

SUBJECT - CHEMISTRY

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Date - 06.05.20

CLASS - BSc(Hons) PART- II

PAPER - III

GROUP - B

TOPIC : WERNER'S THEORY OF CO-ORDINATION COMPOUNDS.

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The main postulates of this theory are as follows:

(1) Metals possess two types of valency, so called (a) primary or principal or ionisable valency and (b) Secondary or non-ionisable valency.

(a) Primary valencies: Primary valencies are those which a metal exercises in the formation of its simple salts. Thus primary valencies of Pt, Co, Cu and Ag in the formation of their simple salts, e.g. $PtCl_4$, $CoCl_3$, $CuSO_4$ and $AgCl$ are 4, 3, 2 and 1 respectively.

These days primary valency is referred to as oxidation state.

(b) Secondary valencies: Secondary valencies are the valencies which a metal cation exercises towards a neutral molecule or an anion in the formation of complex ions. The secondary valency is also termed as the co-ordination number of the metal cation under consideration.

Thus, co-ordination number gives the number of neutral molecules or anions which may be linked to the metal cation in the formation of its complex. For example: In $[Pt(NH_3)_6]Cl_4$, $[Co(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]Cl$, the secondary valencies are 6 for Pt^{4+} , 4 for Co^{3+} , 2 for Ag^+ cations respectively.

(2) Primary valencies are satisfied by negative ions whereas secondary valency may be satisfied by either negative groups or neutral molecules.

(3) Secondary valencies are directed in space and hence such compounds are capable of exhibiting the phenomenon of isomerism.

Determination of the structure of a complex on the basis of Werner's theory: on the basis of his theory, Werner assigned to $\text{CoCl}_3 \cdot 6\text{NH}_3$, the structural formula given in fig(1)

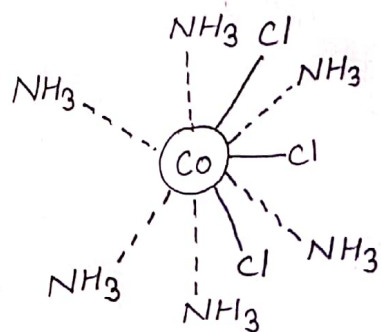


Fig. (1)

In this formula, six ammonia molecules are attached to the Cobalt by Secondary valencies whereas three Chlorine atoms are held to the Cobalt by means of primary valencies. primary valencies are designated by Solid lines and Secondary valencies by dotted lines.

* Experimental evidence in support of Werner's theory: A large number of complexes were studied by Werner and other workers. Werner used molar conductance values to determine the number of ions per molecule thus assigning groups to the first co-ordination sphere. Chemical methods like precipitation of Cl^- by AgNO_3 to determine the number of ionisable Cl^- ions per molecule were also used. example.

(1) Cobalt(III) ammine complexes: When an aqueous Cobalt(II) chloride is treated with ammonia and then oxidised by air, the following six compounds are isolated.

(a) Lureo cobalt chloride, $\text{CoCl}_3 \cdot 6\text{NH}_3$: This is an orange yellow crystalline compound. Its chief characteristics are:

(1) Treatment of this compound in the solid state with sulphuric acid liberates all the chlorine as HCl and leaves sulphate, $\text{Co}_2(\text{SO}_4)_3 \cdot 12\text{NH}_3$. Treatment of its solution with AgNO_3 , precipitates all the chlorines immediately. Thus the bonding between Cobalt and chlorine is purely ionic.