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Choice Based Credit System [CBCS]
(2019 Pattern)

Second Year Bachelors of Science
(S. Y. B. Sc.)
From Academic Year
2020-21
SEMESTER III

Theory Course: CH-302 :
Inorganic and Organic Chemistry (2 credit, 36 L)

Inorganic Chemistry:

Chapter I: Molecular Orbital Theory of Covalent Bonding
Chapter II: Introduction to Coordination chemistry
Chapter 2. Introduction to coordination Chemistry

- Types of Salts.
- Requirements for the formation of coordination compounds.
- Difference between Double salt and complex salt.
- Historical Development.
- Definitions of various terms involved in coordination chemistry.
CHAPTER 2.

INTRODUCTION TO COORDINATION COMPOUNDS

- Coordination compounds or metal complexes or simply complexes are one of the special class of compounds.
- Types of salts - Simple salts, Double salts and Complex salts.
- Simple salts are formed by combination of cation and anion.
- Double salts are stoichiometric mixture of two compounds.
- Complex salts contains metal atom or ion at the centre and is surrounded by ions or molecules.
- The total charge on complex depends upon sum of the charges of central metal atom and surrounding ions or molecules.
- Conditions for the formation of coordination compound-
  1. Metal atom or ion must contain sufficient number of empty orbitals to accept electron pairs for bond formation.
  2. Surrounding atoms, ions or molecules must contain pair of electrons which can be easily donated to the central metal atom or ion.
### Difference Between Double Salt and Complex Salt

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Double Salt</th>
<th>Complex Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Exists only in crystalline state.</td>
<td>Stable both in crystalline and solution state.</td>
</tr>
<tr>
<td>2</td>
<td>All constituent ions can be detected.</td>
<td>All constituent ions can not be detected.</td>
</tr>
<tr>
<td>3</td>
<td>Individual components do not lose their identity in solution.</td>
<td>Individual components lose their identity in solution.</td>
</tr>
<tr>
<td>4</td>
<td>Absence of complex ion.</td>
<td>Presence of complex ion.</td>
</tr>
<tr>
<td>5</td>
<td>Examples: KCl.MgCl₂.6H₂O, K₂SO₄Al₂(SO₄)₃.24H₂O</td>
<td>Examples: K₄[Fe(CN)₆], [Cu(NH₃)₄]SO₄.</td>
</tr>
</tbody>
</table>
Historical Development

- Progress in coordination chemistry is divided into three periods:
  1. Latter part of 18th century to 1893.
  2. Wernerian era – 1893 to 1940.
  3. Modern era 1940 onwards.
- In 1704 a colour marker Diesbach in Berlin heated animal wastes and sodium carbonate in an iron vessel a blue coloured compound was obtained.
- It was Prussian blue (an artist's colour) – $\text{KCN}.\text{Fe(CN)}_2\text{Fe(CN)}_3$, the first recorded compound.
- Today it is prepared by mixing ferric salt with potassium hexacyano ferrate.
- In 1753, Macquer prepared potassium hexacyanoferrate by reacting prussian blue with alkali.
- In 1978, Tassaert prepared orange coloured compound hexaamminecobalt(III) chloride, $\text{CoCl}_3.6\text{NH}_3$, by mixing cobalt chloride solution with aqueous ammonia.
- In 1800 to 1850, large number of complexes were prepared.
Historical Development

- In 1800 to 1850, large number of complexes were prepared as –
  \[ K_3[Fe(CN)_6] \] in 1822,
  \[ [Pt(NH_3)_4], [Pt(Cl)_4] \] in 1828,
  \[ Na_2[Fe(CN)_5NO] \] in 1849.

- Structure of complex compounds were explain by various theories as
  1. Graham theory (1778)
  2. Berzelious theory (1878)
  3. Werner’s theory (1893)

- Werner, in 1893, at the age of 26, put forth his theory to explain
  formation of compounds in which number of bonds formed by the
  central metal atom is greater than that expected from the usual
  valency considerations. He studied the compounds such as:
  \[ \text{Co.Cl}_3.6(\text{NH}_3), \]
  \[ \text{Fe(CN)}_2.4\text{KCN}, \]
  \[ \text{PtCl}_4.6(\text{NH}_3) \text{ etc.} \]

- For this work he was awarded a \textbf{Noble Prize} in Chemistry in \textbf{1913}. 
Definitions of various terms used in coordination chemistry

Following terms are commonly used in coordination chemistry:

1. **Coordination compound:**
   
   A coordination compound is defined as a complex compound in which number of bonds formed by the central metal atom or ion is greater than that expected from the usual valency considerations.

   In a coordination compound metal atom or ion is at the centre and is surrounded by groups or ions. These groups or ions are denoted as ‘L’. They are attached to the metal atom or ion by forming coordinate bond. For e.g. potassium ferricyanide, $\text{K}_3[\text{Fe(CN)}_6]$ in which usual valency of Fe is three but it forms six bonds with CN⁻ ions. Coordination compound are of the following types:

   a. Complex cation – $[\text{Cu(NH}_3)_4]^{2+}$
   b. Complex anion – $[\text{Fe(CN)}_6]^{3-}$
   c. Complex cation and anion - $[\text{Co(NH}_3)_6]^{3+}$ $[\text{Cr(CN)}_6]^{3-}$
   d. Neutral complex - $[\text{Co(NH}_3)_3 \text{Cl}_3]$
Definitions of various terms used in coordination chemistry

2. Complex ion:
Complex ion is a charged species which is formed when a metal atom or ion is directly attached to a group of neutral molecules or ions. These group of neutral molecules or ions are called as ligands. For e.g.

a. \([\text{Cu(NH}_3\text{)}_4]^{2+}\) in which, neutral ammonia molecules are attached to \(\text{Cu}^{2+}\) ion.

b. \([\text{Co(NO}_2\text{)}_6]^{3-}\) in which, negative \(\text{NO}_2^{-}\) ions are attached to \(\text{Co}^{3+}\) ion.

c. \([\text{Co(NH}_3\text{)}_3 \text{Cl}_3]\) in which, both negative \(\text{Cl}^{-}\) ions and neutral ammonia molecules are attached to \(\text{Co}^{3+}\) ion.

