

But some metal ions may exhibit different co-ordination no. in some cases.

e.g: The co-ordination no. of Ni^{2+} is six in $[Ni(NH_3)_6]^{2+}$ and four in $K_2[NiCl_4]$

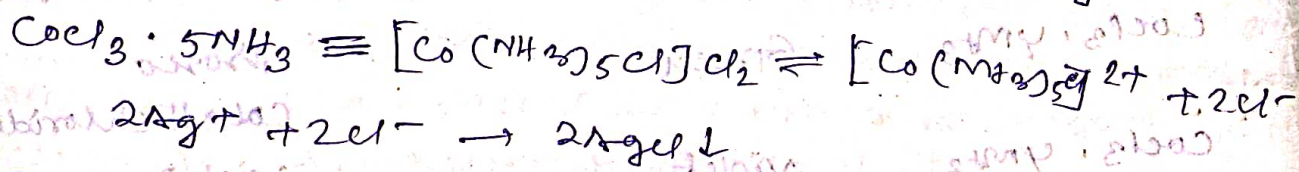
(3) The ligands around the central metal ion have definite arrangement in space.
e.g: octahedral for co-ordination no. = 6 and tetrahedral or square planar for co-ordination no. = 4 while linear for co-ordination no. = 2.

(4) The attachment betn the metal and the species which satisfy both the valencies is shown by a combine solid. broken line (— ···—).

Explanation of Werner's Co-ordination Theory:

In the complex compound $CoCl_3 \cdot 5NH_3$, the primary valency of Co atom in this compound is equal to three (3) and is satisfied three Cl^- ions. The attachment of these ions with Co^{III} ion is shown by broken line.

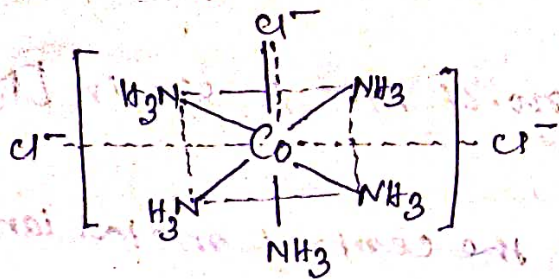
The treatment of this amine with the aqueous solution of $AgNO_3$ precipitates only 2 Cl^- ions as $AgCl$.



The precipitation of only 2 Cl^- ions indicates that, 2 Cl^- ions are outside the co-ordination sphere and the remaining one Cl^- ion and five NH_3 molecules are present inside the co-ordination sphere. The structure of $CoCl_3 \cdot 5NH_3$ can be written as $[Co(NH_3)_5Cl]Cl_2$. This str. shows that the secondary valency of Co atom (C.N=6) is satisfied by one Cl^- ion and 5 NH_3 molecules placed inside the co-ordination sphere.

The attachment of one Cl^- ion and 5 NH_3 molecules to Co atom is shown by solid lines.

The structure of the above compound is shown in figure below:



figs str. of $[Co(NH_3)_5Cl]Cl_2$ molecule.

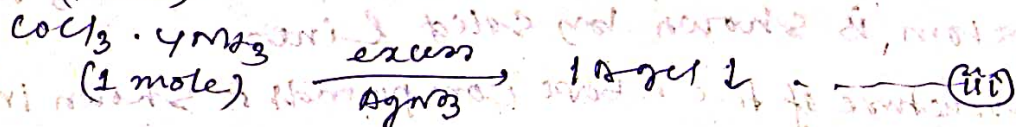
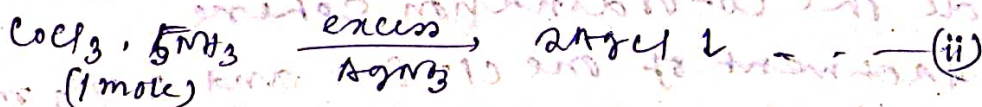
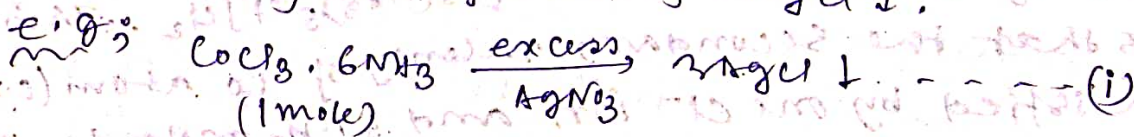
In this structure, one Cl^- ion is attached with Co atom by a combine solid-broken line (---|---), since this ion satisfy both primary as well as secondary valency of Co atom.

Experimental evidences of favours of Werner's Co-ordination theory.

How amine complexes of $CoCl_3$ has been discovered by Werner and named according to their colours;

<u>Complex</u>	<u>Colour</u>	<u>early name</u>
$CoCl_3 \cdot 6NH_3$	yellow	Amo Cobaltichloride
$CoCl_3 \cdot 5NH_3$	purple	Purpuro Cobaltichloride
$CoCl_3 \cdot 4NH_3$	Green	Proscio Cobaltichloride
$CoCl_3 \cdot 4NH_3$	violet	Violeo Cobalti chloride

The reactivities of the Cl^- ions in these above compounds differ considerably. Addition of excess $AgNO_3$ soln to one mole of each complex produced different amounts of precipitated of $AgCl \downarrow$.



The rxn (iii) occurs for both the proseo and violeo complexes. The correlation betn the no. of NH_3 molecules present and the no. of equivalents of AgCl precipitated.

In the series of complexes, $\text{Co}(\text{III})$ exhibits a constant co-ordination no. of six. As NH_3 molecules are removed they are replaced by Cl^- ions. These Cl^- ions are not free. They are co-valently bound to the $\text{Co}(\text{III})$ ion. Werner thus formulated these four salts as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ (proseo and violeo).

Werner studied the conductivities of these compounds in solution. Conductivities of these above complexes co-related and corresponded to those of 1:3, 1:2 and 1:1 electrolytes respectively supporting the above formulation of the complexes.

Werner characterised two isomers proseo and violeo complexes corresponding to the formula $\text{CoCl}_3 \cdot 4\text{NH}_3$ in which co-ordination no. of Co^{III} is six. Hence three possible structures of these complex are planar hexagon, trigonal prism and octahedral. Three isomers are expected from the former two arrangements while only two from the later. Only two isomers are isolated by Werner for the complex $\text{CoCl}_3 \cdot 4\text{NH}_3$. These fact lead Werner to suggest octahedral arrangements of ligand around the metal ion in these complexes and also in other complexes of co-ordination no. equal to six.

8. Molar conductance values of the complexes $\text{PtCl}_4 \cdot 2\text{NH}_3$, $\text{PtCl}_4 \cdot 3\text{NH}_3$ and $\text{PtCl}_4 \cdot 6\text{NH}_3$ are '0', '97' and '520' ohm⁻¹cm² respectively. Rationalised these data in the light of Werner's co-ordination theory.

Molar conductance data indicates that the 1st, 2nd and 3rd complexes behave as non-electrolyte, uni-univalent (1:1) and uni-tetravalent (1:4) electrolyte respectively. According to Werner's theory the Cl^- ions

may satisfy either separately or simultaneously both the primary and secondary valencies of central metal ion. But the neutral NH_3 molecule can satisfy only the secondary valency. The co-ordination no. of Pt^{4+} is six in all the three complexes. Hence in the 1st complex, 4Cl^- ions and 2NH_3 ligands will satisfy the co-ordination no. of Pt^{4+} . The 4Cl^- ions will satisfy the primary valency. In the 2nd complex, 3NH_3 molecules and 3Cl^- ions will satisfy the secondary valency of Pt^{4+} ion while 4Cl^- ions satisfy the primary valency of Pt^{4+} ion. In the 3rd complex, 6NH_3 molecules satisfy co-ordination no. of Pt^{4+} ion and 4Cl^- ions satisfy the primary valency of the Pt^{4+} ion. According to Werner's co-ordination theory, primary valencies are ionisable and secondary valencies are non-ionisable. The second sphere of co-ordination no. (outer) consists of only ions which are held by electrostatic force of attraction. Hence these are completely ionisable. Ligands within the 1st sphere (inner sphere) are held to the central metal cation by co-ordinate bonds, hence are non-ionisable.

In this light of Werner's theory the complexes may be formulated as follows;

