

Coordination Compounds

Studying coordination chemistry helps us understand how metal ions and surrounding molecules or ions bond and interact, leading to the formation of complex compounds with unique properties and applications.

Structure of Coordination complex:



Basic Terms:

- **Coordination Entity:** A coordination entity consists of a central metal atom and its surrounding ligands.
- **Central Atom/Ion:** The main atom or ion in a coordination compound, bonded to ligands.
- Ligand: A molecule or ion bonded to the central atom in a coordination sphere.
- **Coordination Number:** The number of ligands attached to the central atom.
- **Coordination Sphere:** The central atom and its surrounding ligands in a coordination compound.
- **Coordination Polyhedron:** The geometric shape formed by connecting the central atom to its ligands.
- **Oxidation Number:** A charge assigned to an atom in a compound to track electron transfer.
- Homoleptic: A complex where all ligands around the central atom are the same.
- Heteroleptic: A complex with different types of ligands bonded to the central atom.

Chelate Complexes: A polydentate ligand simultaneously coordinates to central metal ion/atom by two or more donor sites and forms a closed stable ring. Chelate complexes are highly stable. Common chelating ligands are en, CO_3^{-2} , EDTA, $C_2O_4^{-2}etc$.

Werner's theory: It suggests that metal ions can form specific coordination bonds with surrounding molecules or ions, leading to the formation of complex compounds with distinct structures and properties. The main postulates are:

- (1) Metals in coordination compounds have two types of linkages: **primary** and **secondary**.
- (2) Primary valences can be satisfied by negative ions and are ionizable.
- (3) Secondary valences are satisfied by neutral molecules or negative ions and are nonionizable. They are equal to the coordination number.
- (4) The arrangement of ions or groups bound by secondary linkages corresponds to different coordination numbers.
- (5) Common geometrical shapes are octahedral, tetrahedral and square planar.
 - Octahedral: $[Co(NH_3)_6]^{+3}$, $[CoCl(NH_3)_5]^{+2}$, $[CoCl_2(NH_3)_4]^{+1}$
 - Tetrahedral: $[Ni(CO)_4]$
 - Square planar: $[PtCl_4]^{-2}$





Octagedral

Tetrahedral

Square planar

Difference between a double salt and a complex:

Characteristic	Double Salt	Complex
Formation	Combination of stable compounds	Combination of compounds
Behaviour in Solution	Dissociates into simple ions	Does not dissociate into simple ions
Example	Carnallite, Mohr's salt, etc.	$[Fe(CN)_6]^{-4}$ in $K_4[Fe(CN)_6]$

Nomenclature of Coordination Compounds:

- Cation first: Name the metal cation at the beginning.
- Anion next: Name anionic ligands with an "-o" ending (e.g., "chlorido" for chloride).

Coordination Compounds

- Ligand prefixes: Use "di-", "tri-", etc., for multiple identical ligands.
- Ligand names: If ligands are complex molecules, use their specific names.
- Coordination number: Indicate the number of ligands with a numeral in parentheses if necessary.
- Overall charge: Specify the complex's overall charge in square brackets.



Valence Bond Theory (VBT):

- In VBT, the metal ion uses its atomic orbitals (s, p, d) for hybridization.
- Hybridized orbitals overlap with ligand orbitals to form coordination bonds.
- Differentiates between inner orbital (low spin) and outer orbital (high spin) complexes.
- Predicts geometry and magnetic behaviour.
 - **Diamagnetic:** Complex which does not contain unpaired electrons.
 - Paramagnetic: Complex which contains unpaired electrons.
 - Magnetic moment = $\sqrt{n(n+2)}$ B.M., n= number of unpaired electrons.

Limitations of VBT:

- i. Doesn't provide a quantitative interpretation of magnetic data.
- ii. Doesn't explain the colour of coordination compounds.
- iii. Can't quantitatively predict stability.
- iv. Doesn't precisely predict tetrahedral and square planar structures.
- v. Doesn't distinguish between weak and strong ligands.

Crystal Field Theory (CFT):

Model Explanation: Describes coordination compound bonding as ionic due to electrostatic interactions between metal ions and ligands.

Degeneracy: In a spherical field, d orbitals of a metal are degenerate (have the same energy).

Crystal Field Splitting (Octahedral):

- Ligands cause splitting of d-orbitals into t_{2g} (lower energy) and ${f e}_g$ (higher energy) sets.
- Δo : Denotes the energy separation between \mathbf{t}_{2g} and \mathbf{e}_{g} orbitals.

Spectrochemical Series: Ranks ligands by their ability to produce strong or weak crystal field splitting.

 $I^- < Br^- < SCN^- < Cl^- < S^{-2} < F^- < OH^- < C_2 O_4^{-2} < H_2 O < NCS < edta^{-4} < NH_3 < en < CN^- < CO$

Weak Field Ligands: $\Delta o < P$, form high spin complexes.

Strong Field Ligands: $\Delta o > P$, form low spin complexes, more stable for d_4 to d_7 ions.

Crystal Field Splitting (Tetrahedral):

- Inverted splitting, smaller than octahedral splitting.
- Low spin configurations are rarely observed in tetrahedral complexes.

Limitations of CFT:

- Assumes ligands as point charges.
- Doesn't consider covalent bonding between ligands and central atom.



Coordination Compounds

Colour of Complexes:

- Coordination compound colours result from absorbing specific light wavelengths, displaying complementary colours.
- CFT explains these colours through **d-d electron transitions** influenced by ligands.
- The d⁰ and d¹⁰ are always colourless.
- The d¹ to d⁹ are always coloured.
- Colour of complex can be decided with the help of colour cycle. (Complementary Colours)

