

Coordination Compounds

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.

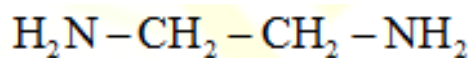
Difference between a double salt and a complex:

- 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, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

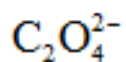
Ligands:

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

- **Didentate** –

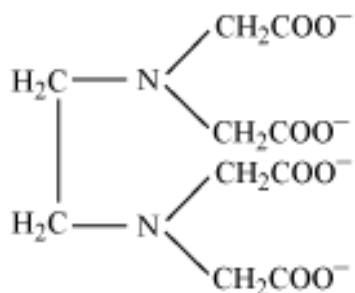


Ethane-1,2-diamine



Oxalate

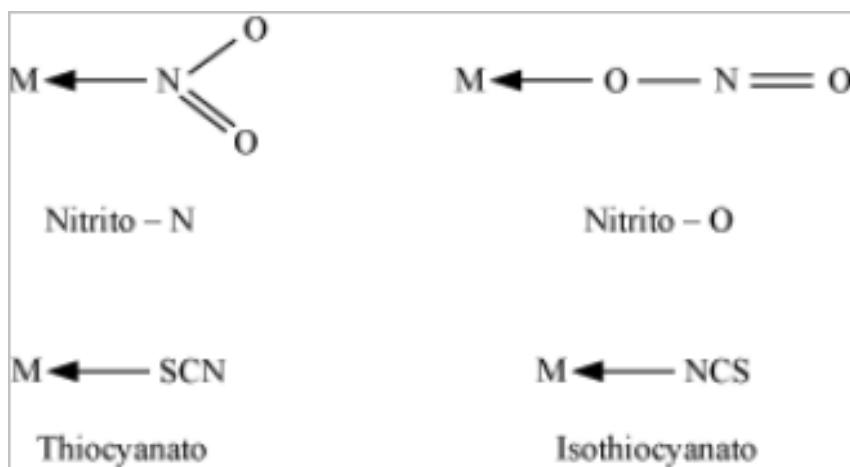
- **Polydentate –**



Ethylenediaminetetraacetate (EDTA^{4-})

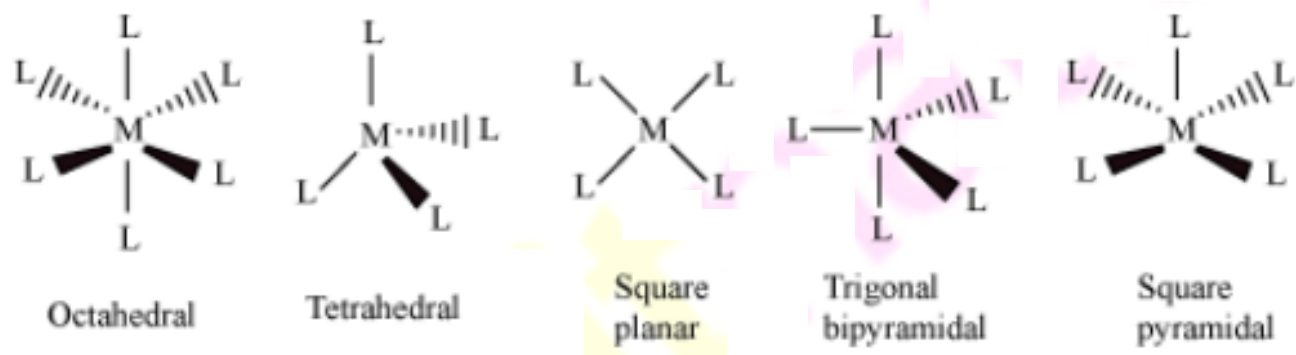
- **Ambidentate –**

(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., $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Heteroleptic complexes: In these complexes, the metal is bound to more than one kind of donor groups, e.g., $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

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 (H_2O), ammine (NH_3), carbonyl (CO), nitrosyl (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.

