
Complex compound

BY..... TIMEPASS EDUCATION



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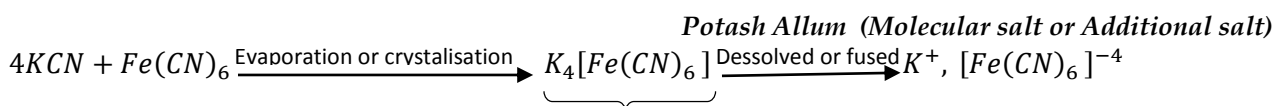
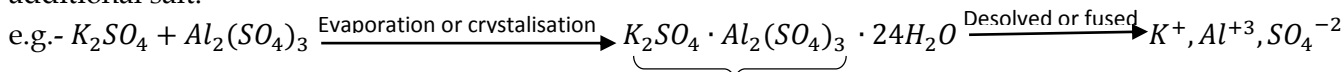
Co-ordination compound Complex compound

It is a branch of inorganic chemistry, which deals with co-ordination compound or complex compound.

e.g.- $K_4[Fe(CN)_6]$, $Cr[(NH_3)_6]Cl_3$, etc

❖ Molecular salt or Additional salt

When two or more simple salts are mixed in simple proportion in fused state or in solution and the mixture is allowed to evaporate, it results formation of new crystal known as molecular salt or additional salt.



Potash Alum (Molecular salt or Additional salt)

Types of molecular salt:-

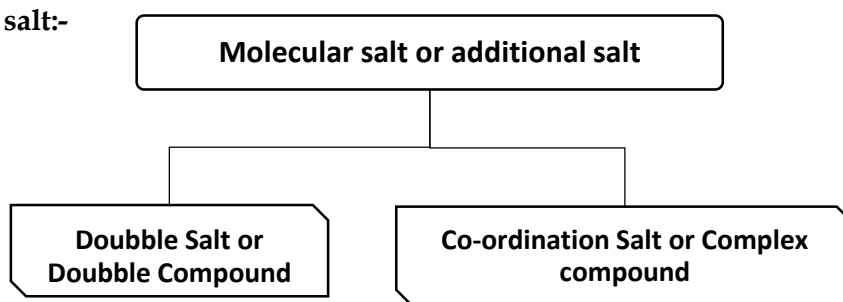


Figure 1

❖ Double salt:-

Those addition salts, which on fusion or dissolving in water dissociate into their all-individual components are called salts or double compound.

They correspond test for all individual ions in solution or in fused state.

e.g.- $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (Potash Alum),
 $KCl \cdot MgCl_2 \cdot 6H_2O$ (Carnalite),
 $FeSO_4 \cdot (NH_4)_2 \cdot 6H_2O$ (Mohr's salt), etc.

❖ Co-ordination compound or Complex:-

Those addition salts or molecular salts which on fusion or dissolving on water does not dissociate into their all components are called co-ordination compounds or complex compounds.

They do not correspond test for all components ions in fused state or in solution.

e.g.- $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Cr(NH_3)_6]Cl_3$, $[Ag(NH_3)_2]Cl$, etc.

