Coordination Compounds - Part I

Coordination sphere consists of the central atom/ion and the ligands attached to it.

Central Atom is bound to a fixed number of ions/groups in a definite geometrical arrangement.

\[
[\text{Co} \quad \text{Cl} \quad (\text{NH}_3)_5 \quad \text{Cl}_2]
\]

Ligands the ions or molecules bound to the central atom/ion in a coordination entity.

Coordination number 5+1=6 The number of ligand donor atoms to which the metal is directly bound.

IUPAC Nomenclature of Coordination

Name the Cation before the anion.

Name Ligands in the alphabetical order

Ligands have a numerical prefix

After ligands, Central metal atom/ion is named

Neutral ligands are given the same name as the uncoordinated molecule

The ligands are named alphabetically, ignoring the prefixes bis, tris, etc...

Anionic ligands are given names that end in the letter “o”.

When the coordination entity is an anion, the name of the metal is altered to end in “ate”

Isomerism

Structural Isomerism

Stereoisomerism (space isomerism)

Ionization isomerism

Hydrate isomerism

Linkage isomerism

Coordination isomerism

Coordination position isomerism
**Coordination Compounds - Part II**

### Structural Isomerism

- **Coordination isomerism** observed in the coordination compounds having both cationic and anionic complex ions.

<table>
<thead>
<tr>
<th>Complex ions</th>
<th>Tetraammineplatinum(II) tetrachloridocuprate(II)</th>
<th>Tetraamminecopper(II) tetrachloridoplutinate(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(NH₃)₄]²⁺</td>
<td>[CuCl₄]⁻</td>
<td>[Cu(NH₃)₄]²⁺</td>
</tr>
</tbody>
</table>

- **Ionization isomerism** afford different anions and cations in solution.

<table>
<thead>
<tr>
<th>Complex ions</th>
<th>Tetraamminedi hydroxo-platinum(IV)sulphate</th>
<th>Tetraamminesulphato-platinum(IV)hydroxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(OH)₂(NH₃)₄]SO₄</td>
<td><a href="OH">PtSO₄(NH₃)₄</a>₂</td>
<td></td>
</tr>
</tbody>
</table>

- **Hydrate isomerism** arises when different number of water molecules are present inside and outside the coordination sphere.

<table>
<thead>
<tr>
<th>Complex ions</th>
<th>Tetraammineaquachlorido-cobalt(III)bromide</th>
<th>Tetraamminebromidocobalt(III)chloride monohydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH₃)₄H₂OCl]Br₂</td>
<td>[Co(NH₃)₄Br₂]ClH₂O</td>
<td></td>
</tr>
</tbody>
</table>

- **Linkage Isomerism** isomerism occurs in complex compounds which contain ambidentate ligands.

<table>
<thead>
<tr>
<th>Complex ions</th>
<th>Pentaamine nitrito-n-cobalt(III) chloride(yellow)</th>
<th>Pentaamine nitrito-o-cobalt(III) chloride(yellow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH₃)₅NO₂]Cl₂</td>
<td>[Co(NH₃)₅ONO]Cl₂</td>
<td></td>
</tr>
</tbody>
</table>

- **Polymerisation Isomerism** it occurs between compounds having the same empirical formula, but different molecular weights.

\[ [\text{Pt(NH₃)}₂\text{Cl}_2] ; [\text{Pt(NH₃)}₄\text{Cl}_4] ; [\text{Pt(NH₃)}₃\text{Cl}]_2[\text{PtCl}_4] \]

- **Coordination position Isomerism** exhibited by polynuclear complexes by changing the position of ligands.

Unsymmetrical

\[
\begin{align*}
\text{(NH₃)₄} & \quad \text{Co} \quad \begin{array}{c}
\text{H}_2 \\
\text{N} \\
\text{O}_2 \\
\text{Co(NH₃)₂} \\
\text{Cl}_2 \\
\end{array}
\end{align*}
\]

Symmetrical

\[
\begin{align*}
\text{(NH₃)₃} & \quad \text{Co} \quad \begin{array}{c}
\text{H}_2 \\
\text{N} \\
\text{O}_2 \\
\text{Co(NH₃)₃} \\
\text{Cl}_2 \\
\end{array}
\end{align*}
\]
**Coordination Compounds - Part III**

**Stereo Isomerism**
- Ligands at different locations relative to one another.

**Geometric**
- Cisplatin
- Transplatin

**Optical**
- Nonsuperimposable mirror images of each other.

**Werner’s Theory**
- Basically explains the structure of the complex compounds

**Postulates**
- Metals consist of two types of valencies; Primary and Secondary
- Primary is fulfilled by anions which are non-directional.
- Secondary are fulfilled by Ligands which are directional.

**Limitations**
- Why Complex compounds are formed by few metals?
- Why Coordinate bonds are directional in nature?
- Why these compounds show magnetic and optical properties?

**Valence Bond Theory**
- Explains Bonding in terms of Hybridisation and explains the magnetic behaviour of the hybridised bonds.

**Postulates**
- Central atom makes available vacant orbitals equal to its coordination number
- These vacant hybrid orbitals form bonds with ligands which are directional in nature

**Limitations**
- Couldn’t explain colour and electronic spectra of complexes
- Couldn’t explain structure of [Cu (NH₃)₄]²⁺
- Couldn’t explain pairing of electrons in presence of ligands

**Hybridisation and Geometry of Complex**

<table>
<thead>
<tr>
<th>Complex Compound or Ion</th>
<th>Magnetic Behaviour</th>
<th>Hybridisation</th>
<th>Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(CN)₆]³⁻</td>
<td>Paramagnetic</td>
<td>d⁶sp³</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Fe(CN)₅(NH₃)]Cl⁻</td>
<td>Diamagnetic</td>
<td>d⁶sp³</td>
<td>Square Planar</td>
</tr>
<tr>
<td>[Ni(CN)₄]²⁻</td>
<td>Paramagnetic</td>
<td>d⁵sp³</td>
<td>Square Planar</td>
</tr>
<tr>
<td>[Cu(NH₃)₂SO₄]⁺</td>
<td>Paramagnetic</td>
<td>dsp²</td>
<td>Square Planar</td>
</tr>
<tr>
<td>[Ni(NH₃)₄]SO₄⁺</td>
<td>Paramagnetic</td>
<td>dsp²</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Cu(CN)₂]⁺</td>
<td>Paramagnetic</td>
<td>dsp²</td>
<td>Square Planar</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]³⁺</td>
<td>Paramagnetic</td>
<td>d⁶sp³</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Cr(CN)₆]³⁻</td>
<td>Paramagnetic</td>
<td>d⁶sp³</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Co(CN)₆]³⁻</td>
<td>Diamagnetic</td>
<td>d⁶sp³</td>
<td>Octahedral</td>
</tr>
<tr>
<td>[Co(NH₃)₆]³⁺</td>
<td>Diamagnetic</td>
<td>d⁶sp³</td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

**Crystal Field Theory**
- Ligand field destroys the degeneracy of d orbitals and splits it into two or more energy levels.

In an octahedral complex, there are six ligands attached to the central transition metal. The d orbitals split into two different levels. The bottom three energy levels are named dₓz, dᵧz, and dₑ (collectively referred to as t₂). The two upper energy levels are named dₒ and dₑ (collectively referred to as eᵧ).

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the dₓz, dᵧz, and dₑ orbitals. The bottom two consist of the dₒ and dₑ orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axis, while the ligands are not.

**Ligands in order of their field strength:**

$1 > Br > Cl > SCN > OH > O₂⁻ > H₂O > SCN > CN > H₂O > Br > Cl > CN > OH