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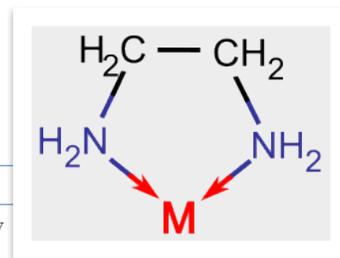
## Coordination Compounds

**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. ethylene diamine,  $\text{C}_2\text{O}_4^{2-}$  (oxalate ion) etc.
- **Tridentate ligands:** Ligands which have three donor atoms per ligand, e.g. (dine) diethyl triamine.
- **Hexadentate ligands:** Ligands which have six donor atoms per ligand, e.g. EDTA.

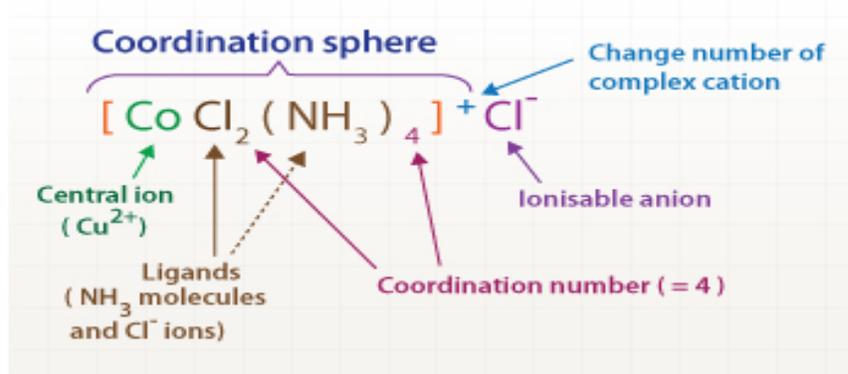
### Chelating Ligands:

- 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]

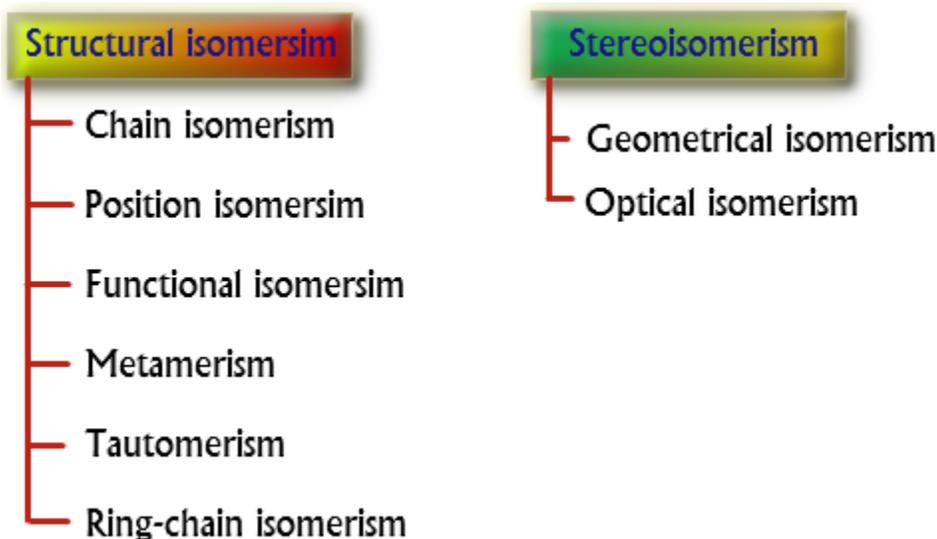
Ligands	Name
<b>Negative</b>	
$\text{CH}_3\text{COO}^-$	Acetato
$\text{CN}^-$	Cyano
$\text{Br}^-$	Bromo
$\text{Cl}^-$	Chloro
$\text{F}^-$	Fluoro
$\text{OH}^-$	Hydrido
$\text{N}^{3-}$	Nitrido
$\text{C}_2\text{O}_4^{2-}$	Oxalato
$\text{SO}_3^{2-}$	Sulfito
$\text{O}_2^-$	Superoxo
$\text{O}_2^{2-}$	Peroxo
$\text{O}^{2-}$	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



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NH <sub>3</sub>	Ammine
CO	Carbonyl
CH <sub>3</sub> NH <sub>2</sub>	Methylamine
NO	Nitrosyl
C <sub>5</sub> H <sub>5</sub> N	Pyridine