❖ Terminology:-

Co-ordination Entities or complex ion

Co-ordination Entities or complex ion

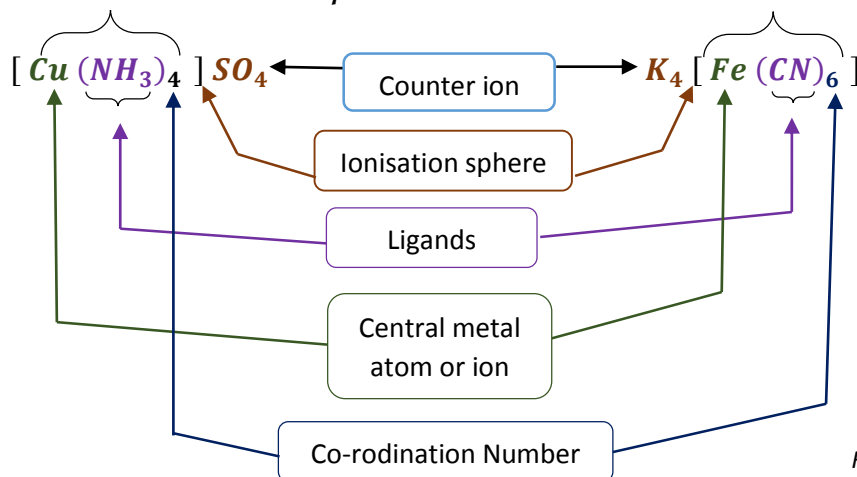


Figure 2

❖ **Complex ion:-**

That part of complex compound, which does not under goes dissociation, is called complex part.

e.g.- [**Cu (NH₃)₄**], [**Fe (CN)₆**], etc

❖ **Co-ordination sphere:-**

Complex part of complex compound, which is enclosed in a square bracket. Tis square bracket is called ionization sphere.

❖ **Counter ion:-**

The part of complex, which is outside of the co-ordination ion, is called counter ion. e.g.- **K₄, SO₄, etc.**

❖ **Central metal atom:-**

The metallic part present in co-ordination sphere is called central metal atom. E.g.- **Fe, Cu, etc.**

❖ **Ligand:-**

The atom or group of atoms attached to central metal atom in complex compound is called ligand.

Ligand donates at least one loan pair of electrons to central metal atom. E.g.- **(NH₃), (CN), etc.**

❖ **Co-ordination number or ligancy denticity:-**

The number of ligands attached with central metal atom are called co-ordination number, ligancy, or denticity. For example, view the figure 2.

❖ **Oxidation number of central metal atom:-**

In a complex compound central metal atom has a particular oxidation state known as the oxidation number of central metal atom. For the example, see the figure 2.

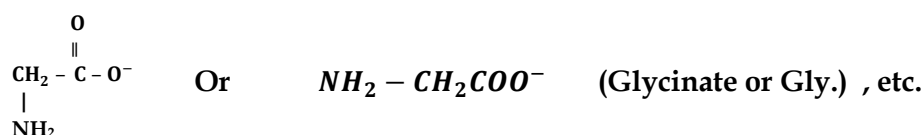
❖ **Types of Ligands:-**

A. On the basis of electronic charge:-

1. **Negative Ligands:-**

Those ligands, which have negative charge, is known as negative ligands. E.g.-

F⁻, Br⁻, I⁻, Cl⁻, C₂O₄⁻ (Oxalate or "ox"), NO₂⁻, CN⁻, NO₃⁻, SO₄²⁻, SO₃²⁻, CO₃²⁻,



2. **Neutral Ligands:-**

H₂O, NH₃, CO, NO, PH₃, Pph₃,  (Pyridine or Py),  (Ethylene diamine or en), etc.

3. **Positive Ligands:-**

NH₂ - N⁺H₃, N⁺O, N⁺H₄, etc.

B. On the basis of linkage:-

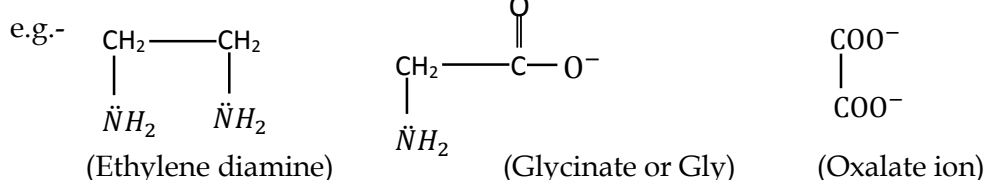
i) Mono-dentate ligands or uni-dentate ligands:-

Those ligands, which have only one linkage or donor site, are called mono-dentate ligands. This type of ligands may donate lone pair of electrons from only one site.

e.g.- NH₃, H₂O, CO, NO₂[⊖], Py, PH₃, F[⊖], Cl[⊖], Br[⊖], I[⊖], etc.

ii) Bi-dentate or Di-dentate ligands:-

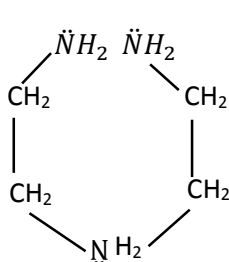
Those ligands, which have two linkages or two donor sites to donate loan pair of electrons to the central metal atom are called bi-dentate ligands. This type of ligands may donate lone pair of electrons from both sites at a same time.



