Discovery and Historical background

Accidental isolation of cobalt-ammine compound (orange colored), $CoCl_3.6NH_3$ by Tassaert from an ammoniacal solution of cobalt chloride exposed to air.

Different cobalt ammine compounds are listed here:

Cobaltammines	**Colour**	**Colour code name**
A. $CoCl_3.6NH_3$	Orange-yellow	Luteocobaltic chloride
B. $CoCl_3.5NH_3.H_2O$	Red	Roseocobalt chloride
C. $CoCl_3.5NH_3$	Purple	Purpurecobaltic chloride
D. Trans-$CoCl_3.4NH_3$	Green	Praseocobaltic chloride
E. Cis-$CoCl_3.4NH_3$	Violet	Violeocobaltic chloride

Though people started understanding the properties and behavior of these compounds after the arrival of Werner's Theory

Properties of Cobaltammines

$CoCl_3.6NH_3$ was isolated in the following way by Tassaert.

$$CoCl_2 \text{ in aqueous } NH_3 \xrightarrow{\text{Exposed to air, colour changed}} \underset{\text{Crystal}}{CoCl_3.6NH_3}$$

Note: In this molecule the NH_3 molecules are so tightly bound that treatment with conc. H_2SO_4 all the chlorides as HCl but NH_3 is lost.

Precipitation of AgCl:

A. $CoCl_3.6NH_3 \longrightarrow 3AgCl$ (i.e. 3 Cl^- remains free per molecule)

B. $CoCl_3.5NH_3.\ H_2O \longrightarrow 3AgCl$ (i.e. 3 Cl^- remains free per molecule)

C. $CoCl_3.5NH_3 \longrightarrow 2AgCl$ (i.e. 2 Cl^- remains free per molecule)

D. $CoCl_3.4NH_3 \longrightarrow 1AgCl$ (i.e. 1 Cl^- remains free per molecule)

E. $CoCl_3.3NH_3 \longrightarrow$ No AgCl (i.e. No Cl^- remains free in solution)

The mode of isolation can also be supported by the molar conductivity measurement

Compound	**Λ_M(Ohm^{-1}cm^{2}mol^{-1}**	**No of ions per molecules**	**No of ionic Cl^{-1} per molecule for AgCl ppt.**
$CoCl_3.6NH_3$	432	1+3=4	3
$CoCl_3.5NH_3.\ H_2O$	261	1+2=3	2
$CoCl_3.5NH_3$	413	1+3=4	3
$CoCl_3.4NH_3$	100	1+1=2	1

People were confused at that time that how a stable metal salt like MCl_x chemically combines with stable molecules like yNH_3 to produce new compound of composition $MCl_x(NH_3)_y$

Alfred Werner got the Noble prize in 1913 for his contribution to understand the coordination compounds.

Basic Postulates of Werner's Coordination Theory

- Metal centre shows two types of valence. Depending on the properties and strength of the valencies showed by the metal centre (acting as the central atom), the valencies can be classified in two groups: primary valence or principal valence and secondary valence or auxiliary valence or residual valence. After satisfaction of the primary valence (ie. ionic charge) of the metal ion, the metal ion still possesses some residual binding capacity that gives the secondary valence.

- The primary valence is utilized to form the ionic bonds while the secondary valence is utilized to form the coordinate covalent bonds in space,

- The primary valence is utilized to bind the unions ionically and these anions are ionisable in solution while the secondary valence is utilized to bind the neural or anionic groups through the coordinate covalent bonds in space. The groups bound by the secondary valence are not ionisable.

- Satisfaction of the primary valence leads to the ordinary molecules like COCI, NH3, etc. While satisfaction of both the primary and secondary valence leads to the coordination compounds like $CoCl_3.6NH_3$; $CoCl_35NH_3$, etc.

