

**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.

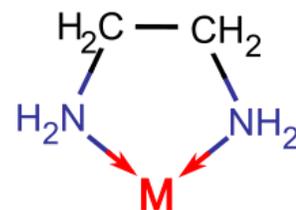
**Hexadentate ligands:** Ligands which have six donor atoms per ligand, e.g. EDTA.

### 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.

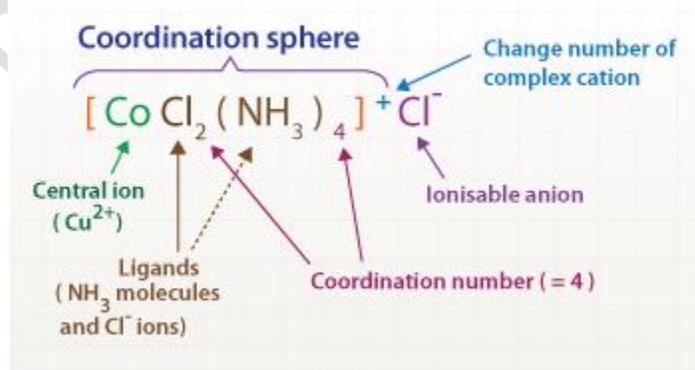


### Werner's Theory:

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:

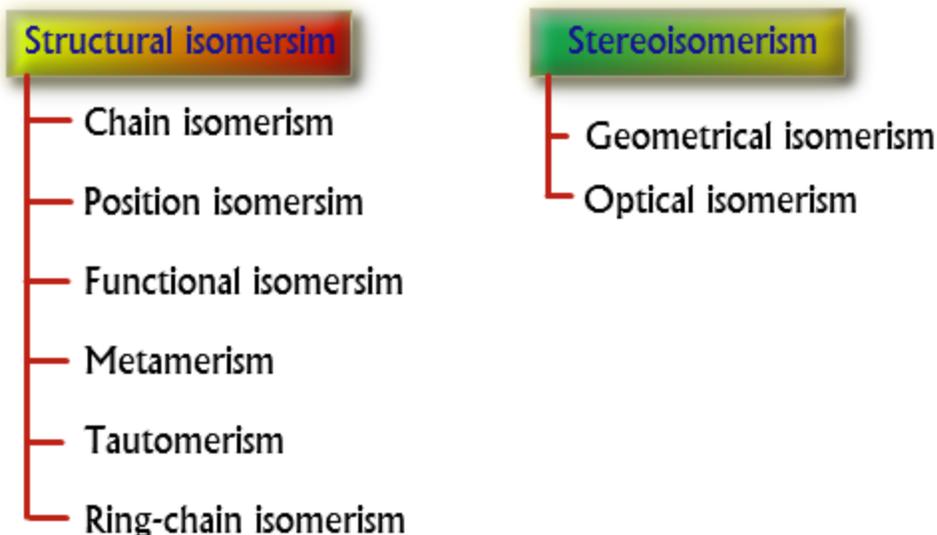
[Name of the groups to the left of bridging ligand (Oxidation state)] - $\mu$  - [Name of the groups to the right of bridging ligand (Oxidation state)] - [Name of negative ion]

Ligands	Name
<b>Negative</b>	
$\text{CH}_3\text{COO}^-$	Acetato
$\text{CN}^-$	Cyano

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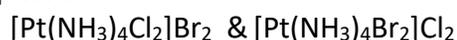
$\text{Br}^-$	Bromo
$\text{Cl}^-$	Chloro
$\text{F}^-$	Fluoro
$\text{OH}^-$	Hydrido
$\text{N}^{3-}$	Nitrido
$\text{C}_2\text{O}_4^{2-}$	Oxalato
$\text{SO}_3^{2-}$	Sulfito
$\text{O}_2^-$	Superoxo
$\text{O}_2^{2-}$	Peroxo
$\text{O}^{2-}$	Oxo
$\text{NH}^{2-}$	Imido
$\text{SO}_4^{2-}$	Sulphato
$\text{S}_2\text{O}_3^{2-}$	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



**Hydrate Isomerism:** Exchange of water molecules between coordinate sphere and ionization sphere



**Linkage Isomerism:** Ambient ligand binds from the different binding sites to the metal atom.



**Coordination Isomerism:** Exchange of the metal atom between coordinate sphere and ionization sphere when both are complex ions.



**Ligand Isomerism:** Different isomers of the same ligands attached to the metal.



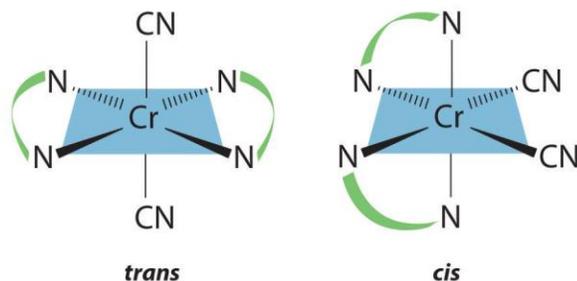
pn = 1,2-Diaminopropane

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.

