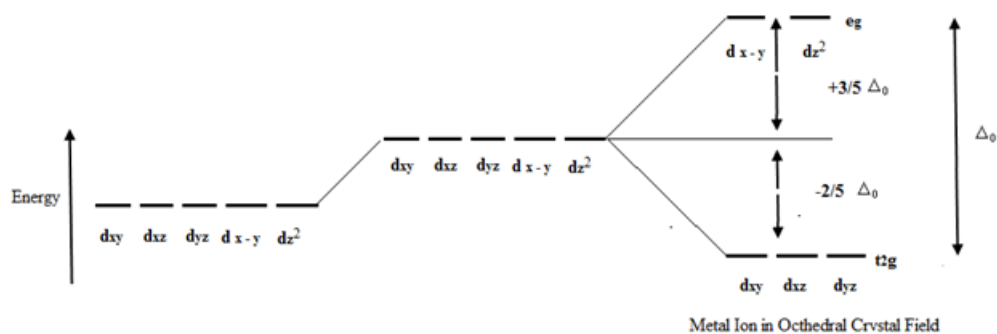
Strong field ligand causes greater repulsion and thus results in the formation of low spin complexes by pairing of electrons.

- Weak field ligands result in the formation of high spin complexes

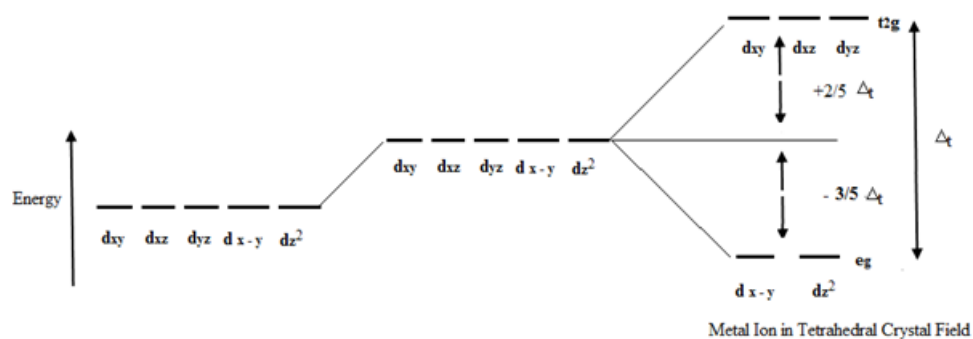
- Order of strength of ligands: $\text{CO} > \text{CN}^- > \text{NO}_2^- > \text{en} > \text{py} = \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$



- Octahedral Complexes: e_g orbital are of higher energy than t_{2g} orbital.



- Tetrahedral Complexes: e_g orbitals are of lower energy than t_{2g} orbitals.



$$\Delta_t = (4/9) \Delta_o$$

Crystal Field Stabilization Energy:

System	High Spin		Low Spin	
	Electronic Configuration	CFSE	Electronic Configuration	CFSE
Octahedral Complex				
d^4	$t_{2g}^3 e_g^1$	$-(3/5)\Delta_0$	$t_{2g}^4 e_g^0$	$-(8/5)\Delta_0 + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-(10/5)\Delta_0 + 2P$
d^6	$t_{2g}^4 e_g^2$	$-(2/5)\Delta_0 + P$	$t_{2g}^6 e_g^0$	$-(12/5)\Delta_0 + 3P$
d^7	$t_{2g}^5 e_g^2$	$-(4/5)\Delta_0 + 2P$	$t_{2g}^6 e_g^1$	$-(9/5)\Delta_0 + 3P$
Tetrahedral Complexes				
d^4	$e_g^2 t_{2g}^2$	$-(2/5)\Delta_t$	$e_g^4 t_{2g}^0$	$-(12/5)\Delta_t + 2P$
d^5	$e_g^2 t_{2g}^3$	0	$e_g^4 t_{2g}^1$	$-2\Delta_t + 2P$
d^6	$e_g^3 t_{2g}^3$	$-(3/5)\Delta_t + P$	$e_g^4 t_{2g}^2$	$-(8/5)\Delta_t + 2P$

Magnetic Properties: Complexes with unpaired electrons are paramagnetic while with no unpaired electron are diamagnetic.