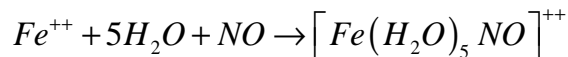
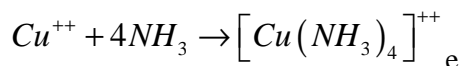


CO-ORDINATION COMPOUNDS

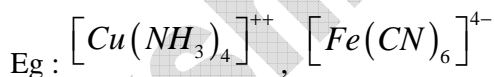
Characteristics of complex compounds:

- * A new ion formed by the combination of a simple cation with anions or neutral molecules or even cations is known as a complex ion.



Ligands:

- * An ion or a molecule which can donate pair of electrons to a metal atom or a metal ion and can form dative bond is called ligand.
- * Ligands are of three types
Negative ligands Eg : X^{-} , SO_4^{-2} , CN^{-} , $C_2O_4^{-2}$; etc.,
Neutral ligands Eg: H_2O , NH_3 etc.,
Positive ligands Eg : NO^{+}
- * A molecule or ion which donates only one pair of electrons is called monodentate ligand. The monodentate ligand is said to have only one co-ordinating center.
Eg : CN^{-} , HO^{-} , NH_3 , H_2O
- * A molecule or ion which donates two lone pairs of electrons is called bidentate ligand. The bidentate ligand will have two co-ordinating centers.
Eg: 1) Oxalate ion 2) Glycinate ion 3) Ethylene diamine
- * A Polydentate ligand will have more than two co-ordinating centers.
Eg : EDTA is a hexa dentate ligand.
- * The central metal atom or metal ion and the ligands put together is called the co-ordination sphere. While writing the formula of a complex the co-ordination sphere is enclosed in square brackets.



Co-ordination number:

- (i) The number of co-ordinate covalent bonds formed by the ligands with the central metal ion in a complex is called co-ordination number.
- (ii) The co-ordination number is generally 2, 4 (or) 6, occasionally 8 (in Osmium complexes).
- (iii) It is equal to the number of monodentate ligands which are bound to central metal atom or ion through a dative bonds.
- * The transition metal ions form co-ordinate compounds because
 - i) They have small size.
 - ii) They have high nuclear charge
 - iii) They have vacant orbitals
 - iv) They can accept lone pairs of electrons.

- * The ions that lie outside the square bracket are only ionisable and are released as free ions in solutions.
- * $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in aqueous solutions gives four ions. They are $[\text{Co}(\text{NH}_3)_6]^{3+}$ and three .
- * The central metal atom generally exhibits +ve oxidation state except in metal carbonyls in which it carries zero oxidation state.

Werner theory VBT and shapes of co-ordination compounds: Valence Bond Theory, Crystal Field Theory

- * According to Werner (father of Co-ordination chemistry) transition metals possess two types of valencies.
 - a) Primary valency (Ionisable valency)
 - b) Secondary valency (non ionisable valency)
- * **Primary valency (Ionisable valency) :**
 - i) It is satisfied by only anions.
 - ii) It is referred to as oxidation state.
 - iii) It is represented by dotted lines while writing the structure of complex.
- * **Secondary valency (Non-Ionisable valency):**
 - i) It is satisfied by anions or neutral molecules or rarely with cations.
 - ii) The groups satisfying secondary valencies are called ligands.
 - iii) The number of secondary valencies is called coordination number.
 - iv) It is represented by solid lines while writing the structure of the complex.
- * In some complexes the same groups satisfies both primary and secondary valencies.
- * The ligands are directed in space around the central metal atom in different ways. This leads to a definite geometry to the molecule.
- * The number of ions given by some complexes :
 - i) $\text{CoCl}_3 \cdot 6\text{NH}_3$ gives $[\text{Co}(\text{NH}_3)_6]^{3+}$ & 3 Cl^-
 - ii) $\text{CoCl}_3 \cdot 5\text{NH}_3$ gives $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ & 2 Cl^-
 - iii) $\text{CoCl}_3 \cdot 4\text{NH}_3$ gives $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ & 1 Cl^-
 - iv) $\text{CoCl}_3 \cdot 3\text{NH}_3$ is not ionised
- * By adding excess of AgNO_3 solution to one mole each of the above complexes the number of moles of AgCl formed is 3, 2, 1, 0 respectively.
- * When $\text{CoCl}_3 \cdot 5\text{NH}_3$ is added to silver nitrate in aqueous solutions, two moles of AgCl is precipitated as one chloride ion is in the co-ordination sphere and two chloride ions are free outside.
- * Shape of the complex species depends on its co-ordination number.