Basic Postulates of Werner's Coordination Theory

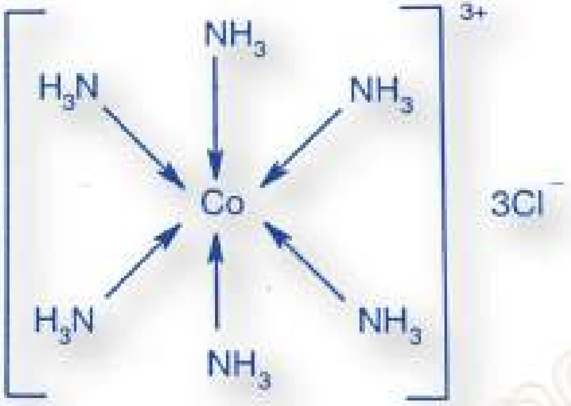
- For a particular metal centre, the secondary valence is generally fixed and it gives the coordination number of the metal centre.
- The secondary valencles are directed in space around the metal centre to constitute coordination sphere (more correctly, 1st coordination sphere). The directional property of secondary valence (i.e. coordinate covalent bonds) gives a definite geometrical shape of coordination sphere.
- To determine the structure (i.e. geometry) of the complex species (i.e coordination sphere, Wener considered the number of isolated isomers for a certain geometry, Different geometries for a certain coordination number can produce different numbers of geometrical isomers. From the actual number of geometrical isomers, the geometry was predicted. In some cases, possibility of optical isomerism was considered by Werner to determine a particular geometry.

Illustration of primary and secondary valencies

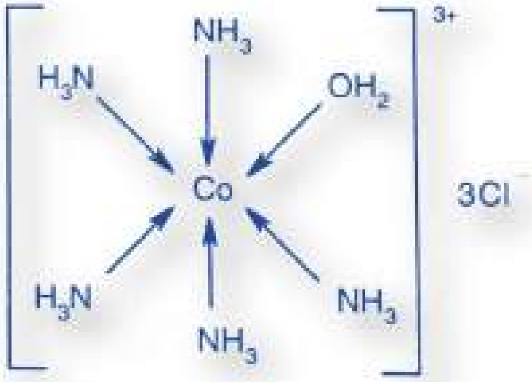
Complex series	Primary valency	Oxidation state	Secondary valency
$[Co(NH_3)_6]^{+3}$	3	+3	6
$[CoCl_2(NH_3)_4]^{+}$	3	+3	6
$[Fe(CN)_6]^{-3}$	3	+3	6
$[Fe(CN)_6]^{-4}$	2	+2	6
$[FeCl_4]^{-}$	3	+3	4
$[PtCl_2(NH_3)_4]^{+2}$	4	+4	6
$[PtCl_2(NH_3)_2]^{0}$	2	+2	4

Formulation of cobalt(III) ammine compounds

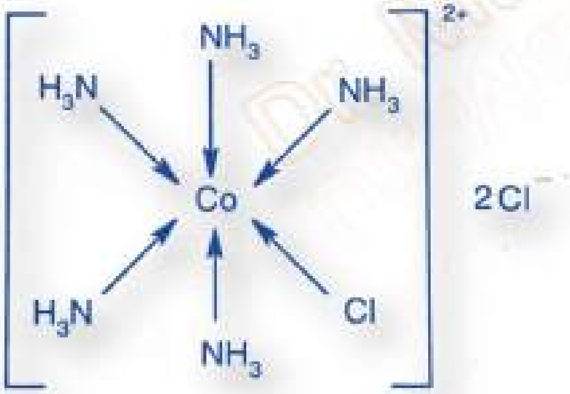
$CoCl_3 \cdot 6NH_3$:



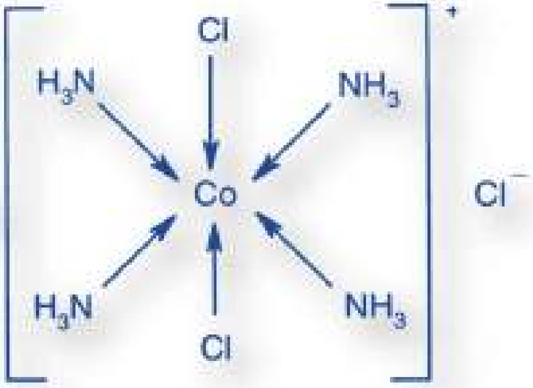
$CoCl_3 \cdot 5NH_3 \cdot H_2O$:



