

### Werner's theory:

- Every complex compound has a central metal ion or atom.
- The metal in a complex exhibits two types of valencies
  - a) Primary valency
  - b) Secondary valency
- Central metal ion/ atom forms dative bonds with electron pair donors or ligands.

#### Primary valency or Ionizable valency:

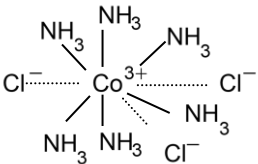
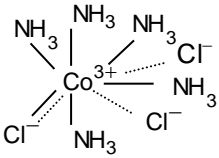
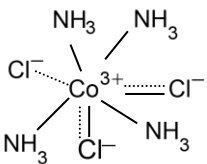
- It is equal to oxidation state of metal ion
- It is satisfied by negative ions. The groups bound by primary valency will ionise.
- These are held by electrostatic attraction by the metal ion, like ionic bond.
- These group are connected to the metal- ions, shown by broken line in the formula, or shown outside the square bracket.
- These are non-directional.

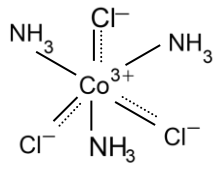
#### Secondary valency or non-ionizable valency:

- Secondary valency is equal to co-ordination number or number of coordinate covalent bonds.
- Secondary valency may be satisfied by neutral groups  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  or negative ions.  $\text{CN}^-$ ,  $\text{Cl}^-$  or even positive ion like  $\text{NO}^+$ .
- The groups satisfying secondary valency are called ligands.
- The number of unidentate ligands around the metal is known as coordination number.
- Ligands donate lone pairs to the metal atom or ion and form coordinate covalent bonds.
- Ligands act as Lewis bases and metal ion/atom acts as Lewis acid.
- Ligands are connected to the metal by thick line or shown inside the square bracket.
- Some ligands may satisfy both primary and secondary valences and they do not ionize.
- Ligands are directed in space around the metal in a symmetric order and acquired a specific shape. Secondary valency is directional in nature and it determines the shape of the complex.

No of ligands	Shape of complex
2	Linear
3	Trigonal planar
4	Tetrahedral (or) Square planar
5	Square pyramidal (or) Trigonal bipyramidal
6	Octahedral
7	Pentagonal bipyramidal

Example:

Complex	No of ligands (or) Coordination no.	Werner Structure	
1. $\text{CoCl}_3 \cdot 6\text{NH}_3$	6	Octahedral – Three $\text{Cl}^-$ ions satisfy primary valency – Six $\text{NH}_3$ molecules satisfy secondary valency – No. of ions in solution = 4 – $\text{AgCl}$ molecules precipitated on adding excess of $\text{AgNO}_3 = 3\text{AgCl}$	
2. $\text{CoCl}_3 \cdot 5\text{NH}_3$	6	Octahedral – 2 $\text{Cl}^-$ satisfy primary valency – One $\text{Cl}^-$ satisfies both primary and secondary valency – 5 $\text{NH}_3$ molecules satisfy secondary valency – No. of ions in solution = 3 – $\text{AgCl}$ molecules precipitated on adding excess of $\text{AgNO}_3 = 2$	
3. $\text{CoCl}_3 \cdot 4\text{NH}_3$	6	Octahedral – 2 $\text{Cl}^-$ & 4 $\text{NH}_3$ molecules satisfy both primary and secondary valency – One $\text{Cl}^-$ satisfies only	

		primary valency – No. of ions in solution = 2 – AgCl molecules precipitated = 1	
4. $\text{CoCl}_3$ $3\text{NH}_3$	6	Octahedral – The three $\text{Cl}^-$ ions satisfy both primary and secondary valencies and $3\text{NH}_3$ molecules satisfy secondary valency – No. of species in solution = 1 – AgCl molecules precipitated by adding excess of $\text{AgNO}_3$ is zero.	

#### Defects in Werner's theory:

- This theory does not explain the role of the electronic configuration of metal in forming complexes.
- It is known now in through coordinate bond formation that the metal tries to acquire the nearest inert gas configuration during the formation of complex.
- This theory does not explain the reason for the color of the complex.
- This theory does not explain the magnetic behavior of complex.