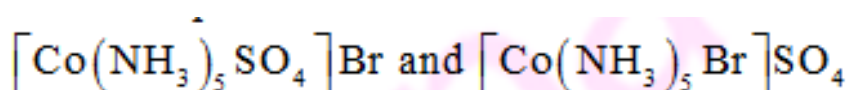
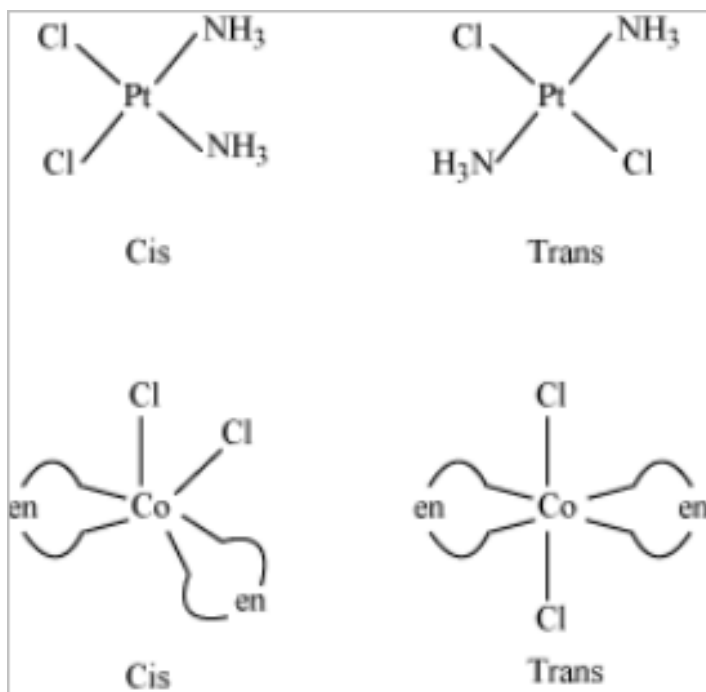
- The neutral complex molecule is named as the complex cation.

Isomerism in coordination compounds:

- Stereoisomerism –**

Geometrical isomerism:

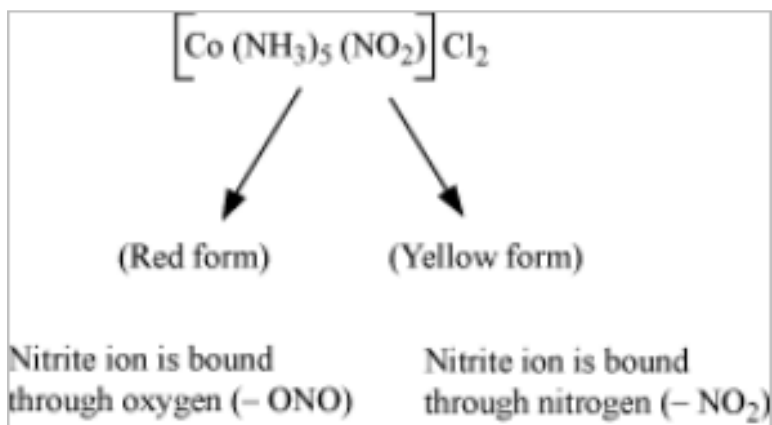
This type of isomerism arises in heteroleptic complexes due to different geometric arrangements of the ligands.



- Optical isomerism:**

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

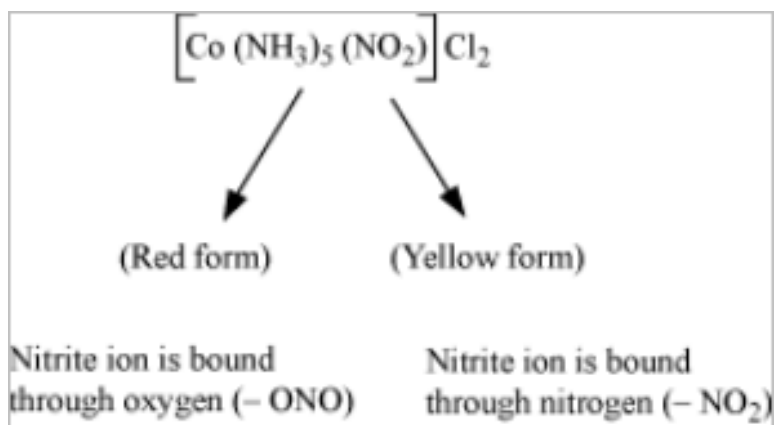
- The molecules or ions which cannot be superimposed on their mirror images are called **chiral** or **optically active**.



