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 ($KCl.\ MgCl_2.\ 6H_2O$), Mohr's salt [$FeSO_4.\ (NH_4)_2\ SO_4.\ 6H_2O$]
- Complex ions do not dissociate further to give simpler ions. For example, $[Fe(CN)_6]^{4-}$, $[Fe(C_2O_4)_3]^{3-}$

Ligands:

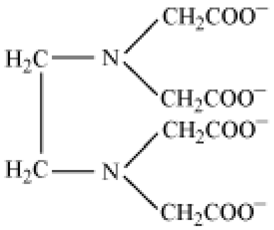
Ions or molecules bound to the central metal atom or ion in the coordination entity

- **Didentate –**

$H_2N-CH_2-CH_2-NH_2$ Ethane – 1, 2 – diamine

$C_2O_4^{2-}$ Oxalate

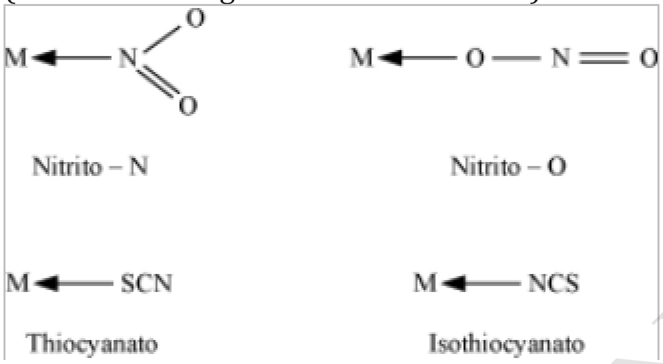
- **Polydentate –**



Ethylenediaminetetraacetate ($EDTA^{4-}$)

- **Ambidentate –**

  (Can bind through two different atoms)



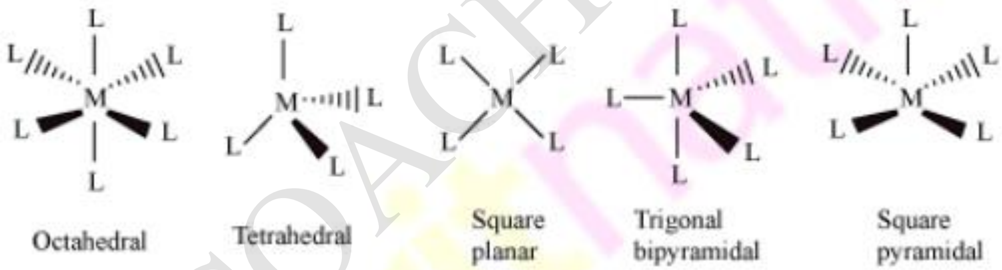
Nitrito – N

Nitrito – O

Thiocyanato

Isothiocyanato

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



Octahedral

Tetrahedral

Square planar

Trigonal bipyramidal

Square pyramidal

Homoleptic and heteroleptic complexes:

- Homoleptic complexes: In these complexes, the metal is bound to only one kind of donor group, e.g., $[Co(NH_3)_6]^{3+}$
- Heteroleptic complexes: In these complexes, the metal is bound to more than one kind of donor groups, e.g., $[Co(NH_3)_4Cl_2]^{+}$

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.

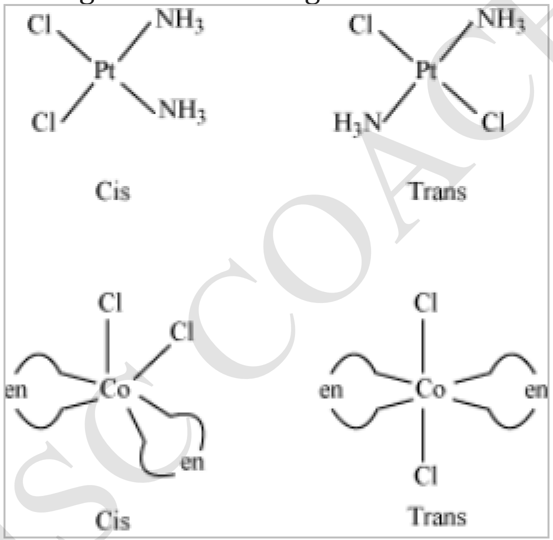
  [Exceptions: aqua (H_2O), ammine (NH_3), carbonyl (CO), nitrosyl (NO)]
- To indicate the number of the individual ligands, the prefixes mono–, di–, tri–, etc., are used. If these prefixes are present in the names of ligands, then the terms bis–, tris–, tetrakis–, etc., are used.
- Oxidation state of 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 –**

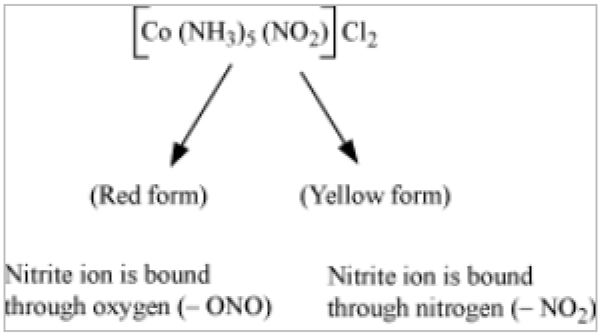
  Geometrical isomerism:
  This type of isomerism arises in heteroleptic complexes due to different geometric arrangements of the ligands.