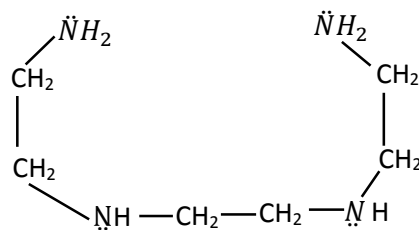
iii) Poly-dentate ligands or multi-dentate ligands:-

Those ligands, which have three or more than three linkages or donor sites to donate the lone pair of electrons to central metal atom are called poly-dentate ligands. This type of ligand may donate lone pair of electrons from three or more than three sites at the same time.

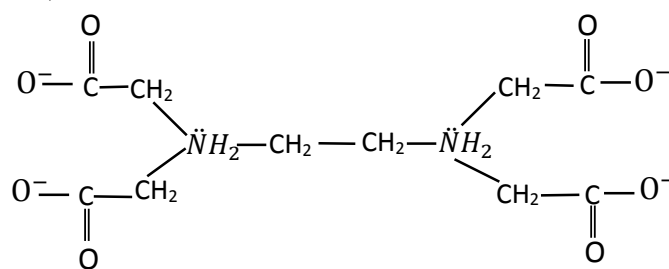
e.g.-



Diethylene triamine or dien
(Three donor sites)



Triethylene tetraamine or trien
(Four donor sites)



Ethylene diamine tetra acetate ion or EDTA

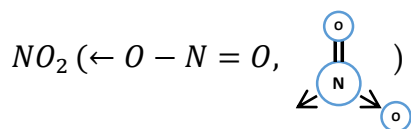
(Six donor sites)

C. Some other types of ligands:-

➤ Ambidentate ligands:-

Those ligands which have two donor sites but they may donate lone pair of electrons to the central metal atom from one only one site at the same time are called ambidentate ligands.

e.g.- Cyanide ($\leftarrow \text{C} \equiv \text{N}$, $\leftarrow \text{N} \equiv \text{C}$),



➤ flaxydentate ligands:-

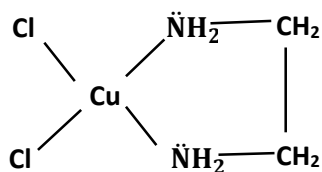
Those poly-dentate ligands are those ligands, which may donate lone pair of electrons from different sites are called flaxydentate ligands

e.g.- EDTA

❖ Chelate:-

Bi-dentate ligands and poly-dentate ligands may form a ring structure with central metal atom is called, 'chelate ring' and such types of complexes are called 'chelate complex' and the process is called 'chelation'.

e.g.-



Note:- Chelate complexes are more stable than complexes formed by mono-dentate ligands.

❖ **Types of complexes**

- i. Cationic complexes
- ii. Anionic complexes
- iii. Neutral complexes
- iv. Mixed complexes

i. Cationic complexes:-

Those complexes in which complex part is in cation are called cationic complexes.

e.g.- $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ ($[\text{Cr}(\text{NH}_3)_6]^{3+}$, Cl^{3-}), $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$, etc.

Cation complex part - $[\text{Cr}(\text{NH}_3)_6]^{3+}$

ii. Anionic complexes:-

Those complexes in which complex part is anion are called anionic complexes.

e.g.- $\text{K}_4[\text{Fe}(\text{CN})_6]$ (K^{4+} , $[\text{Fe}(\text{CN})_6]^{4-}$), $\text{K}_3[\text{Fe}(\text{CN})_6]$, etc.