CO-ORDINATION NUMBER SHAPE OF THE COMPLEXES

2	Linear
3	trigonal planar
4	tetrahedral or square planar

- | | |
|---|--|
| 5 | square pyramidal or trigonal bipyramidal |
| 6 | octahedral |
| 7 | pentagonal bi pyramidal |

Defects in Werner's theory:

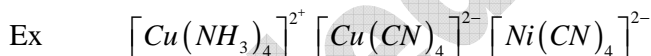
- * This theory does not relate the electronic configuration of metal with the formation of the complex.
- * It is known now that the metal tries to acquire the nearest inert gas configuration during the formation of complex

VBT and shapes of co-ordination compounds:

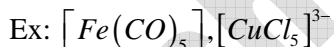
Valence Bond Theory:

According to this theory

- * The vacant orbitals of central metal atom hybridise and overlap with the orbitals of the ligands each containing lone pair of electrons.
 - * A ligand contains at least one lone pair of electrons which can be used for bonding with the central metal ion.
- A complex formed will be paramagnetic if unpaired electrons are present. If unpaired electrons are not present then the complex will be diamagnetic.
- The electrons in the metal orbitals may undergo regrouping even against Hund's rule.
- * Ligand orbitals overlap the vacant metal orbitals to form a strong co-ordinate covalent bond to the extent possible.
 - * sp^3 hybridisation: The structure of the complex is tetrahedral. $[Ni(CO)_4], [NiCl_4]^{2-}$
 - * dsp^2 hybridisation: The Structure of the complex is square planar.

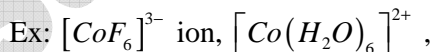


- * dsp^3 hybridisation: The Structure of the complex is trigonal bipyramid.



Inner and outer orbital octahedral complexes.

- * In an inner **orbital complex**, inner (n-1)d orbitals and the outer ns and np orbitals hybridise.
- * Inner orbital complexes are also called spin paired or low spin or strong field or covalent complexes.
- * In an outer **orbital complex**, outer ns, np and nd-orbitals hybridise.



The hybridisation involved is sp^3d^2 .

- * Outer orbital complexes are also called spinfree or high spin or weak field or low field or ionic complexes.
- * The spin only magnetic moment of the complex can be calculated by the formula

$$\mu_s = \sqrt{n(n+2)} \text{ BM}$$

(= number of unpaired electrons)

arrangements are known as isomers. The coordination compounds show the following types of isomerism.

- * According to Valence Bond theory :
 - i) the central ion furnishes the orbitals for hybridization.
 - ii) the hybridized orbitals overlap with the orbitals of those ligands which can donate electron pairs,
 - iii) if the complex contains unpaired electrons, it is paramagnetic in nature.
- * The commonly found spatial arrangements in coordination compounds are square planar, trigonal - bipyramidal or square - pyramidal and octahedral.
- * The geometry of the coordination entity can be predicted if its magnetic behaviour is known.
- * For square planar geometry, dsp^2 hybrid orbitals are required.
- * For trigonal - bipyramidal or square - pyramidal geometry, dsp^3 hybrid orbitals are required.
- * For octahedral geometry, d^2sp^3 hybrid orbitals are required.

ISOMERISM IN COMPLEXES:

- * Compounds which have the same molecular formulae but differ in their structural arrangements are known as isomers. The coordination compounds show the following types of isomerism.

a) Ionisation Isomerism :

- This type of isomerism occurs when the counter ion in a coordination compound is itself a potential ligand. As a result the counter ions and the ligand can change their places. The following pairs of compounds are examples of ionization isomers.
- The ionization isomers produce different ions in solution, e.g., an aqueous solution of $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ gives white ppt. of BaSO_4 with BaCl_2 confirming the presence of free SO_4^{2-} ions in solution. But a solution of $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ does not give a positive test with BaCl_2 .

- b) **Hydrate Isomerism** is a special form of ionization isomerism. It occurs when water is a part of coordination entity or is outside it. For example there are three isomers of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$

$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Violet
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$	pale green
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$	dark green

- c) **Linkage Isomerism** : This type of isomerism occurs in those complex compounds which contain ambidentate ligands such as SCN^- , CN^- , NO_2^- , ETC. these ligands have two donor atoms. However, at a time only one is linked to the central metal atom of the complex, e.g.,
 $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$
 pentaamminenitrito-N-cobalt (III) chloride
 Pentaamminenitrito-O-cobalt(III) Chloride

e) **Geometrical Isomerism :**

- It is also known as **cis-trans isomerism**.
- It is shown by complexes in which the coordination entities have the general formula, $[Ma_2b_2]$ and $[Ma_2b_4]$ where M is the central metal atom/ion; a and b are donor atoms (ligands).
- $[Ma_2b_2]$ coordination entities are square planar whereas $[Ma_2b_4]$ are octahedral.
- In cis-isomer the same ligands are on the same side of the coordination polyhedron whereas in trans-isomers they are on the opposite side. For example.

Geo metric isomers of square planar type $[Ma_2b_4]$

f) **Optical Isomerism :**

- Isomers which are not superimposable on their mirror images are known as **optical isomers**. They are also known as enantiomorphs or enantiomers.
- The optical isomers of a compound have identical physical and chemical properties but they rotate the plane of polarized light either to the left or to the right.
- The optical isomers which rotate the plane of polarized light to the left as laevorotatory (l or -). The isomers which rotate the plane of polarized light are known as **dextrorotatory** (d or +).
- A **racemic mixture** is a mixture of equal parts of the laevorotatory isomer and the dextrorotatory isomer of the same substance.
 - Optical isomerism is exhibited by octahedral complexes having bidentate ligands.