## Isomerism in coordination compounds



### Structural Isomerism

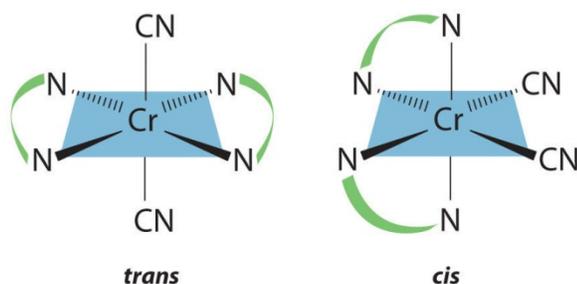
- **Ionization Isomerism:** Exchange of ligands between coordinate sphere and ionization sphere  
 $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  &  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
- **Hydrate Isomerism:** Exchange of water molecules between coordinate sphere and ionization sphere  
 $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Br}_3$  &  $[\text{Cr}(\text{NH}_3)_2_3(\text{H}_2\text{O})_2\text{Br}]\text{Br}_2\text{H}_2\text{O}$
- **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:



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**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, CN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, en, py, NH<sub>3</sub>.

**Weak Filed Ligands:** H<sub>2</sub>O, OH<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>

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<sup>2</sup>sp<sup>3</sup> hybridization of [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> 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:** sp<sup>3</sup>d<sup>2</sup> hybridization of [CoF<sub>6</sub>]<sup>3-</sup> involves 4d, 4s and 4p orbital, hence it is an inner orbital complex.

## Geometry:



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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:

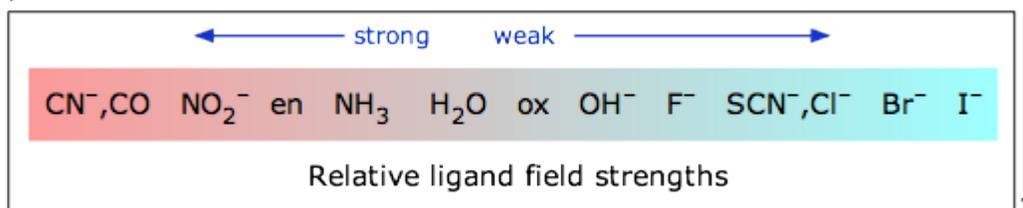
Compound must contain free electrons in order to show colour.

### 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

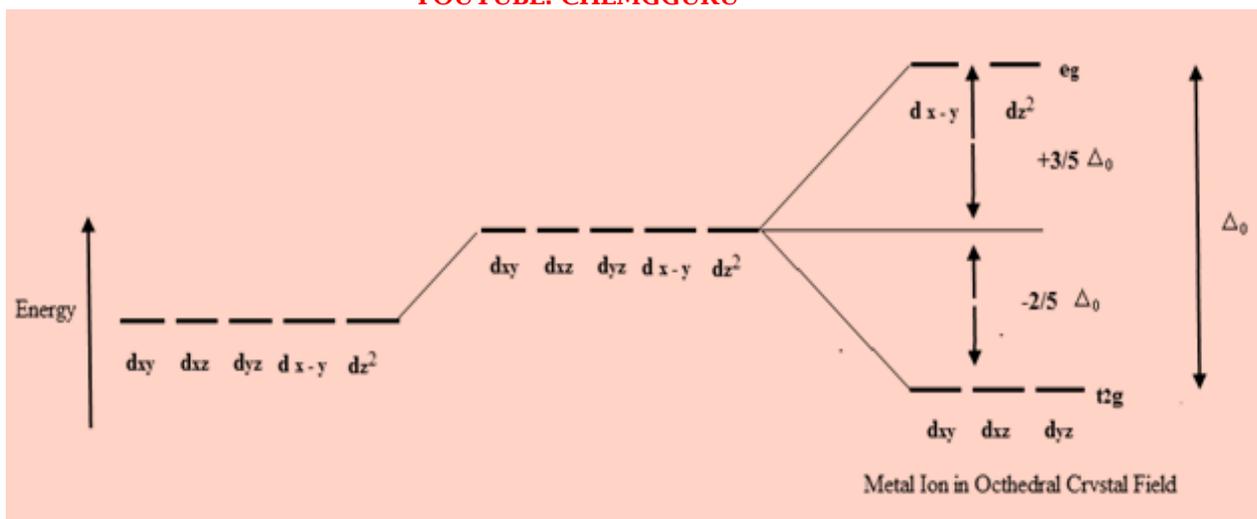
**Order of strength of ligands:**  $CO > CN^- > NO_2^- > en > py = NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$