Anion complex part - $[\text{Fe}(\text{CN})_6]^{4-}$

iii. Neutral complexes:-

Those complexes in which complex part is in anion are called anion complexes.

e.g.- $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$, etc.

iv. Mixed complexes:-

Those complexes in which have both cation and anion complex parts are called mixed complexes.

e.g.- $[\text{Cr}(\text{NH}_3)_6][\text{CoF}_6]$, etc.

❖ **Method to calculate oxidation state on central metal atom:-**

To learn how to calculate oxidation state of a central metal atom concentrate the following examples-

e.g.1.- Let us consider we have a complex $[\text{NiCl}_4]^{2-}$ and we have to calculate the oxidation state of Ni.

Let,

Oxidation state of 'Ni' is 'x' and we know that.....

Oxidation number of Cl is -1 also,

Oxidation number of whole complex (i.e. $[\text{NiCl}_4]^{2-}$) is -2.

Now, we know that the sum of oxidation number of all components of a complex is equal to the oxidation number of a complex.

Then,

$$x + (-4) = -2$$

$$\text{or, } x - 4 = -2$$

$$\text{or, } x = 4 - 2$$

$$\text{or, } x = 2 \text{ (i.e. } +2)$$

Thus, the oxidation state of Ni in $[\text{NiCl}_4]^{2-}$ is +2.

e.g.2- calculate the oxidation state of central metal atom 'Fe' in complex compound $\text{K}_4[\text{Fe}(\text{CN})_6]$.

let the oxidation state of Fe in given complex is 'x'.

Now, we know that -

oxidation number of K = +1

oxidation number of CN = -1 and

oxidation number of whole complex i.e. $\text{K}_4[\text{Fe}(\text{CN})_6] = 0$

(Note:- The oxidation no. of whole complex means the total charge on complex compound.)

\therefore oxidation no. of K + oxidation no. of Fe + oxidation no. of CN = oxidation no. of $\text{K}_4[\text{Fe}(\text{CN})_6]$

$$\text{or, } (+1) \times 4 + x + (-1) \times 6 = 0$$

$$\text{or, } 4 + x - 6 = 0$$

Complex compound

or, $x = +2$

Thus the oxidation state of Fe in $K_4[Fe(CN)_6]$ is +2.

Note:- " we know that most of students have problem to determine the oxidation state of other components of complex as like counter ion, ligands, etc. during the calculation the oxidation state of central metal atom but don't worry about it there are some tips to remember the oxidation number of other components of complex excepting central metal atom."

Periodic Table of the Elements

The periodic table includes the following series and groups:

- Group 1:** 1IA, 11A
- Group 2:** 2IA, 2A
- Groups 3-10:** IIIA, 4A, 5A, 6A, 7A, 8, 9, 10, 11A, 11B, 12A, 12B
- Group 11:** 11A, 11B
- Group 12:** 12A, 12B
- Group 13:** 3A
- Group 14:** 4A
- Group 15:** 5A
- Group 16:** 6A
- Group 17:** 7A
- Group 18:** 8A, 18A
- Lanthanide Series:** 57-71
- Actinide Series:** 89-103

Let's concentrate on above periodic table and remember the following tips:-

- Oxidation number of first group (H, Li, Na, K, Rb, Cs, Fr) is +1.
- Oxidation number of second group (Be, Mg, Ca, Sr, Ba, Ra) is +2.
- Oxidation number of group 18th (F, Cl, Br, I, At, Uus) is -1.
- Oxidation number of bi-molecular compound (i.e. O_2 , H_2 , Cl_2 , etc.) is 0
- Oxidation number of neutral ligands (i.e. H_2O , NH_3 , CO , NO , PH_3 , Pph_3 , Py , en , NO , PH_3 , etc.) is 0.
- Oxidation number of ligands, $C_2O_4^{2-}$ (Oxalate or "ox"), NO_2^- , CN^- , Gly , etc. is -1.
- Oxidation number of ligands, SO_4^{2-} , SO_3^{2-} , CO_3^{2-} , etc. is -2.
- Oxidation number of ligands, $NH_2 - N^+H_3$, N^+O , N^+H_4 , etc. is +1.
- Oxidation number of EDTA is -4.

e.g.3.- $[Pt(NH_3)ClBr(H_2O)]$ calculate the oxidation number of central metal atom.

