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DEPARTMENT OF CHEMISTRY

A Project work on

"WERNER'S THEORY"

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WERNER'S THEORY

In 1893 Werner produced a theory to explain the structures, formation and nature of bonding in the coordination compounds. This theory is known as Werner's theory of coordination compounds.

Werner was the first inorganic chemist to be awarded the Nobel Prize for chemistry 1913. He studied many complex compounds obtained from the reaction between cobalt chloride and ammonia.

The Postulate of Werner's Theory

The central metals of coordination compounds exhibit two types of valencies

Primary Valency
Secondary valency

1. Primary Valency

Primary valencies are those which a metal exhibits in the formation of simple salts. e.g. CoCl3 , NaCl, CuSO4 etc. In modern terminology it represents the oxidation number of metal.

e.g. the primary valencies of Co in $CoCl_3$ is 3, and oxidation state +3

Similarly, for NaCl, oxidation state of Na is +1, for $CuSO_4$, oxidation state of Cu is +2

The primary valencies are ionizable.
These are written outside the coordination sphere.
These are non-directional and do not give any geometry to complex compound
Example: $[Co(NH_3)_6]Cl_3$, number of primary valencies 3, oxidation state +3

Primary ValencyLimitation of Werner's theory

Though Werner explained some properties of the coordination compound, he failed to explain the colour of the coordinate compound.

He could not explain the magnetic and optical properties of coordination compounds.

He could not answer the question, why does the coordination sphere have a definite geometry.

$$[Co(NH_3)_6]Cl_3$$

Primary valency

2. Secondary Valency

The secondary valency of metals is either by negative ions or neutral molecules or both.
In modern terminology it represents the coordination number of the metal.
Secondary valencies are written inside the coordination sphere.
These are directional in nature and give definite geometry to the complex.
These are non-ionisable.

Example: [Co (NH3)6]Cl3 coordination number is 6.

$[Co(NH_3)_6]Cl_3$

Secondary valency

Structure and Properties on the basis of Wener's Theory:

Werner explained the Structure and properties of following four complexes of Co (III) chloride with ammonia.

Compounds		Colour	Old Name	No. of charges on complex ion	No. of Ions		
Old Formulae	New Formulae				Cation	Anion	Total
$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$	Yellow	Luteo complex	+3	1	3	4
$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$	Purple	Purpureo complex	+2	1	2	3
$CoCl_3 \cdot 4NH_3$	Trans-$[Co(NH_3)_4Cl_2]Cl$	Green	Praseo complex	+1	1	1	2
$CoCl_3 \cdot 4NH_3$	Cis-$[Co(NH_3)_4Cl_2]Cl$	Violet	Violeo complex	+1	1	1	2
$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$	Blue green	—	—	—	—	—

- *Werner added the above four cobalt(III) complexes in table with an excess silver nitrate solution. Which resulted in different amounts of silver chloride precipitate*
- *He concluded that in CoCl3.6NH3, 3Cl- ions react with 3 silver ion form 3 silver chloride precipitates which act as primary valency and 6NH3 molecules act as secondary valency.*

Thus in modern term the compound is written as $[Co(NH_3)_6]Cl_3$.

- Similarly, for $CoCl_3.5NH_3$, $2Cl^-$ ions act as primary valency, the remaining $1Cl^-$ and $5NH_3$ ions act as secondary valency. So the compound is $[Co(NH_3)_5Cl]Cl_2$
- For $CoCl_3.4NH_3$, $1Cl^-$ is primary valency, $2Cl^-$ and $4NH_3$ is secondary valency. So the compound is $[Co(NH_3)_5Cl_2]Cl$
- For $CoCl_3.3NH_3$, all $3Cl^-$ and $3NH_3$ ion act as secondary valency So the compound is $[Co(NH_3)_5Cl_3]$
- Limitation of Werner's theory
- Though Werner explained some properties of the coordination compound, he failed to explain the colour of the coordinate compound.
- He could not explain the magnetic and optical properties of coordination compounds.
- He could not answer the question, why does the coordination sphere have a definite geometry. He represents the primary valencies by dotted lines(.......) and secondary valencies by solid line (–)
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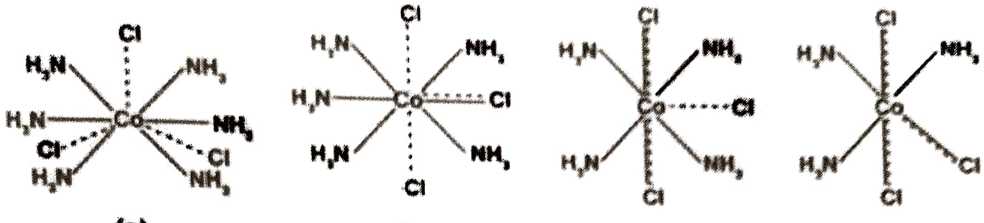
For $CoCl_3.3NH_3$, all 3Cl- and $3NH_3$ ion act as secondary valency
So the compound is $[Co(NH_3)_5 Cl_3]$



(a) (b) (c) (d)

2. Electrical Conductance Measurement:
The conductance of solution depends upon the numbers of charge particles present in that solution.

