Unit - I

1. Co-ordination compounds

Introduction:

When solutions containing two or more salts are mixed in simple molecular proportions and are allowed to evaporate crystals of new compounds called *molecular or addition compounds* are got.

These are of two types.

i. Double salts.

ii. Co-ordination compounds.

Double salts are molecular compounds, which exist only in crystal lattice. They break down into their constituent compounds or ions when dissolved in water or in any other solvent. Their physical and chemical properties are the same as those of their constituents

E.g., i. Mohr's salt: $FeSO_4 (NH_4)_2SO_4 . 6H_2O$

ii. Potash alum: $K_2SO_4 Al_2 (SO_4)_3 . 24H_2O$ and

iii. Carnallite: $KCl.MgCl_2 . 6H_2O$.

Co-ordination compounds are molecular compounds. They retain their identities even when they are dissolved in water or in any other solvent. Their properties are entirely different from those of their constituents.

E.g., i. $[Ag (NH_3)_2Cl]$

ii. $[Ni (NH_3)_6]Cl_2$

1. Methods by which the presence of complex ions are detected in solution:

i. By cryoscopic measurements:

It is possible to calculate the number of particles in a solution by cryoscopic measurements like measurement of depression in freezing point etc. To find out whether a molecular compound is a double salt or a complex has been formed in a solution, we have to determine the number of particles in the solutions of the molecular compound. If the number of particles in the solution of the molecular compound is the same as the total number of particles of the constituents of the molecular compound then we conclude that a double salt has been formed. On the other hand if the number of particles in solution of the molecular compound is different from the total number of particles of the constituents of the molecular compound then we conclude that a complex has been formed.

For example :

i. Potash alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. Its solution showed the presence of 8 particles in solution, which is equal to the total number of particles of the constituents of potash alum, namely, K_2SO_4 and $Al_2(SO_4)_3$. So we conclude that potash alum is a double salt.

K_2SO_4	$\longrightarrow$	$2K^+ + SO_c^{2-}$	(3 particles)
$Al_2(SO_4)_3$	$\longrightarrow$	$2Al^{3+} + 3(SO_4)^{2-}$	(5 particles)
		Total	(8 particles)

ii. Potassium ferrocyanide is $K_4[Fe(CN)_6]$. Its solution showed the presence of only 5 particles in solution. This is different from the total number of particles of the constituents of potassium ferrocyanide namely 4KCN and $Fe(CN)_2$. So we conclude that a complex has been formed in solution.

4KCN	$\longrightarrow$	$4K^+ + 4CN^-$	(8 particles)
Fe (N)$_2$	$\longrightarrow$	$Fe^{2+} + 2CN^-$	(3 particles)
		Total	(11 particles)
$K_4[Fe(CN)_6]$	$\longrightarrow$	$4K^+ + [Fe(CN)_6]^{4-}$	(5 particles)

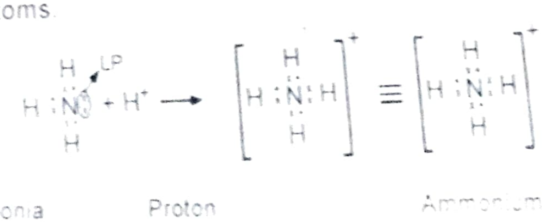
2 Precipitation methods:

Ions in complex compounds will not be precipitated by normal precipitating agents. For example Ni^{2+} will not be precipitated as NiS from its complex $K_2[Ni(CN)_4]$ by S^{2-} and Cl^- will not be precipitated as AgCl from $[Co(NH_3)_3Cl_3]$ by Ag^+.

Thus if normal precipitating agents fail to precipitate relevant ions from a solution of a molecular compound we can come to the conclusion that a complex has been formed in solution.

Co-ordinate bond:

A co-ordinate bond is formed between two elements when both the electrons required for the bond formation are contributed by one of the two combining atoms.