Note:- Remember that we always calculate the oxidation state of that atom which is linked with ligands in complex part.

(If, you have problem to understand any theory of this topic you can watch or download our video lecture on this topic on [Youtube](#) (Timepass Educatuion), [Facebook](#) (Timepass Education))

In the above complex, Pt is the central metal atom which is linked with the ligands NH_3 , Cl , Br and H_2O . It is clear that the central metal atom is Pt. Let the oxidation state of Pt is 'x'.

We have,

Complex compound

oxidation no. of $NH_3 = 0$,
oxidation no. of $Cl = -1$,
oxidation no. of $Br = -1$ and
oxidation no. of $H_2O = 0$
oxidation no. of whole complex ($[Pt(NH_3)ClBr(H_2O)]$) = 0
 $\therefore x + (0) - 1 - 1 + 0 = 0$
or, $x - 2 = 0$
or, $x = +2$
Thus, the oxidation state of Pt is +2.

e.g.4.- $[Co(en)_2Cl_2]^+$ find central metal atom and calculate the oxidation state of central metal atom.

Central metal atom = Co

Let, oxidation state of Co in given complex is x.

We have,

Oxidation no. of en = 0

Oxidation no. of $Cl_2 = -1$

Oxidation no. of whole complex (i.e. $[Co(en)_2Cl_2]^+$) = +1

$\therefore x + (0) \times 2 - 1 \times 2 = +1$

or, $x - 2 = +1$

or, $x = +3$

Thus the oxidation state of Co is +3.

❖ Method to calculate the effective atomic number (EAN) or Effective atomic number rule (EAN Rule):-

This rule was proposed by Sidwick. It states that - "The total number of electron possessed by the central metal atom in a complex including electrons donated by ligands is equal to atomic number of any inert element. This number is called effective atomic number and this rule is called effective atomic rule.

EAN = Z - oxidation state of central atom + 2×number of loan pair of electron

Or,

EAN = Z - oxidation state of central atom + 2×co-ordination number

Where,

EAN = Effective atomic number and Z = Atomic number.

❖ Method to calculate co-ordination number (C.N.):-

$$\text{Co-ordination number} = \sum(\text{Number of ligands} \times \text{donate character})$$

e.g.- 1. Find the co-ordination number of $[Co(C_2O_4)(NH_3)(Cl)]$

Firstly we have to find the number of ligands and their donate character.

No. of $(C_2O_4) = 1$ and its donate character is 2 (because it donates two loan pair of electrons)

No. of $(NH_3) = 3$ and its donate character is 1 (because it is unidentate ligand)

No. of $(Cl) = 1$ and its donate character is 1 (because it is unidentate ligand)

$\therefore C.N. = \text{no. of } (C_2O_4) \times \text{donate character} + \text{no. of } (NH_3) \times \text{donate character} + \text{no. of } (Cl) \times \text{donate character}$

or, $C.N. = 1 \times 2 + 3 \times 1 + 1 \times 1 = 2 + 3 + 1 = 6$

e.g.-2 find the co-ordination of $[Fe(NH_3)(en)_2(Br)]$

$C.N. = 1 \times 1 + 2 \times 2 + 1 \times 1 = 1 + 4 + 1 = 6$

❖ Examples:-

a. Calculate the EAN of $K_4[Fe(CN)_6]$

In this complex central metal atom (C.M.A) is Fe.

Let, x = oxidation state (O.S.) of Fe.