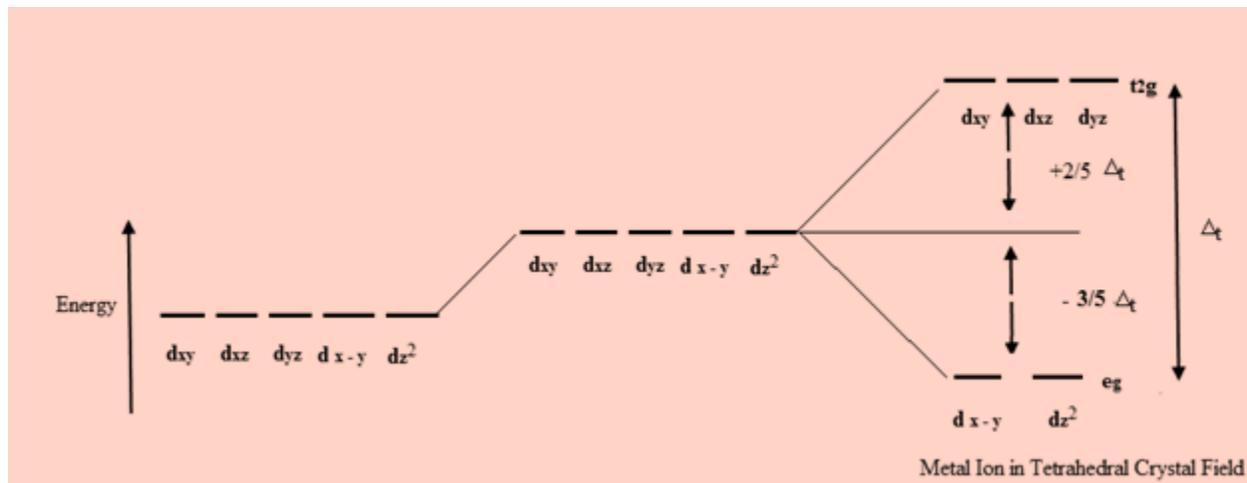
- **Octahedral Complexes:**  $e_g$  orbital are of higher energy than  $t_{2g}$  orbital.



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



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



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### Crystal Field Stabilization Energy:

System	High Spin		Low Spin	
	Electronic Configuration	CFSE	Electronic Configuration	CFSE
<b>Octahedral Complex</b>				
d <sup>4</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>1</sup>	-(3/5)Δ <sub>0</sub>	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>0</sup>	-(8/5)Δ <sub>0</sub> +P
d <sup>5</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>2</sup>	0	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>0</sup>	-(10/5)Δ <sub>0</sub> +2P
d <sup>6</sup>	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>2</sup>	-(2/5)Δ <sub>0</sub> +P	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>0</sup>	-(12/5)Δ <sub>0</sub> +3P
d <sup>7</sup>	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>2</sup>	-(4/5)Δ <sub>0</sub> +2P	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>1</sup>	-(9/5)Δ <sub>0</sub> +3P
<b>Tetrahedral Complexes</b>				
d <sup>4</sup>	e <sub>g</sub> <sup>2</sup> t <sub>2g</sub> <sup>2</sup>	-(2/5)Δ <sub>t</sub>	e <sub>g</sub> <sup>4</sup> t <sub>2g</sub> <sup>0</sup>	-(12/5)Δ <sub>t</sub> +2P
d <sup>5</sup>	e <sub>g</sub> <sup>2</sup> t <sub>2g</sub> <sup>3</sup>	0	e <sub>g</sub> <sup>4</sup> t <sub>2g</sub> <sup>1</sup>	-2 Δ <sub>t</sub> +2P
d <sup>6</sup>	e <sub>g</sub> <sup>3</sup> t <sub>2g</sub> <sup>3</sup>	-(3/5)Δ <sub>t</sub> +P	e <sub>g</sub> <sup>4</sup> t <sub>2g</sub> <sup>2</sup>	-(8/5)Δ <sub>t</sub> +2P

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