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**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:**

Coordination Number	Hybridization	Geometry
4	sp <sup>3</sup>	Tetrahedral

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	$dsp^2$	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:

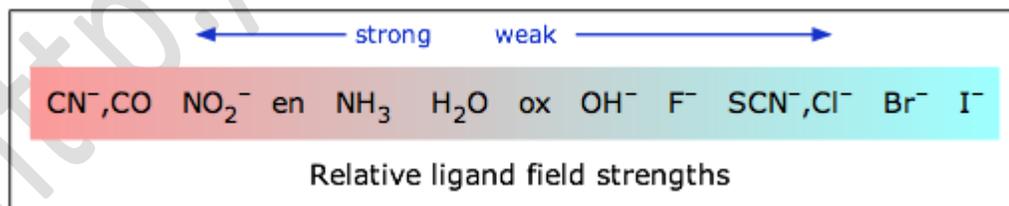
Compound must contain free electrons in order to show colour.

### Crystal Field Theory:

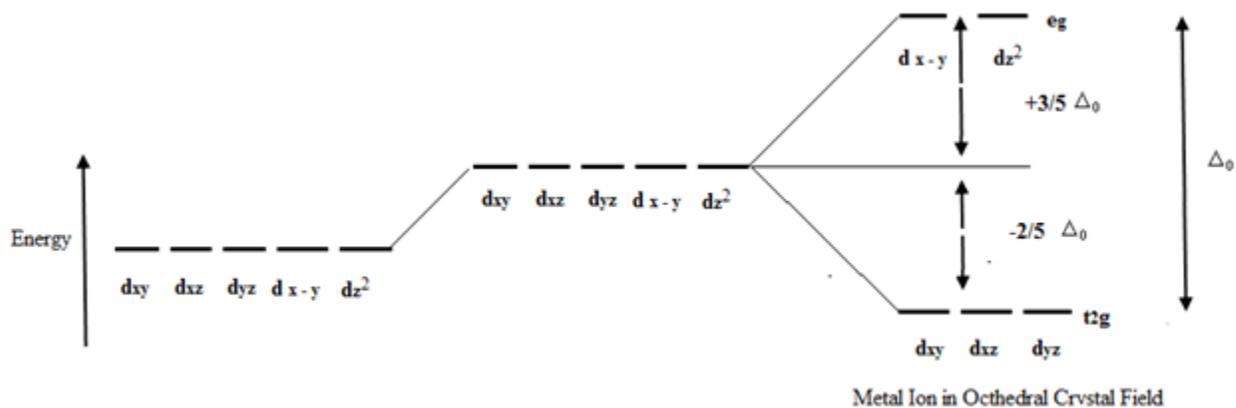
Strong field ligand causes greater repulsion and thus results in the formation of low spin complexes by pairing of electrons.

Weak field ligands result in the formation of high spin complexes

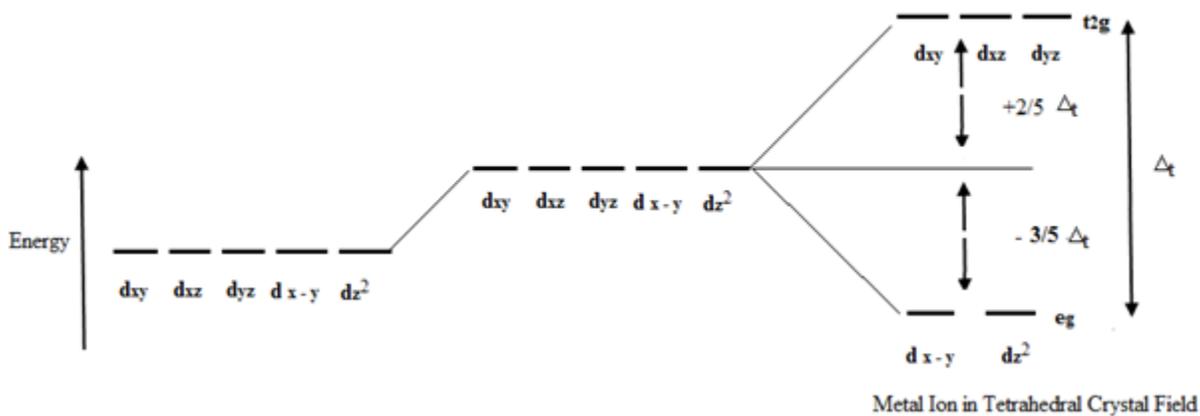
Order of strength of ligands:  $CO > CN^- > NO_2^- > en > py = NH_3 > H_2O > OH^- > F^- > Cl^- > Br^- > I^-$



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



**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	$t_{2g}^5 e_g^0$	$-(10/5)\Delta_0 + 2P$
$d^6$	$t_{2g}^4 e_g^2$	$-(2/5)\Delta_0 + P$	$t_{2g}^6 e_g^0$	$-(12/5)\Delta_0 + 3P$
$d^7$	$t_{2g}^5 e_g^2$	$-(4/5)\Delta_0 + 2P$	$t_{2g}^6 e_g^1$	$-(9/5)\Delta_0 + 3P$

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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.

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