

# 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.  $\text{NH}_3$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  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.
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- Secondary valencies have a fixed orientation around the metal in space.



Primary Valencies = 3  $\text{Cl}^-$

Secondary Valencies = 6  $\text{NH}_3$

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:

[Name of the groups to the left of bridging ligand (Oxidation state)] – $\mu$  – [Name of the groups to the right of bridging ligand (Oxidation state)] – [Name of negative ion]

Ligands	Name
<b>Negative</b>	
$\text{CH}_3\text{COO}^-$	Acetato
$\text{CN}^-$	Cyano
$\text{Br}^-$	Bromo
$\text{Cl}^-$	Chloro
$\text{F}^-$	Fluoro
$\text{OH}^-$	Hydrido
$\text{N}^{3-}$	Nitrido
$\text{C}_2\text{O}_4^{2-}$	Oxalato
$\text{SO}_3^{2-}$	Sulfito
$\text{O}_2^-$	Superoxo
$\text{O}_2^{2-}$	Peroxo
$\text{O}^{2-}$	Oxo
$\text{NH}^{2-}$	Imido
$\text{SO}_4^{2-}$	Sulphato
$\text{S}_2\text{O}_3^{2-}$	Thiosulfato
$\text{HS}^-$	Mercapto
<b>Positive</b>	
$\text{NO}^+$	Nitrosonium
$\text{NH}_2\text{NH}_3^+$	Hydrazinium
<b>Neutral</b>	
$\text{H}_2\text{O}$	Aqua
$\text{NH}_3$	Ammine
$\text{CO}$	Carbonyl
$\text{CH}_3\text{NH}_2$	Methylamine
$\text{NO}$	Nitrosyl
$\text{C}_5\text{H}_5\text{N}$	Pyridine

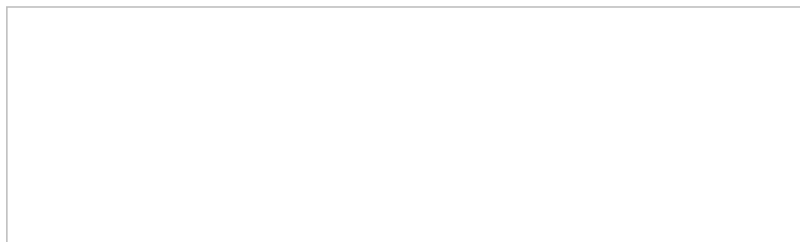
## Isomerism in coordination compounds

## 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 ligand 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 when 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 plane 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,  $\text{CN}^-$ ,  $\text{NO}_2^-$ , en, py,  $\text{NH}_3$ .  
**Weak Field Ligands:**  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$

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:**  $d^2sp^3$  hybridization of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  involves 3d, 4s and 4p orbital, hence it is an inner orbital complex.

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

**Example:**  $sp^3d^2$  hybridization of  $[\text{CoF}_6]^{3-}$  involves 4d, 4s and 4p orbital, hence it is an outer orbital complex.

#### Geometry:

Coordination Number	Hybridization	Geometry
4	$sp^3$	Tetrahedral
	$dsp^2$	Square Planar
6	$d^2sp^3$ & $sp^3d^2$	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
<b>Octahedral Complex</b>				
$d^4$	$t_{2g}^3 e_g^1$	$-(3/5)\Delta_0$	$t_{2g}^4 e_g^0$	$-(8/5)\Delta_0 + P$
$d^5$	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-(10/5)\Delta_0 + 2P$
$d^6$	$t_{2g}^4 e_g^2$	$-(2/5)\Delta_0 + P$	$t_{2g}^6 e_g^0$	$-(12/5)\Delta_0 + 3P$
$d^7$	$t_{2g}^5 e_g^2$	$-(4/5)\Delta_0 + 2P$	$t_{2g}^6 e_g^1$	$-(9/5)\Delta_0 + 3P$
<b>Tetrahedral Complexes</b>				
$d^4$	$e_g^2 t_{2g}^2$	$-(2/5)\Delta_t$	$e_g^4 t_{2g}^0$	$-(12/5)\Delta_t + 2P$
$d^5$	$e_g^2 t_{2g}^3$	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.