$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

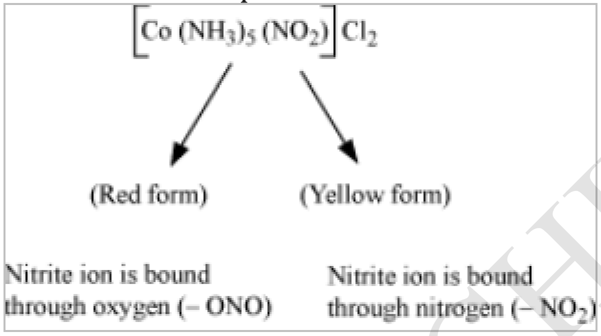
- **Optical isomerism:**
  Optical isomers (enantiomers) are mirror images which cannot be superimposed on one another.

- 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

  $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

- **Ionisation isomerism:**

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

  $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$

- **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.

$$\left[\mathrm{Cr}\left(\mathrm{H_2O_6}\right)\right]\mathrm{Cl_3} \text{ and } \left[\mathrm{Cr}\left(\mathrm{H_2O}\right)_5\mathrm{Cl}\right]\mathrm{Cl_2}\cdot\mathrm{H_2O}$$

(violet) (grey – green)

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., $[Co(NH_3)_6]^{3+}$

- **Outer-orbital or high spin or spin-free complexes:** Complexes that use outer *d*–orbitals in hybridisation, e.g., $[CoF_6]^{3-}$

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.

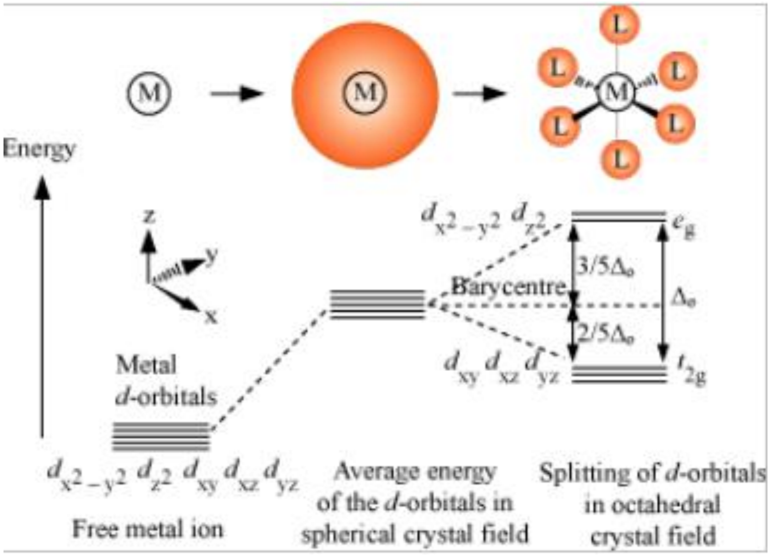
- Whether a complex of coordination number 4 is tetrahedral or square planar cannot be exactly predicted.

- 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:



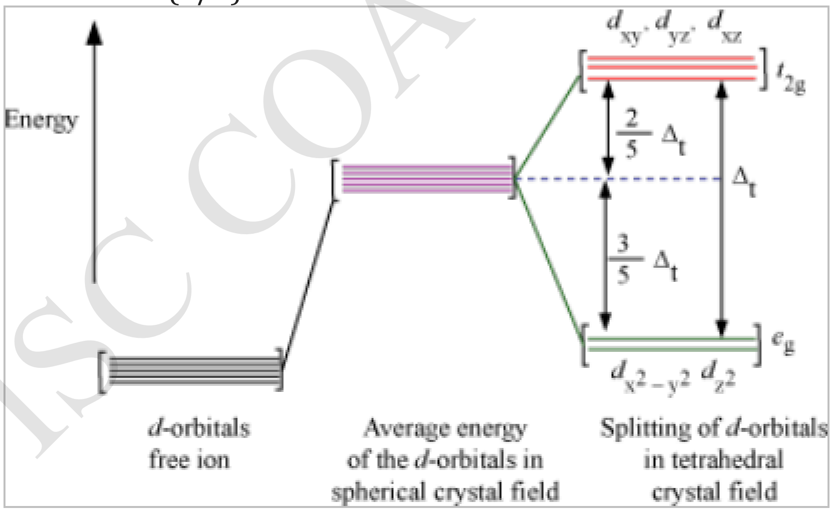
- **Spectrochemical series:**

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-}$$
$$< H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$$

- Ligands for which Δ_0 (crystal-field splitting) < P (pairing energy) are called **weak-field** ligands, and form **high-spin** complexes.

- Ligands for which Δ_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.

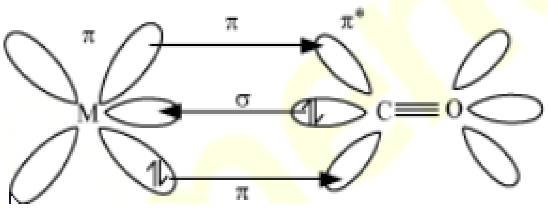
Limitations of the crystal-field theory:

- 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:
$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots K_n$
Where,
β → Overall stability constant
K → 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.