Then $1 \times 4 + x - 6 = 0$

or, $x - 2 = 0$

Complex compound

or, $x = +2$

In this complex Fe is in +2 oxidation state.

$\therefore EAN = Z - O.S. \text{ of C.M.A.} + 2 \times \text{coordination number}$

or, $EAN = 26 - (+2) + 2 \times 6$

or, $EAN = 36$ (Atomic number of Kr)

b. Calculate the EAN of $K_3[CoF_6]$

In this complex central metal atom (C.M.A) is Cobalt (Co).

It is in +3 o.s. in this complex.

$\therefore EAN = 27 - 3 + 2 \times 6 = 24 + 12 = 36$ (atomic number of Kr)

$$+3 + x - 6 = 0$$

$$\text{or, } x = +3$$

c. $K_3[Fe(CN)_6]$

C.M.A. = Fe

O.S. of Fe = +3

$\therefore EAN = 26 - 3 + 2 \times 6 = 23 + 12$

or, $EAN = 35$ (Approximately equal to atomic number of Kr(36))

$$+3 + x - 6 = 0$$

$$\text{or, } x = +3$$

d. $[NiCl_4]^{2-}$

$[NiCl_4]^{2-} \rightarrow Ni^{2+}$ (i.e. o.s. of Ni is +2)

$\therefore EAN = 28 - 2 + (2 \times 4) = 34$ (Approximately equal to atomic number of Kr(36))

Note:- Some students have problem to remember to calculate EAN. We suggest you can use tricks to remember the atomic number of atoms as following trick-

FeCoNi, company has 262728 million dollars i.e. atomic numbers of Fe, Co and Ni are 26, 27, and 28 respectively.

If, you have problem to understand any theory of this topic you can watch or download our video lecture on this topic on [Youtube](#) (Timepass Educatuion), [Facebook](#) (Timepass Education)

❖ **Limitations of EAN Rule:-**

In some complexes, EAN is approximate rule.

❖ **Method to calculate hybridization of central metal ion:-**

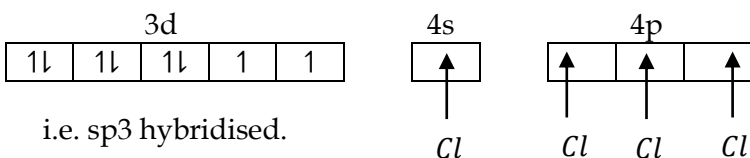
First concentrate on following example:-

Let, we have to find the hybridization of Ni in the complex $[NiCl_4]^{2-}$.

We know that, the atomic number of Ni is 28 but in the complex $[NiCl_4]^{2-}$ Ni is in +2 oxidation satate.

In normal state Ni = $[Ar]^{18}3d^84s^24p^0$

$[NiCl_4]^{2-} \rightarrow Ni^{2+} = [Ar]^{18}3d^84s^04p^0$



$Ni^{2+} \rightarrow 3d^84s^04p^0$

28 (atomic no. of Ni)
 -2 (no. of lost electrons)
-18 (atomic no. of Ar)
 8 (total no. of electrons in outer orbit)

❖ **Magnetic moment:-**

$Magnetic\ moment(\mu) = \sqrt{n(n+2)}\ BM$ (Bohr magneton)

Where n is number of unpaired electron.

For Ni^{2+} $\mu = \sqrt{2(2+2)} = 2\sqrt{2} = 2 \cdot 82\ BM$

Note:-

i. For paired electrons, substance behaves as diamagnetic substance and we know that the diamagnetic substance is repelled by magnet and its weight increases in magnetic field.