$CoCl_3 \cdot 5NH_3$:



$CoCl_3 \cdot 4NH_3$: (*trans*-form)



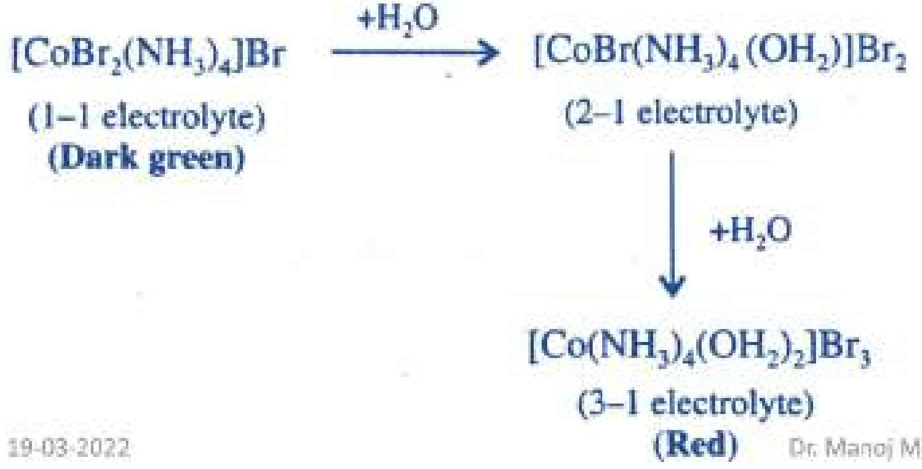
Formulation of a series of Platinum(IV) ammine complexes from Werner's theory

Compound	**Λ_M(Ohm^{-1}cm^{2}mol^{-1}**	**No. of ions per molecule**	**Formulation**
$PtCl_4.6NH_3$	520	4+1=5	$[Pt(NH_3)_6]Cl_4$
$PtCl_4.5NH_3$	400	3+1=4	$[PtCl(NH_3)_5]Cl_3$
$PtCl_4.4NH_3$	230	2+1=3	$[PtCl_2(NH_3)_4]Cl_2$
$PtCl_4.3NH_3$	100	1+1=2	$[PtCl_3(NH_3)_3]Cl$
$PtCl_4.2NH_3$	5	0	$[PtCl_4(NH_3)_2]$
$PtCl_4.NH_3.2KCl$	110	1+1=2	$K[PtCl_5(NH_3)_6]$
$PtCl_4.2KCl$	255	2+1=3	$K_2[PtCl_6]$

Complications of the interpretation of conductance data and results of silver halide (AgX) precipitation due to solvation at the kinetically labile centres

It has been assumed that the moieties remaining outside the coordination sphere are ionically bound by the primary valence only and these remain as the free ions in solution. On the other hand, the moieties present within the coordination sphere are bound by the secondary valence and these do not come out from the coordination sphere as the free species. **This assumption is true only for the kinetically inert metal centres.**

For the labile centres, the moieties present in the coordination sphere come out due to solvation to complicate the interpretation. For example, the **dark green bromopraseo salt**, $[CoBr_2(NH)_4]Br$ on dissolution gives a dark green solution which gradually changes in colour to red. This colour change is accompanied with the gradual increase in molar conductance. This has been explained by considering the **aquation**, i.e substitution of bromides by water molecules in the coordination sphere as follows:



To avoid the complication from the solvation which is likely to occur in labile centres, Werner used the inert complexes formed by Co(III) (octahedral complexes), Pt(IV) (octahedral complexes), Cr(III) (octahedral complexes) and Pt(II) (square planar complexes). Though at that time, the reason behind the **kinetic lability** and **inertness** was not clearly understood.

