Short Notes for CUET UG Chemistry

Unit V: Coordination Compounds

1. Introduction: Double Salts vs. Coordination Compounds

- **Double Salts:** Addition compounds that dissociate completely into simple ions when dissolved in water. They lose their identity in solution.
    - *Example:* Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$) dissociates into Fe^{2+}, NH_4^+, and SO_4^{2-} ions.
- **Coordination (Complex) Compounds:** Addition compounds that do not dissociate completely into simple ions in water. The complex ion retains its identity.
    - *Example:* Potassium ferrocyanide $K_4[Fe(CN)_6]$ dissociates into $4K^+$ and the complex ion $[Fe(CN)_6]^{4-}$, but does not give Fe^{2+} or CN^- ions.

2. Werner's Theory of Coordination Compounds

Alfred Werner proposed that metals in coordination compounds exhibit two types of valencies:

1. **Primary Valency:** Ionizable, non-directional, and corresponds to the **oxidation state** of the central metal. Satisfied by negative ions (anions).
2. **Secondary Valency:** Non-ionizable, directional, and corresponds to the **coordination number** of the central metal. Satisfied by neutral molecules or negative ions (ligands). It determines the geometry of the complex.

3. Basic Definitions

- **Coordination Entity:** Constitutes a central metal atom or ion bonded to a fixed number of ions or molecules (e.g., $[CoCl_3(NH_3)_3]$).
- **Central Atom/Ion:** The atom or ion to which a fixed number of ligands are bound in a definite geometrical arrangement. It acts as a Lewis acid (electron pair acceptor).
- **Ligands:** The ions or molecules bound to the central atom/ion. They act as Lewis bases (electron pair donors).
    - *Unidentate:* Binds through one donor atom (e.g., Cl^-, H_2O, NH_3).
    - *Didentate:* Binds through two donor atoms (e.g., ethane-1,2-diamine/en, oxalate/$C_2O_4^{2-}$).
    - *Polydentate:* Binds through several donor atoms (e.g., EDTA^{4-} is hexadentate).
    - *Chelate Ligand:* A di- or polydentate ligand that forms a ring structure with the central metal, increasing the stability of the complex (Chelate effect).
    - *Ambidentate Ligand:* A unidentate ligand that can ligate through two different atoms (e.g., NO_2^- can bind through N or O; SCN^- can bind through S or N).
- **Coordination Number (CN):** The total number of ligand donor atoms directly bonded to the central metal ion.
- **Coordination Sphere:** The central atom and the ligands directly attached to it are enclosed in square brackets and are collectively termed the coordination sphere.
- **Coordination Polyhedron:** The spatial arrangement of the ligand atoms directly attached to the central atom.
- **Oxidation Number:** The charge the central metal would carry if all ligands were removed along with the electron pairs shared with it.
- **Homoleptic Complexes:** Complexes in which the metal is bound to only one kind of donor group (e.g., $[Co(NH_3)_6]^{3+}$).
- **Heteroleptic Complexes:** Complexes in which the metal is bound to more than one

kind of donor group (e.g., $[Co(NH_3)_4Cl_2]^+$).

4. IUPAC Nomenclature

1. **Order of naming:** The cation is named first in both positively and negatively charged coordination entities.
2. **Ligands:** Named in alphabetical order before the name of the central atom/ion. Anionic ligands end in *-o* (e.g., chlorido, cyanido), neutral ligands keep their names (exceptions: aqua for H_2O, ammine for NH_3, carbonyl for CO, nitrosyl for NO).
3. **Prefixes:** *di-, tri-, tetra-* are used to indicate the number of individual ligands. If the ligand name already includes a numerical prefix (like ethane-1,2-diamine), the terms *bis-, tris-, tetrakis-* are used.
4. **Metal Name:** If the complex ion is an anion, the metal name ends with the suffix *-ate* (e.g., ferrate, cuprate). If the complex is a cation or neutral, the metal name remains unchanged.
5. **Oxidation State:** Written in Roman numerals in parentheses immediately after the metal name.

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5. Isomerism in Coordination Compounds

Isomers have the same chemical formula but different spatial arrangements of atoms.

A. Structural Isomerism

- **Ionisation Isomerism:** Occurs when the counter ion in a complex salt is itself a potential ligand and can displace a ligand, generating a different ion in solution (e.g., $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$).
- **Hydrate (Solvate) Isomerism:** Similar to ionisation isomerism, but the differing ligand is a solvent molecule, usually water (e.g., $[Cr(H_2O)_6]Cl_3$ vs $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$).
- **Linkage Isomerism:** Arises in complexes containing ambidentate ligands (e.g., bonding via N in $-NO_2$ vs bonding via O in $-ONO$).
- **Coordination Isomerism:** Interchange of ligands between cationic and anionic entities of different metal ions present in a complex.

B. Stereoisomerism

- **Geometrical Isomerism:** Different spatial arrangement of ligands around the central metal. Common in square planar and octahedral complexes.
    - *Cis/Trans:* Similar ligands are adjacent (cis) or opposite (trans) to each other.
    - *Fac/Mer:* In octahedral complexes of type $[Ma_3b_3]$, if three identical ligands occupy one face of the octahedron, it is facial (fac); if around the meridian, it is meridional (mer).
- **Optical Isomerism:** Chiral molecules that form non-superimposable mirror images (enantiomers). They rotate plane-polarized

light in opposite directions (dextro 'd' and laevo 'l'). Common in octahedral complexes involving didentate ligands.