- **Structural isomerism –**

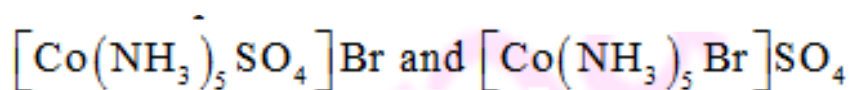
- **Linkage isomerism:**

Arises due to the presence of ambidentate ligand



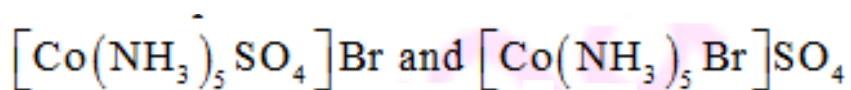
- **Coordination isomerism:**

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



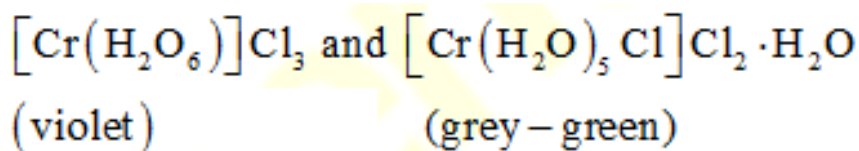
- **Ionisation isomerism:**

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:

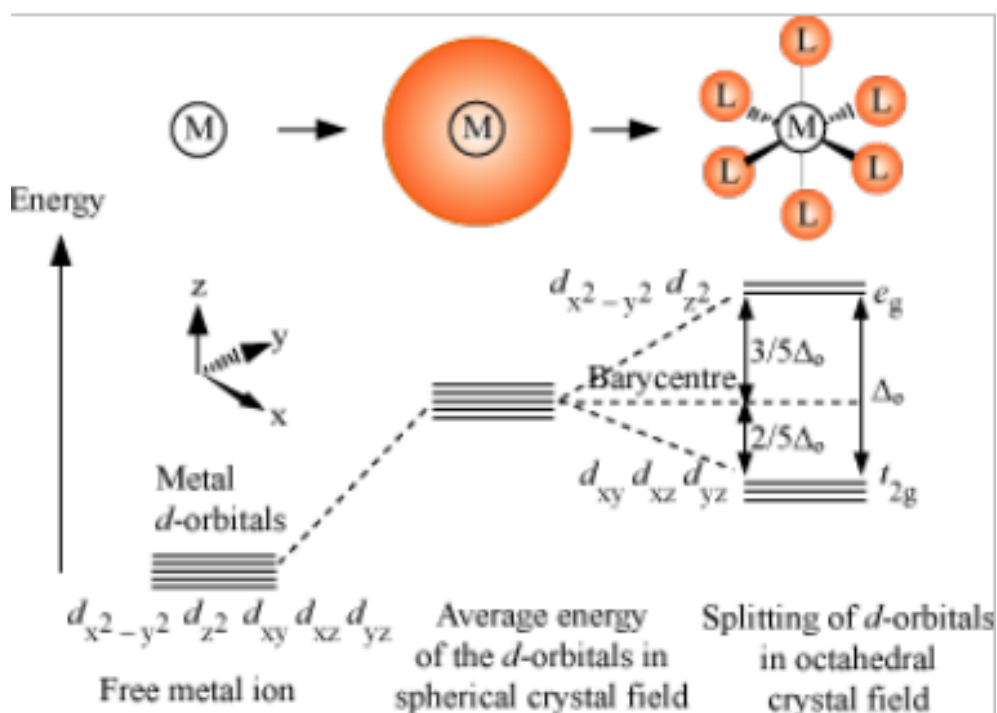
- A number of assumptions are involved.
- Quantitative interpretation of magnetic data is not given.
- The exhibition of colour by coordination compounds is not explained.
- The thermodynamic or kinetic stabilities of coordination compounds are not quantitatively interpreted.