3. Central atom:
The central metal atom in neutral coordination compound to which two or more neutral molecules are attached.

For e.g. \(\text{Ni(CO)}_4\), \(\text{Fe(CO)}_5\) etc.
Definitions of various terms used in coordination chemistry

4. **Central ion:**
   The central metal ion in a coordination compound to which two or more neutral molecules or ions are attached.
   For e.g. \([\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}\), the Co\(^{2+}\) is central ion to which both neutral ammonia molecules and negative Cl\(^{-}\) ions are attached.

5. **Ligand:**
   Any atom, ion or molecule having capacity to donate a electron pair to the central metal atom or ion is called as ligand or coordinating group. In a ligand the particular atom which donates electron pair is called as donor atom or donor site. As ligands donates electron pair are also called as Lewis bases. Ligands may be negative ions, positive ions or neutral molecules. Depending upon number of donor atoms in a ligand, ligands are classified as –
   a. Monodentate or unidentate ligands.
   b. Bridged ligands
   c. Polynodentate ligands.
Definitions of various terms used in coordination chemistry

- **Monodentate or unidentate ligands**: Monodentate ligand contains only one donor atom. e.g. \([\text{Ni (Cl)}_4]^{2-}\), \([\text{Fe(H}_2\text{O)}_6]\)

- **Bridging ligand**: It is the unidentate ligand which simultaneously coordinate with two or more metal ions. \([\text{Fe}_2(\text{Cl})_6]\)

- **Polydentate ligand**: They contain two or more donor atoms which coordinate to same central metal atom or ion. These ligands are also called as chelating ligands. The complex formed by these ligand is called as chelate. e.g. \([\text{M(H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}\)

Ligands can be –

- **Negative ions** – 1. Monatomic halides, F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\)
  2. Polyatomic ions, CN\(^-\), SCN\(^-\), NO\(_2^\)\(^-\)

- **Positive ions** – \(\text{N}_2\text{H}_5^+\), (\(\text{NH}_2\text{NH}_3^+\))

- **Neutral molecules** – \(\text{NH}_3\), \(\text{H}_2\text{O}\) etc.
Definitions of various terms used in coordination chemistry

- **Coordinate or dative bond:**
  Coordinate bond is defined as, the bond formed between two atoms when sharing of two electrons takes place from only one atom.
  - The atom which shares an electron pair is known as donor atom.
  - The atom which accepts the electron pair is known as acceptor.
  - The electron pair which is donated is called as lone pair.
  - The coordinate bond is shown by an arrow ( → ), pointing away from donor to the acceptor.

- **Coordination number (C.N.)**
  - The number of monodentate ligands that are directly attached to the central metal atom or ion is known as coordination number of that metal atom or ion.
  - When the coordinating groups are polydentate ligands the coordination number of the central metal atom or ion is the number of metal – ligand (M ← L) bonds formed in a complex compound.
Definitions of various terms used in coordination chemistry

- Common coordination numbers of shown by metal atom or ion are = 2, 3, 4, and 6.
- Light transition metals shows coordination numbers 4 and 6.
- Heavy transition metals shows coordination numbers > 6.
- Metal atom or ion may show different coordination numbers in different complexes. For e.g. \( \text{Fe}^{3+} \) ion shows C.N. 4 in \([\text{FeCl}_4]^–\) and 6 in \([\text{FeCl}_6]^{3–}\).
- Coordination numbers of some common metal ions are given in following table -

<table>
<thead>
<tr>
<th>Ion</th>
<th>C.N.</th>
<th>Complex Ion</th>
<th>Ion</th>
<th>C.N.</th>
<th>Complex Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^+)</td>
<td>2</td>
<td>([\text{Cu (NH}_3]_2]^+)</td>
<td>Ni(^{2+})</td>
<td>4</td>
<td>([\text{Ni (Cl)}_4]^{2–})</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>2</td>
<td>([\text{Ag (CN)}_2]^–)</td>
<td>Ni(^{2+})</td>
<td>6</td>
<td>([\text{Ni F}_6]^{4–})</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>4</td>
<td>([\text{Zn (NH}_3]_4]^{2+})</td>
<td>Pt(^{2+})</td>
<td>4</td>
<td>([\text{Pt (NH}_3]_4]^{2+})</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>4</td>
<td>([\text{Cu (NH}_3]_4]^{2+})</td>
<td>Pt(^{4+})</td>
<td>6</td>
<td>([\text{Pt (NH}_3]_6]^{4+})</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>6</td>
<td>([\text{Co (H}_2\text{O)}_6]^{2+})</td>
<td>Fe(^{3+})</td>
<td>4</td>
<td>([\text{Fe (Cl)}_4]^–)</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>6</td>
<td>([\text{Cr (H}_2\text{O)}_6]^{3+})</td>
<td>Fe(^{3+})</td>
<td>6</td>
<td>([\text{Fe (H}_2\text{O)}_6]^{3+})</td>
</tr>
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