LP = Lone pair of electrons

Explanation:

Let us consider the formation of amm
nitrogen atom contains a lone pair of electro
sharing an electron each with three hydrog
there are no electrons. So the hydrogen ion a
from the nitrogen atom of the ammonia a
formation H^+ attains helium configuration.
and H is called a *Co-ordinate bond*. Such
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combining atom contributes one electron

However after the formation, there is
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called the *acceptor* atom. In our examp
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1. The nuclei of co-ordinate compo
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2. The co-ordinate compounds ar
of them are soluble in organic
3. They show stereo isomerism.
4. The co-ordinate compounds lie
compounds in their volatility.
5. These compounds have highe
and higher viscosity as comp
6. The co-ordinate compounds
ionise and are poor conduct

Co-ordination compounds:

Co-ordination compounds a
or ion, usually a metal, surroun
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Explanation:

Let us consider the formation of ammonium ion. In ammonia, the nitrogen atom contains a lone pair of electrons after completing its octet by sharing an electron each with three hydrogen atoms. In a hydrogen ion, there are no electrons. So the hydrogen ion accepts the lone pair of electrons from the nitrogen atom of the ammonia and forms a bond. By this bond formation H^+ attains helium configuration. Such a bond formed between N and H is called a *Co-ordinate bond*. Such a bond is also known as *dative bond or semipolar bond*. (We know covalent bond is formed also by sharing a pair of electrons between two combining atoms, but here, each of the combining atom contributes one electron for sharing)

However after the formation, there is no difference between a co-ordinate bond and a covalent bond. Thus, all the four bonds in NH_4^+ ion are identical.

The atom , which gives a pair of electrons for bond formation is called *donor* atom; while the atom, which accepts a lone pair of the electrons, is called the *acceptor* atom. In our example N is the donor atom; the H^+ is the acceptor atom.

Characteristics of co-ordinate compounds:

The properties of co-ordinate compounds are very much similar to those of covalent compounds in many respects.

1. The nuclei of co-ordinate compounds are held firmly by the electrons and therefore they do not form ions in water.
2. The co-ordinate compounds are sparingly soluble in water. A number of them are soluble in organic solvents.
3. They show stereo isomerism.
4. The co-ordinate compounds lie in between electrocovalent and covalent compounds in their volatility.
5. These compounds have higher melting points and higher boiling points and higher viscosity as compared with the covalent compounds.
6. The co-ordinate compounds, being partly covalent in nature, do not ionise and are poor conductors of electricity.

Co-ordination compounds:

Co-ordination compounds are compounds that contain a central atom or ion, usually a metal, surrounded by a cluster of ions or molecules, bound b y co-ordinate bonds. There are also known as metal complexes or complexes. The complex tends to retain its identity even in solution.

When solutions of $Fe(CN)_2$ and KCN are mixed together and evaporated, potassium ferrocyanide, $K_4[Fe(CN)_6]$ is obtained. This in aqueous solution does not give test for Fe^{2+} and CN^- ions but answers the test for K^+ ion and ferrocyanide ion $[Fe(CN)_6]^{4-}$.

$$Fe(CN)_2 + 4KCN \longrightarrow \underset{\text{Complex Salt}}{K_4[Fe(CN)_6]} \rightleftharpoons 4K^+ + \underset{\text{Complex ion}}{[Fe(CN)_6]^{4-}}$$

Thus in the molecular compound like $K_4[Fe(CN)_6]$, the individual compounds lose their identity. *Such molecular compounds are called co-ordination (or complex) compounds.*

Complex ion :

Definition: A complex ion is an electrically charged radical, which is formed by the union of a simple cation with one or more neutral molecules or simple ions.

Example: $Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$

$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$

Central ion:

Definition: In a co-ordination compound, the central metal ion, which is attached to various ions or neutral molecules, is called the central ion.

Example: In $[Fe(CN)_6]^{4-}$, Fe^{2+} ion is the central ion. Similarly in $[Cu(NH_3)_4]^{2+}$, Cu^{2+} ion is the central ion.

Ligand: *Definition:* The neutral molecules or ions (usually anions), which are attached with the central metal ions, are called ligands.

Example: In the complex ion, $[Fe(CN)_6]^{4-}$, Fe^{2+} ion is the central metal ion and the six CN^- ions are the ligands.

In most of complex as a ligand acts as a donor of electrons to the central metal ion, which acts as the acceptor. In a ligand, the particular atom, which actually donates the electron pair to the metal atom, is called the donor atom.

Example: In CN^- ion nitrogen acts as the donor atom.