Hence $n = 0 \therefore \mu = \sqrt{0(0+2)} = 0\ BM$

Complex compound

ii. For unpaired electrons, substance behaves as paramagnetic substance and we know that the paramagnetic substance is attracted by magnet and its weight increases in magnetic field

Hence *Magnetic moment* (μ) = $\sqrt{n(n+2)} \text{ BM}$

If, $n = 1$; $\mu = 1.732 \text{ BM}$

If, $n = 2$; $\mu = 2.82 \text{ BM}$

If, $n = 3$; $\mu = 3.87 \text{ BM}$

If, $n = 4$; $\mu = 4.89 \text{ BM}$

If, $n = 5$; $\mu = 5.90 \text{ BM}$

❖ Bonding in complexes

Different theories have been to explain bonding in complexes-

- Werner's Theory (W.T.)
- Valence bond theory (V.B.T.)
- Crystal field theory (C.F.T.)

➤ Werner's Theory (W.T.):-

It was proposed by Werner to explain bonding in complexes.

Main points of Werner's theory are as follows:-

- i. In a complex central metal atom exhibits two types of valencies one is called primary valency and another is called secondary valency.
- ii. Primary valency is ionisable while secondary valency is non-ionisable.
- iii. Primary valency shows oxidation number of central metal atom while secondary valency shows co-ordination number of central metal atom.
- iv. Primary valency is satisfied by anion while secondary valency is satisfied by anion, molecule or in some case cation.
- v. Secondary valency is represented by solid line (—) while primary valency is represented by broken line (.....) or dotted line.

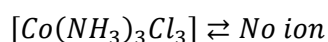
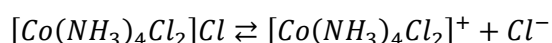
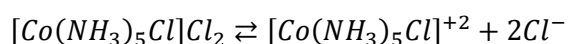
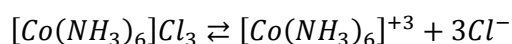
Werner studied on Cobalt (Co) complex in co-ordination number-

- a. $\text{Co}(\text{NH}_3)_6\text{Cl}_3$
- b. $\text{Co}(\text{NH}_3)_5\text{Cl}_3$
- c. $\text{Co}(\text{NH}_3)_4\text{Cl}_3$
- d. $\text{Co}(\text{NH}_3)_3\text{Cl}_3$

Study of above complexes gives following information:-

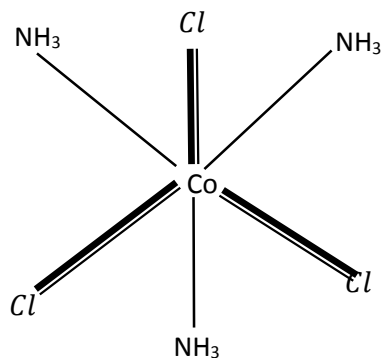
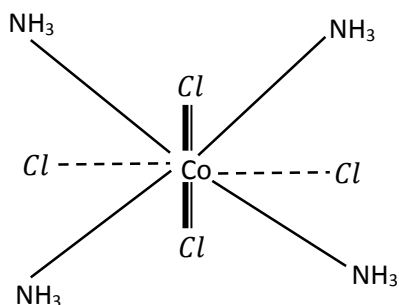
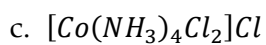
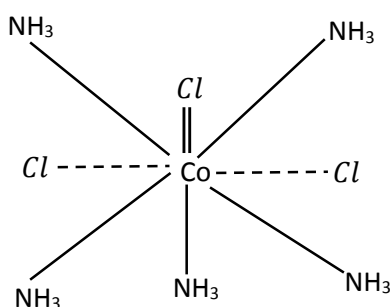
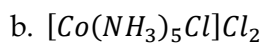
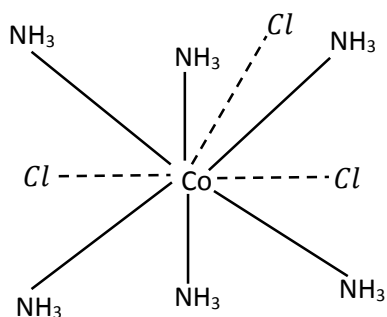
Complex	Ag NO_3 Test	Fevident E.J no. Cl^-	Numbers of ions by conducting measurement	Parent ion of complex
$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	+ve AgNO_3 Test	3	4	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{Co}(\text{NH}_3)_5\text{Cl}_3$	"	2	3	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{Co}(\text{NH}_3)_4\text{Cl}_3$	"	1	2	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{Co}(\text{NH}_3)_3\text{Cl}_3$	"	0	0	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