- Whether a complex of coordination number 4 is tetrahedral or square planar cannot be exactly predicted.
- Weak and strong ligands cannot be distinguished.

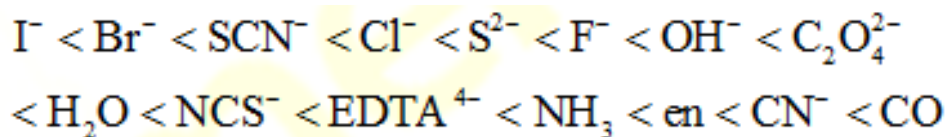
Crystal-field theory:

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

- Crystal-field splitting in octahedral coordination entities:



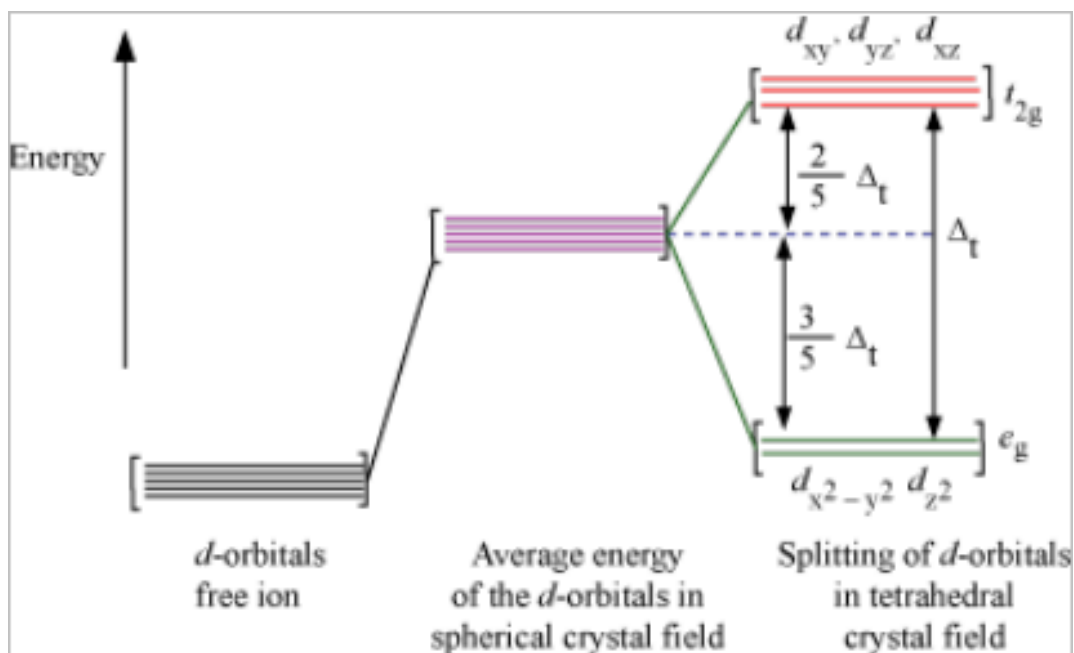
- Spectrochemical series:



- Ligands for which Δ_o (crystal-field splitting) $<$ P (pairing energy) are called **weak-field** ligands, and form **high-spin** complexes.
- Ligands for which Δ_o (crystal-field splitting) $>$ P (pairing energy), are called **strong-field** ligands, and form **low-spin** complexes.

- Crystal-field splitting in tetrahedral coordination entities:

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



Colour in coordination compounds:

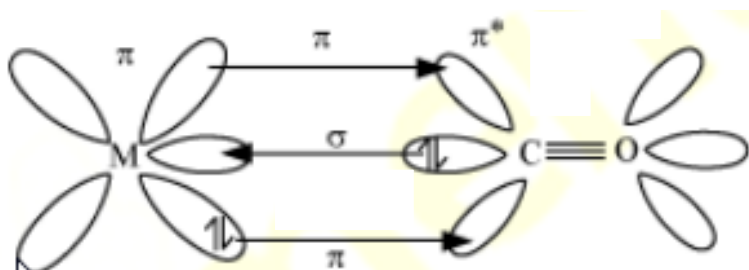
The colour of the coordination compounds is attributed to $d-d$ transition of electrons.

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.