THEORIES OF COMPLEX COMPOUNDS

Werner's Theory of Coordination Compounds

The geometries and properties of coordination compounds were first deduced by swiss chemist alfred werner in 1893, who was awarded the 1913 Noble prize in chemistry for his pioneering studies. This theory was put forward before the electron had been discovered by J.J.Thomson in 1896 and before the electronic theory of valency.

Postulates of This Theory

(1) In coordination compounds, metal exhibits two types of valencies—primary or ionizable valency (also called principle valency) and secondary or non-ionizable valency (also called auxiliary valency).

The combining power of a metal atom is divided into two spheres of attraction: The inner or the coordination sphere and the outer or the ionisation sphere.

The ionization sphere constitutes the entities which satisfy the primary valency of the metal. Hence it is also called primary sphere. The coordination sphere constitutes the entities which satisfy the secondary valency of the metal. Hence it is also called secondary sphere. In a complex compound, coordination sphere is represented by square bracket [ ] and the ionisation sphere is outside the coordination sphere as shown below:

$$\underbrace{[Co(NH_3)_6]}_{\substack{\text{Coordination sphere}\\ \text{or inner sphere}}}\quad\underbrace{Cl_3}_{\substack{\text{ionisation sphere}\\ \text{or outer sphere}}}$$

(2) Every metal has a fixed number of secondary valencies. The number of secondary valencies equals the number of ligand atoms coordinated to the metal. (i.e., coordination number).

(3) Primary valencies are satisfied by negative ions whereas secondary valencies may be satisfied by either neutral molecules or negative ions or in rare cases by positive ions.

(4) Metal ion has tendency to satisfying its both valences primary and secondary. Hence sometimes some anions satisfy both primary and secondary valences at same time.

According to modern concept of coordination compounds, the species satisfying the secondary valency are called ligands. And the primary valency is oxidation state of central metal ion.

The charge on the complex ion varies with the number of negative ions which may enter into the coordination sphere to replace neutral molecules. Consequently, the total no. of ions also varies. Consider for example, the complexs of Co(III) incorporating ammonia molecules and Cl^- as ligands and having coordination number of six. Replacement of NH_3 by Cl^-, changes the charge on complex ion and total no. of ions.

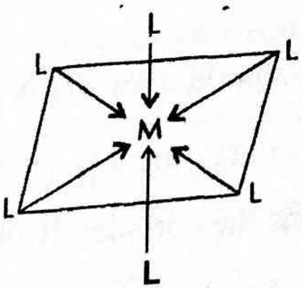
Compound	No. of Charges on Complex Ion	No. of Ions		
		Cation	Anion	Total
$CoCl_3 \cdot 6NH_3$ or $[Co(NH_3)_6]Cl_3$	+3	1	3	4
$CoCl_3 \cdot 5NH_3$ or $[Co(NH_3)_5Cl]Cl_2$	+2	1	2	3
$CoCl_3 \cdot 4NH_3$ or $[Co(NH_3)_4Cl_2]Cl$	+1	1	1	2

(5) The complex ion commonly exists as a positive ion.

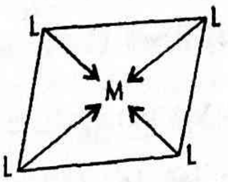
(6) Primary valencies are non directional whereas the secondary valencies are directional. The secondary valencies have a fixed orientation in space around the metal.

The number of species satisfying the secondary valency gives a definite geometry to the coordination compound. For example, when C.N. is 2, 3, 4 or 6 the geometry of the coordination compound would be linear, trigonal planar, tetrahedral or square planar and octahedral repectively. If a complex has a C.N. six, then irrespective of the nature of metal ion and ligand, the secondary valencies would be directed towards the corner of octahedron.

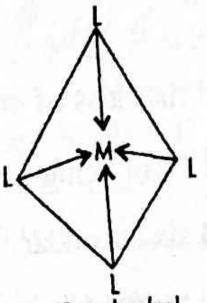
Likewise, when C.N. is 4, the geometry of the coordination compound is either tetrahedral or square planar. If the geometry is tetrahedral, the secondary valencies are directed towards the corners of square planar. If the geometry is square planar, the secondary valenceis are directed towards the corners of tetrahedron. If the geometry is square planar, the secondary valenceis are directed towards the corners of the square.



Octahedral geometry

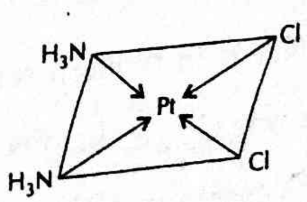


Square planar geometry

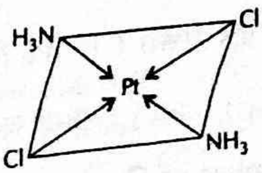


Tetrahedral geometry

The directional nature of secondary valencies makes possible the existence of stereoisomers amongst norganic complexes. Thus the complex, $PtCl_2 \cdot 2NH_3$ exists in two geometrical isomeric forms: *cis* and *trans*. Their structures may be represented as follows.

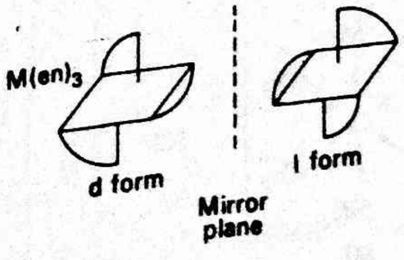


cis



trans

The isomeric forms arise because the four coordinating groups (two ammonias and two chlorines), are directed at the corners of a square. ather than having random orientations around platinum, are directed at the corners of a square.



More recently, with a bidentate ligand such as ethylenediamine (1, 2-diaminoethane), two optically active isomers have been found.

In a similar way, Werner studies a range of complexes which included $[Pt^{II}(NH_3)_2Cl_2]$ and $[Pd^{II}(NH_3)_2Cl_2]$. The coordination number is 4, and the shape could be either tetrahedral or square planar. Werner was able to prepare two different isomers for these complexes. A tetrahedral complex can only exist in one form, but a square planar complex can exist in two isomeric forms. This proved these complexes are square planar rather than tetrahedral.

(7) When a coordination compound undergoes ionisation in aqueous solution, the species satisfying the primary valency can be obtained in their free state whereas the species satisfying the secondary valency can not be obtained in free state.

Werner treated cold solutions of a series of coordination complexes of Co(III) with NH_3 and Cl^- with an excess of silver nitrate, and weighed the silver chloride precipitated. The stoichiometries of complex–AgCl formed were as follows:

$$CoCl_3 \cdot 6NH_3 \rightarrow 3AgCl$$
$$CoCl_3 \cdot 5NH_3 \rightarrow 2AgCl$$
$$CoCl_3 \cdot 4NH_3 \rightarrow 1AgCl$$

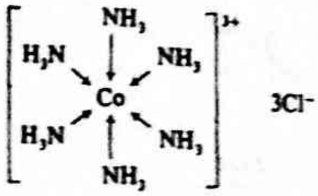
Werner deduced that in $CoCl_3 \cdot 6NH_3$ the three chlorines acted as primary valencies, and the six ammonias as secondary valencies. In modern terms the complex is written $[Co(NH_3)_6]Cl_3$. The three Cl^- are ionic and hence are precipitate as AgCl by $AgNO_3$. The six NH_3 ligands form coordinate bonds to Co^{3+}, forming a complex ion $[Co(NH_3)_6]^{3+}$.

Werner deduced that loss of one NH_3 from $CoCl_3 \cdot 6NH_3$ should give $CoCl_3 \cdot 5NH_3$, and at the same time one Cl^- changed from being a primary valency to a secondary valency. Thus this complex has two primary valencies and six secondary valencies. In modern terms the complex $[Co(NH_3)_5Cl]Cl_2$ ionizes to give $[Co(NH_3)_5Cl]^{2+}$ and two Cl^- ions. Thus only two of the three chlorine atoms are ionic and thus only two are precipitated as AgCl with $AgNO_3$. Five NH_3 and one Cl form coordinate bonds to Co^{3+}, forming a complex ion.

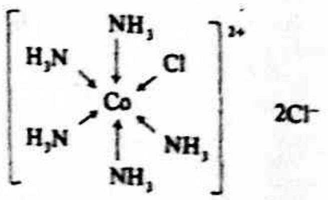
Similarly in $CoCl_3 \cdot 4NH_3$ Werner deduced that one Cl formed a primary valency, and that there were six secondary valencies (two Cl and four NH_3). In modern terms the complex $[Co(NH_3)_4Cl_2]Cl$ ionizes to give $[Co(NH_3)_4Cl_2]^+$ and Cl^- and so only one Cl^- can be precipitated as AgCl.

The coordination number of Co^{3+} is 6; in this case four NH_3 and two Cl^- form coordinate bonds to Co^{3+}.

Thus Werner established that the number of secondary valenceis (that is the coordination number) was 6 in these complexes.



(a)



(b)