The ionization of above complexes may be shown as follows:-



Complex compound

Some Examples:-



Drawbacks of Werner's theorem:-

- This theory does not explain the fact that complex formation tendency is limited to few metals.
- This theory does not explain geometry of complexes.
- This theory does not explain magnetic behavior of complexes

Complex compound

- This theory does not explain colour of complexes.

➤ Valence bond theory (V.B.T):-

'Ponting' and 'Slates' proposed this theory.

Main points of this theory:-

- In a complex central metal atom has vacant d-orbital. If it has not vacant d-orbital then it makes available vacant d-orbital having appropriate energy.
- Ligands donate at least one lone pair of electrons to the vacant hybrid orbital of central metal atom.
- There is co-ordinate bond between central metal atom and ligands.
- Central metal may form complexes in co-ordination number 6 or co-ordination number 4.
- In co-ordination 6 hybridization of central metal atom is sp^3d^2 or d^2sp^3 having octahedral structure.
- In co-ordination 4 hybridization of central metal atom may be sp^3 having tetrahedral geometry or in co-ordination 4 hybridization of central metal atom may be dsp^2 or sp^2d having square planer geometry.
- If inner d-orbital involved in hybridization then such complexes are called outer orbital complexes.
- Magnetic moment of complexes can be calculated by following formula:-

$$\text{Magnetic moment}(\mu) = \sqrt{n(n+2)} \text{ BM (Bohr magneton)}$$

Where μ = Magnetic moment and
n = number of unpaired electron.

Examples:-

Let us consider following examples in C.N. 6.

Hybridization $\rightarrow d^2sp^3$ (inner) or sp^3d^2 (outer)

Structure \rightarrow Octahedral

a. $[Cr(NH_3)_6]^{+3}$

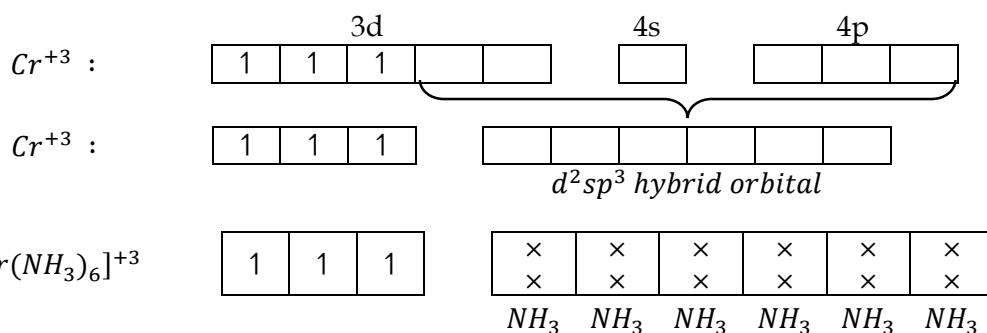
In this complex Cr is in +3 O.S.

$Cr(24) : [Ar]183d^54s^14p^0$

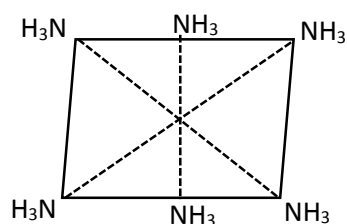
$Cr^{+3}(24) : [Ar]183d^34s^04p^0$

Hence it is d^3 system.

$$\begin{aligned} x + 0 &= 3 \\ \text{or, } x &= +3 \end{aligned}$$



Structure - octahedral



Complex compound

a. ah

we are working on this we will upload the full lecture on this topic soon.

- re
- ❖ tb
- ❖ efvev