Defect of Werner's Theory

(i) **Nature of bonding:** It cannot explain the nature of bonding, i.e. metal-ligand interaction within the coordination sphere. Consequently, it fails to explain the magnetic properties, spectral properties, thermodynamic stabilities and kinetic stabilities (ie. lability and inertness) of the complexes.

(ii) **Structure determination from the number of isolated isomers:** This method applied by Werner is not absolutely correct. One may not be able to isolate an isomer and based on this, it cannot be concluded that the isomer does not exist.

(iii) **Preference to a certain coordination number and stereochemical configuration:** At the time of Werner, most of the complexes known were of either 4 C.N. or 6 C.N. But Werner's theory could not explain the preference among these complexes for the 4- and 6- coordination numbers. For C.N. 4, some complexes are tetrahedral while some complexes are square planar. This aspect cannot be understood Werner's theory.

(iv) Even a particular metal centre may adopt different coordination numbers and different geometries in different conditions. It is illustrated by the following examples. $[Ni(Co)_4]$ (C.N. = 4, tetrahedral): $[Ni(CN)_4]^{2-}$ (C.N. = 4, square planar); $[Ni(NH_3)_6]^{2+}$ (C.N. = 6, octahedral). This aspect cannot be understood from Werner's theory.

Double salt and complex salt

Double salt: A large number of molecular compounds can be produced through the combinations of simple molecular inorganic salts which are capable of their independent existence. **Examples:**

(i) Potash alum: $K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$
(ii) Mohr's salt: $(NH_4)_2SO_4.\ FeSO_4.6H_2O$

- A double salt is an aggregate of two simple inorganic salt and the aggregate simply splits into the constituent ions in solution. i.e. **aggregate maintain individuality of the constituent salts.**
- A double salt shows its distinct identity in the solid crystalline state but it **lose its identity in solution.**

$$K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O \xrightarrow{H_2O} 2K^+ + 4SO_4^{2-} + 2Al^{3+} + 24H_2O$$

$$(NH_4)_2SO_4.\ FeSO_4.6H_2O \xrightarrow{H_2O} 2NH_4^+ + Fe^{2+} + 2SO_4^{2-} + 6H_2O$$

Double salt differ from mixed crystals formed by the isomorphous crystals as the mixed crystals do not maintain the fixed composition. The composition of a mixed crystals can vary depending on the relative concentrations of the constituent salts in the solution from which the mixed crystal is isolated through crystallization. E.g. $KMnO_4$ and $KClO_4$ are isomorphous and they can produce a continuous series of solid solution (i.e. mixed crystals) with one another.

Complex salt:

- The individual identity of the constituent salt are lost. Thus the complex salt on being ionized cannot produce all the constituent ions in solution.

$K_4[Fe(CN)_6]$ is obtained by the action of KCN on $FeSO_4$.

$2KCN + FeSO_4 \longrightarrow Fe(CN)_2 + K_2SO_4,$
$4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$

$K_4[Fe(CN)_6]$ ionizes in the aqueous solution in the following way:

$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

But not
$K_4[Fe(CN)_6] \longrightarrow 4K^+ + 6CN^- + Fe^{2+}$

The complex ions are capable of maintaining their independent existence in both the solid and solution phase as written within [], i.e. $[Fe(CN)_6]^{4-}$

Perfect and Imperfect Complexes

For perfect complexes, the constituent ions fails to respond their **common chemical test**. E.g. in complex $K_3[Fe(CN)_6]$, the Cu^{2+} ion can not be precipitated by using H_2S as the complex is quite stable and it can not undergo dissociation producing Cu^{2+} ions.
Examples of perfect complexes: $[Ni(CN)_4]^{2-}$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, etc.