$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^+ + 3Cl^-$

$[Co(NH_3)_5Cl]Cl_2 \rightarrow [Co(NH_3)_5Cl]^+ + 2Cl^-$

$[Co(NH_3)_4Cl_2]Cl \rightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$

So that the molar conductance of the compound should be the following order which also satisfies the observed conductance value.

$[Co(NH_3)_6]Cl_3 > [Co(NH_3)_5Cl]Cl_2 > [Co(NH_3)_4Cl_2]Cl > [Co(NH_3)_3Cl_3]$

3. Precipitation Reaction:
On the addition of silver nitrate solution, with chloride complex. The chloride ions which present outside the coordination sphere undergo precipitation reaction. As the number of chloride ions present outside the sphere increases, the number of formation of precipitates increases vice versa. Examples Based on Postulates of Werner's Theory

Werner's theory is responsible for the formation of structures of various cobalt amines. We will look at its explanation now. Cobalt has a primary valency (oxidation state) of three and exhibits secondary valency (coordination number) of 6. We represent the secondary valencies by thick lines and the primary valency by broken lines.

Cryoscopic Measurement:

The cryoscopic measurement (i.e., measurement of depression in freezing point) gives the number of ions formed by the dissociation of an ionic compound. The depression in freezing point is a colligative property and depends upon the number of particles in the solution. Greater the number of particles, the more will be the freezinLimitation of Werner's theory

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Compound	Number of particles Determined from Cryoscopic Measurement
$CoCl_3.6NH_3$	4
$CoCl_3.5NH_3$	3
$CoCl_3.4NH_3$	2
$CoCl_3.3NH_3$	0

g point.
He represents the primary valencies by dotted lines (.......) and secondary valencies by solid line (–)

Evidence in favour Werner's theory

1. Cryoscopic Measurement:

The cryoscopic measurement (i.e., measurement of depression in freezing point) gives the number of ions formed by the dissociation of an ionic compound. The depression in freezing point is a colligative property and depends upon the number of particles in the solution. Greater the number of particles, the more will be the freezing point.

1) CoCl3.6NH3 Complex: In this compound, the coordination number of cobalt is 6 and NH3 molecules satisfy all the 6 secondary valencies. Chloride ions satisfy the 3 primary valencies. These are non-directional in character. These chloride ions instantaneously precipitate on the addition of silver nitrate. The total number of ions, in this case, is 4, three chloride ions and one complex ion.

2) CoCl3.5NH3 complex: In this compound, cobalt has the coordination number of 6. However, we see that the number of NH3molecule 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.

3) CoCl3.4NH3 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 $[CoCl_2(NH_3)_4]Cl$.

Werner's Theory and Isomerism

Werner turned his attention towards the geometrical arrangements of the coordinated groups around the central cation. He was successful in explaining the cause behind optical and geometrical isomerism of these compounds. Some examples are as follows:

1) [CoCl2(NH3)4]Cl complex: According to Werner, there are three structures possible for this complex. These are planar, trigonal prism, octahedral. The number of possible isomers is 3 for planar, 3 for trigonal prism and 2 for octahedral structure.

However, as we could isolate only two isomers of the compound, he concluded that geometrical arrangement of the coordinated group around the central atom in this compound was octahedral. In the case of several other complexes in which the coordination number of the central atom was six, Werner was of the opinion that in all these cases the six coordinated complex have octahedral geometry.

He also read the geometry of the complexes where the coordination number of the central metal atom is 4. He gave two possible structures for such compounds: Square Planar and Tetrahedral. Let us look at an example of the same.

2] [PtCl2(NH3)2] complex: In this complex, the coordination number of the metal is 4. According to Werner, this complex exists in two isomeric forms, cis and trans. This shows that all the four ligands lie in the same plane. Therefore, the structure should be a square planar or tetrahedral.

Limitation of Werner's theory

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