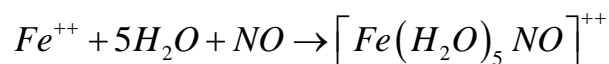
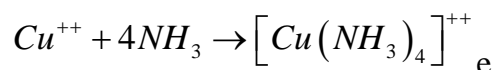


Co-Ordination Compounds

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

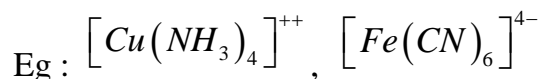
- * A molecule or ion which donates two lone pairs of electrons is called bidentate ligand. The bidentate ligand will have two co-ordinating centers.

Ex: 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

- The number of co-ordinate covalent bonds formed by the ligands with the central metal ion in a complex is called co-ordination number.
- The co-ordination number is generally 2, 4 (or) 6, occasionally 8 (in Osmium complexes).
- It is equal to the number of monodentate ligands which are bound to central metal atom or ion through a dative bond.

- * The transition metal ions form co-ordinate compounds because

- They have small size.
- They have high nuclear charge
- They have vacant orbitals
- 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.

- * $[Co(NH_3)_6]Cl_3$ in aqueous solutions gives four ions. They are $[Co(NH_3)_6]^{3+}$ 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 $[\text{Co}(\text{NH}_3)_6]^{3+}$ & 3Cl^-
- ii) $\text{CoCl}_3 \cdot 5\text{NH}_3$ gives $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{+2}$ & 2Cl^-
- iii) $\text{CoCl}_3 \cdot 4\text{NH}_3$ gives $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ & 1Cl^-
- 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, and 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.

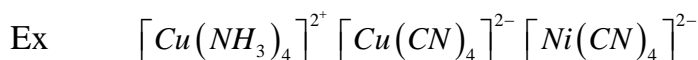
A complex formed will be paramagnetic if unpaired electrons are present. If unpaired electrons are not present then the complex will be diamagnetic.

The electrons in the metal orbitals may undergo regrouping even against Hund's rule.

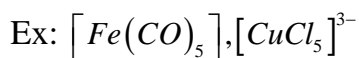
* Ligand orbitals overlap the vacant metal orbitals to form a strong co-ordinate covalent bond to the extent possible.

* 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.

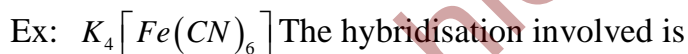


* dsp^3 hybridisation: The Structure of the complex is trigonal bipyramid.



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.

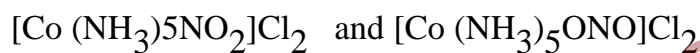
a) Ionisation Isomerism

- 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 $[Co(NH_3)_5Br]SO_4$ gives white ppt. of $BaSO_4$ with $BaCl_2$ confirming the presence of free SO_4^{2-} ions in solution. But a solution of $[Co(NH_3)_5SO_4]Br$ 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,



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, $[\text{Ma}_2\text{b}_2]$ and $[\text{Ma}_2\text{b}_4]$ where M is the central metal atom/ion; a and b are donor atoms (ligands).
- $[\text{Ma}_2\text{b}_2]$ coordination entities are square planar whereas $[\text{Ma}_2\text{b}_4]$ 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 $[\text{Ma}_2\text{b}_4]$

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.**