For imperfect complexes, the constituent ions respond to some of the chemical test for the metal and involved ligands. E.g. $K_2[Cd(CN)_4]$ ionizes sufficiently to allow the detection of Cd^{2+} ion as CdS by passing H_2S.

$$K_2[Cd(CN)_4] \longrightarrow 2K^+ + [Cd(CN)_4]^{2-}$$

$$[Cd(CN)_4]^{2-} \longrightarrow Cd^{2+} + 4CN^-$$

$$Cd^{2+} + S^{2-} \longrightarrow \text{CdS (Yellow ppt.)}$$

Stability constant plays an important role in determining the complexes as perfect or imperfect

$$M + xL \Longleftrightarrow [ML_x], \; K_{stab} = \frac{[ML_x]}{[M][L^x]}$$

K_{stab}, a thermodynamic parameter, denotes the overall stability constant of the complex.

Similarly, the dissociation constant of the complex can be shown as:

$$[ML_x] \Longleftrightarrow M + xL,$$

$$K_{instab} = \frac{1}{K_{stab}} \frac{[M][L^x]}{[ML_x]}$$

$K_{instab,}$ denotes the instability constant of the complex.

If k_{stab} is very high (i.e. k_{instab} is very low), then the extent of dissociation of the complex into its constituents is very small and such complexes are referred to as the **perfect complexes.**
On the other hand, if K_{stab} is low, (i.e. high vale of K_{instab}), then the complex dissociates to a significant extent and such complexes are described as the **imperfect complexes.**

The stability constants of the complexes $K_2[MCl_4]$ (M = Zn, Cu, Pt) differ significantly.

K_{stab} runs as: $Pt^{2+} >> Cu^{2+} >> Zn^{2+}$, K_{instab} runs as: $Pt^{2+} << Cu^{2+} << Zn^{2+}$

In fact, $[ZnCl_4]^{2-}$ breaks down into its constituent ion completely while $[PtCl]^{2-}$ remains almost unchanged and $[CuCl_4]^{2-}$ shows intermediate behavior

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Thus the perfectness in the complexes increases in the sequence:

$[ZnCl_4]^{2-} << [CuCl_4]^{2-} << [PtCl_4]^{2-}$

Inner sphere, outer sphere and second sphere coordination Complexes

When ligands coordinate with the metal produced **inner sphere complex**. Inner sphere complex may be **ionic or neutral** depending on the conditions. If the complex is ionic then it can hold the oppositely charged ion outside the coordination sphere.
This association between the inner sphere complex and the oppositely charged ions produces **outer sphere complex**.

$$M^{x+} + nL \overset{K}{\Longleftrightarrow} [ML_n]^{x+},$$

(Inner sphere complex)

$$[ML_n]^{x+} + Y^{m-} \overset{K_{O.S}}{\Longleftrightarrow} [ML_n]^{x+} \,.\, Y^{m-}$$

Outer sphere
association constant

Ion pair (Outer sphere complex)

Besides the ion pair interaction, other types of interaction like ion-dipole interaction, dipole-dipole interaction can also produce the outer sphere complex.

$[Co(NH_3)_6]^{3+}.H_2O$	**(ion-dipole interaction)**
$[CoCl_3(NH_3)_3].H_2O$	**(dipole-dipole interaction)**

Note: The outer sphere association constant increases with the increase of the product of charges on the ions and decreases with increase of sixe of the ions.

Outer sphere association constants ($K_{O.S}$) for some outer sphere complexes

Ion-pair	$K_{O.S}$
$[Co(NH_3)_6]^{3+}.Cl^-$	74
$[Co(NH_3)_6]^{3+}.Br^-$	46
$[Co(NH_3)_6]^{3+}.I^-$	17
$[Co(en)_3]^{3+}.Cl^-$	52
$[Co(en)_3]^{3+}.SO_4^{2-}$	2.8×10^3

Binary and mixed ligand complexes

In the coordination sphere, if only one type of ligand excluding the solvent molecules is present, the complex is called **binary complex or homoleptic complex**. E.g. $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5OH_2]^{3+}$

If there are different types of ligands (excluding the solvent) within the coordination sphere, then complex is called mixed ligand complex or heteroleptic complex.

Note: If there are two types of ligands, the complex is referred to as the **ternary complex**. Similarly, a **quarternary complex** posses three different types of ligands within the coordination sphere. Example of ternary complexes are: