

# Coordination Compounds

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## Coordination compounds:

These are the complex compounds in which transition metal atoms are bound to a number of anions or neutral molecules.

## Postulates of Werner's theory of coordination compounds:

- In coordination compounds, there are two types of linkages (valences) – primary and secondary.
- The primary valences are ionisable and are satisfied by negative ions.
- The secondary valences are non-ionisable and are satisfied by negative ions or neutral molecules. The secondary valence is equal to the coordination number of a metal and remains fixed for a metal.
- Different coordination numbers have characteristic spatial arrangement of the ions or groups bound by the secondary linkages.

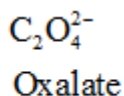
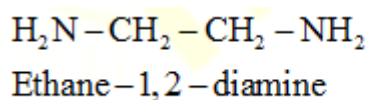
## Difference between a double salt and a complex:

- In water, a double salt dissociates completely to give simpler ions. Examples of double salt: carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), Mohr's salt [ $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ ]
- Complex ions do not dissociate further to give simpler ions. For example,  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

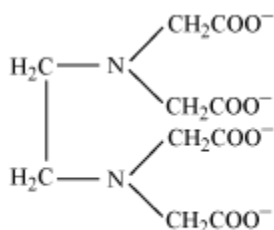
## Ligands:

Ions or molecules bound to the central metal atom or ion in the coordination entity

- **Didentate –**



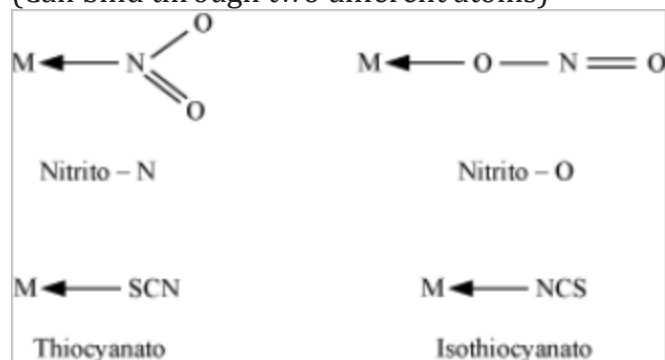
- **Polydentate –**



Ethylenediaminetetraacetate (EDTA<sup>4-</sup>)

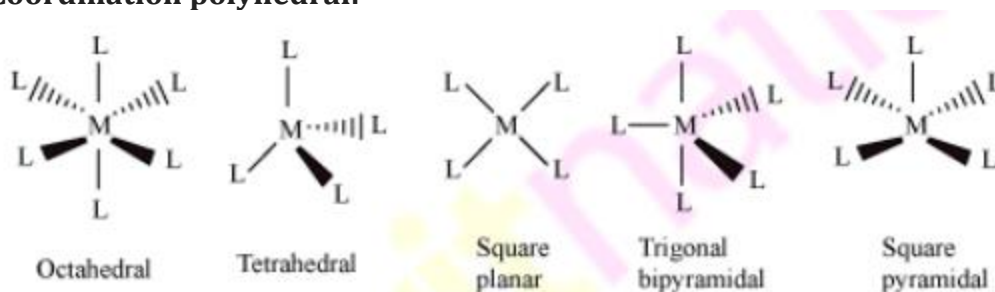
- **Ambidentate –**

(Can bind through two different atoms)



**Coordination number:** Number of ligand donor atoms bonded directly to the metal

**Coordination polyhedral:**



**Homoleptic and heteroleptic complexes:**

- Homoleptic complexes: In these complexes, the metal is bound to only one kind of donor group, e.g., [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
- Heteroleptic complexes: In these complexes, the metal is bound to more than one kind of donor groups, e.g., [Co(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup>

**Naming of mononuclear coordination compounds:**

- The cation is named first in both positively and negatively charged coordination entities.

- The ligands are named in alphabetical order, before the name of the central atom/ion.
- Names of the anionic ligands end in -o.

[Exceptions: aqua ( $\text{H}_2\text{O}$ ), ammine ( $\text{NH}_3$ ), carbonyl ( $\text{CO}$ ), nitrosyl ( $\text{NO}$ )]

- To indicate the number of the individual ligands, the prefixes mono-, di-, tri-, etc., are used. If these prefixes are present in the names of ligands, then the terms bis-, tris-, tetrakis-, etc., are used.
- Oxidation state of the metal is indicated in Roman numerals, in parentheses.
- If the complex ion is cation, then the metal is named as the element.

If the complex ion is anion, then the metal is named with '-ate' ending.

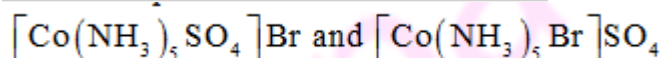
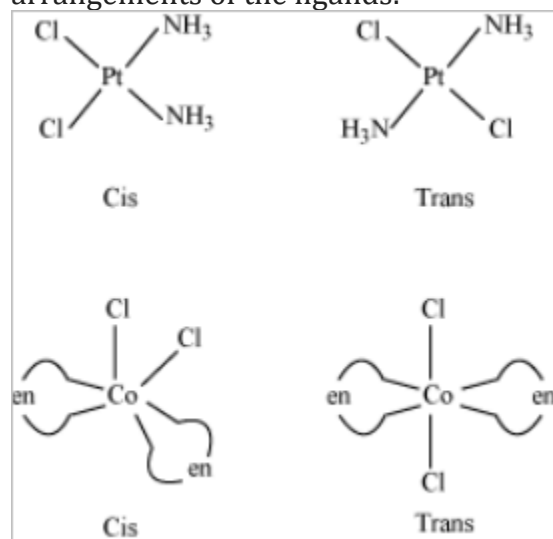
- The neutral complex molecule is named as the complex cation.

### Isomerism in coordination compounds:

- **Stereoisomerism –**

#### Geometrical isomerism:

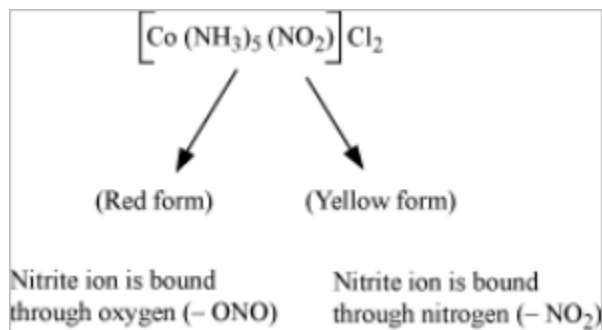
This type of isomerism arises in heteroleptic complexes due to different geometric arrangements of the ligands.



- **Optical isomerism:**

Optical isomers (enantiomers) are mirror images which cannot be superimposed on one another.

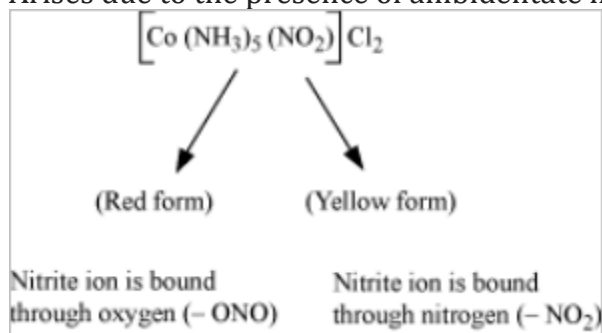
- The molecules or ions which cannot be superimposed on their mirror images are called **chiral** or **optically active**.



- Structural isomerism –**

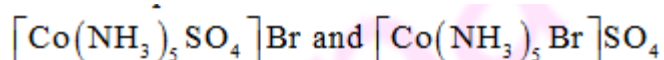
- Linkage isomerism:**

Arises due to the presence of ambidentate ligand



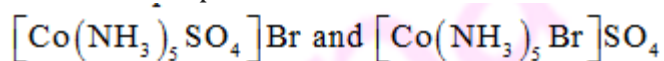
- Coordination isomerism:**

Arises due to the interchange of ligands between cationic and anionic entities of different metal ions



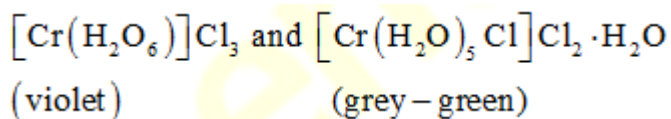
- Ionisation isomerism:**

Arises due to the interchange of ligands between the inside and the outside of the coordination sphere



- Solvate isomerism (Hydrate isomerism when solvent is water):**

Arises depending upon whether a solvent molecule is directly bonded to the metal ion or is present as a free solvent molecule.



**Valence bond theory:**

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	$sp^3$	Tetrahedral
4	$dsp^2$	Square planar
5	$sp^3d$	Trigonal bipyramidal
6	$sp^3d^2$	Octahedral
6	$d^2sp^3$	Octahedral

- **Inner-orbital or low spin or spin-paired complexes:** Complexes that use inner  $d$ -orbitals in hybridisation, e.g.,  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- **Outer-orbital or high spin or spin-free complexes:** Complexes that use outer  $d$ -orbitals in hybridisation, e.g.,  $[\text{CoF}_6]^{3-}$

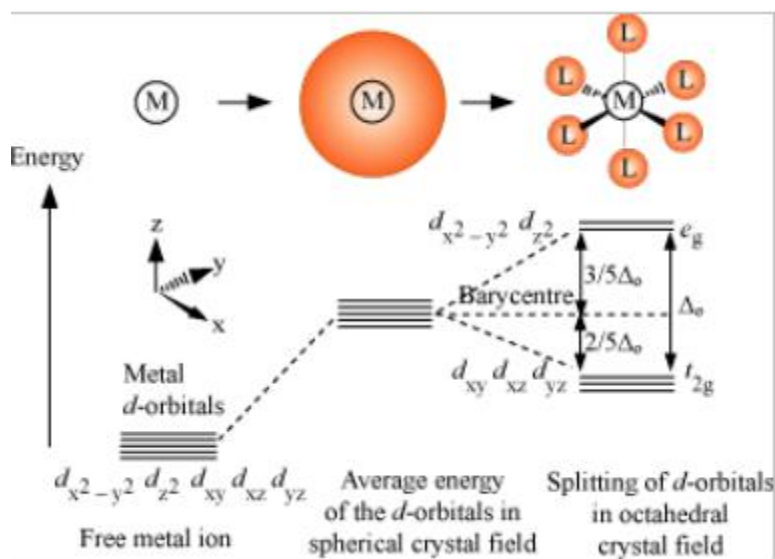
**Limitations of valence bond theory:**

- A number of assumptions are involved.
- Quantitative interpretation of magnetic data is not given.
- The exhibition of colour by coordination compounds is not explained.
- The thermodynamic or kinetic stabilities of coordination compounds are not quantitatively interpreted.
- Whether a complex of coordination number 4 is tetrahedral or square planar cannot be exactly predicted.
- Weak and strong ligands cannot be distinguished.

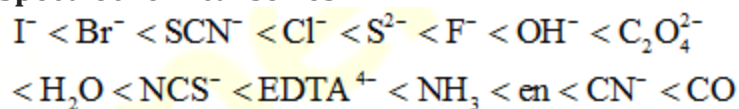
**Crystal-field theory:**

[Crystal-field splitting is the splitting of the degenerate energy levels due to the presence of ligands.]

- Crystal-field splitting in octahedral coordination entities:

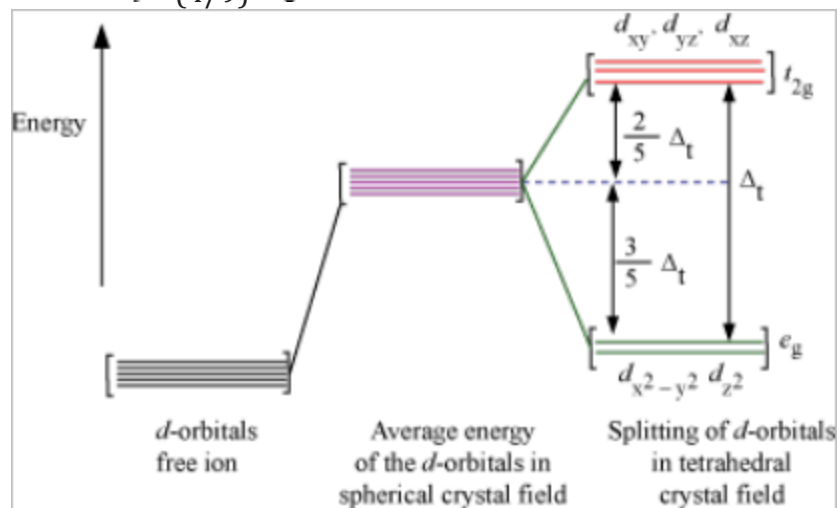


- Spectrochemical series:**



- Ligands for which  $\Delta_0$  (crystal-field splitting)  $< P$  (pairing energy) are called **weak-field** ligands, and form **high-spin** complexes.
- Ligands for which  $\Delta_0$  (crystal-field splitting)  $> P$  (pairing energy), are called **strong-field** ligands, and form **low-spin** complexes.
- Crystal-field splitting in tetrahedral coordination entities:

$$\Delta_t = (4/9) \Delta_0$$



**Colour in coordination compounds:**

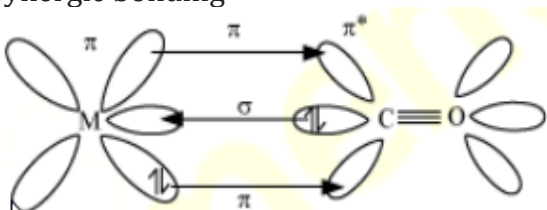
The colour of the coordination compounds is attributed to  $d-d$  transition of electrons.

**Limitations of the crystal-field theory:**

- Anionic ligands are assumed to exert the greatest splitting effect. But the anionic ligands are found at the lower end of the spectrochemical series.
- Crystal-field theory does not take into account the covalent character of bonding between ligand and the central metal atom.

**Bonding in metal carbonyls:**

- Synergic bonding –



Stability of coordination compounds:

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \dots K_n$$

Where,

$\beta \rightarrow$  Overall stability constant

$K \rightarrow$  Stepwise stability constant

**Applications of coordination compounds:**

- EDTA is used in the treatment of lead poisoning.
- Cis-platin is used in the treatment of cancer.