B.Sc. (Honours) Part-II

Paper-IIIB

Topic: Werner's postulates

UG

Subject-Chemistry

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Werner's postulates

Postulates of Werner's theory

1) Every metal atom has two types of valencies

i) Primary valency or ionisable valency

ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature where as the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called

coordination compounds.

In brief:-

Metals exhibit two types of valencies in the formation of complexes. These are primary valencies and secondary valencies.

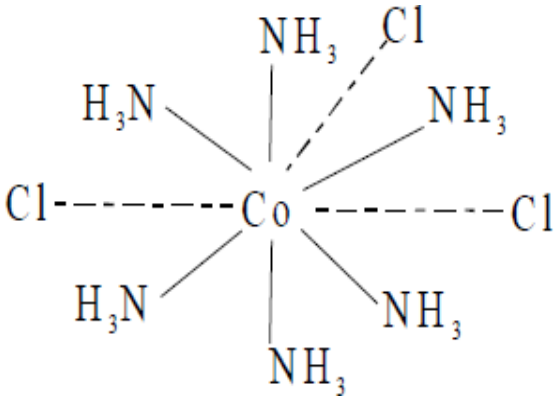
1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.

2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Examples of Werner's representation

1. Werner represented the first member of the series $[Co(NH_3)_6]Cl_3$ as follows.

In this representation, the primary valency (dotted lines) are satisfied by the three chloride ions. The six secondary valencies (solid lines) are satisfied by the six ammonia molecules.



2. $CoCl_3.5NH_3$ complex:

In this compound, cobalt has the coordination number of 6. However, we see that the number of NH_3molecule decreases to 5. The chloride ion occupies the remaining one position. This chloride ion exhibits the dual behaviour as it has primary as well as secondary valency.

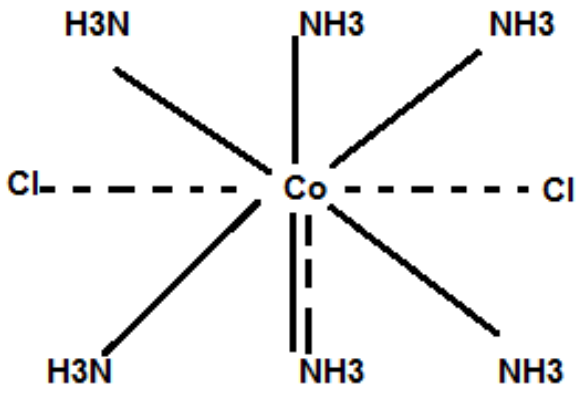


fig. structure of CoCl3.5NH3 complex
Number of Cl- ions precipiated = 2
total numbers of ions = 3

3) $CoCl_3.4NH_3$ complex:

In this compound, two chloride ions exhibit the dual behaviour of satisfying both Primary and Secondary Valencies. This compound gives a precipitate with silver nitrate corresponding to only one Cl^- ion and the total number of ions, in this case, is 2. Hence, we can formulate it as $[CoCl_2(NH_3)_4]Cl$.

Defects of Werner's theory

Werner's theory describes the structures of many coordination compounds successfully. However, it does not explain the magnetic and spectral properties.

Like all the major theories, Werner's Theory was not free from limitations. The common limitations of the theory are:

- It could not explain the inability of all elements to form coordination compounds.
- The Werners theory could not explain the directional properties of bonds in various coordination compounds.
- It does not explain the colour, the magnetic and optical properties shown by coordination compounds.