6. Bonding in Coordination Compounds

A. Valence Bond Theory (VBT)

VBT explains the structure and magnetic properties based on orbital hybridization. The metal provides empty orbitals (s, p, d) that hybridize to accept electron pairs from ligands.

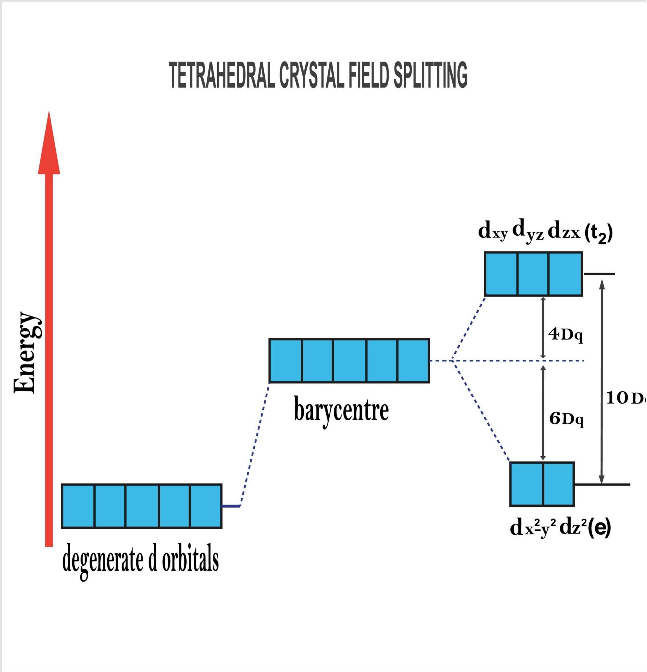
- **Inner Orbital Complexes:** Use inner $(n-1)d$ orbitals for hybridization (e.g., d^2sp^3). These are generally **low-spin** complexes and are formed with strong-field ligands.
- **Outer Orbital Complexes:** Use outer nd orbitals for hybridization (e.g., sp^3d^2). These are generally **high-spin** complexes and are formed with weak-field ligands.
- **Limitations of VBT:** It does not explain the color of complexes, offers no quantitative interpretation of magnetic data, and does not distinguish between weak and strong ligands.

B. Crystal Field Theory (CFT)

CFT considers ligands as point charges (or dipoles) and the metal-ligand bond as purely ionic. It focuses on the splitting of the five degenerate d-orbitals of the metal ion in the presence of the ligand's electric field.

- **Octahedral Splitting (Δ_o):** The d-orbitals split into two sets: lower energy t_{2g} (d_{xy}, d_{yz}, d_{zx}) and higher energy e_g ($d_{x^2-y^2}$, d_{z^2}).
- **Tetrahedral Splitting (Δ_t):** The splitting is inverted and smaller than octahedral splitting. The lower energy set is e and the higher energy set is t_2.

$$\Delta_t = \frac{4}{9}\Delta_o$$



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Spectrochemical Series: An experimentally determined arrangement of ligands in increasing order of crystal field splitting power (Δ):

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < N$$

Applications of CFT:

1. **Magnetic Properties:** Depends on the relationship between crystal field splitting energy (Δ_o) and pairing energy (P).
    - If $\Delta_o < P$ (Weak field ligand): Electrons prefer to occupy higher energy e_g orbitals rather than pair up. Forms **high-spin** complexes.
    - If $\Delta_o > P$ (Strong field ligand): Electrons prefer to pair up in lower energy t_{2g} orbitals. Forms **low-spin** complexes.
2. **Colour:** Due to **d-d transitions**. An electron jumps from the lower energy d-orbital to the higher energy d-orbital by absorbing a specific wavelength of visible light. The complex transmits the complementary color.

- **Limitations of CFT:** It completely ignores the covalent character of metal-ligand bonds.

7. Shape and Bonding in Metal Carbonyls

Homoleptic metal carbonyls (e.g., $[Ni(CO)_4]$, $[Fe(CO)_5]$) contain only carbonyl (CO) ligands.

- **Synergic Bonding:** The metal-carbon bond possesses both σ and π character.
  1. The ligand donates a lone pair of electrons into an empty metal orbital to form a σ**-bond**.
  2. The metal donates electrons from a filled d-orbital into the empty antibonding π^* orbital of the CO ligand to form a π**-back bond**. This creates a synergic effect, strengthening the bond between CO and the metal.

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8. Importance & Applications

- **Analytical Chemistry:** Used in qualitative and quantitative analysis (e.g., Ni^{2+} detection using dimethylglyoxime; hardness of water estimated using Na_2EDTA).
- **Metallurgy:** Extraction of gold and silver involves the formation of cyanide complexes ($[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$). Purification of Nickel via Mond's process involves $[Ni(CO)_4]$.
- **Biological Systems:** * Chlorophyll (photosynthesis) is a coordination compound of Magnesium.
  - Hemoglobin (oxygen transport) is a complex of Iron.
  - Vitamin B12 (cyanocobalamin) is a complex of Cobalt.
- **Catalysis:** Wilkinson's catalyst $[RhCl(PPh_3)_3]$ is used for the hydrogenation of alkenes.
- **Medicine:** Cisplatin $[Pt(NH_3)_2Cl_2]$ is highly effective in inhibiting the growth of tumors (cancer treatment).