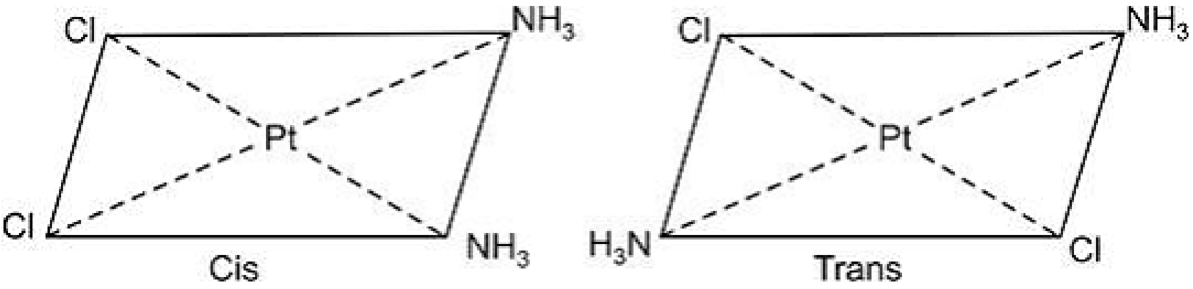
Co-Ordination Compounds

Q. 1. Explain the geometrical isomerism with example.

Ans. Geometrical isomerism: - This type of isomerism occurs in disubstituted complexes with coordination number 4 or 6 having square planar and octahedral arrangement respectively. It does not occur in tetrahedral complexes. When similar groups are opposite to each other, it is called trans isomers, whereas when similar groups same side with each other, it is called cis isomers.



Q. 2. Describe the crystal field theory.

Ans. The crystal field theory is based on the following assumptions.
1. The attraction between the central metal and the ligand is purely electrostatic.
2. The transition metal atom or ion is considered as a positive ion of charge equal to the oxidation state.
3. The transition metal atom or ion is surrounded by a definite number of ligands. The ligands may be negative ions or neutral molecules having lone-pair of electrons.
4. The attraction between the central metal ion and the ligands in a complex is purely electrostatic. The negative end of the dipole of the neutral molecule ligand is directed towards the metal ion.
5. The ligands are considered as point charges and produce an electric field. This electric field changes the energy of the orbitals on the metal atom or ion.
6. The electrons on the central metal ion experience repulsive force from those on the ligands. As a result, electrons on the metal ion occupy the d-orbitals as far away as possible from the direction of approach of ligands.
7. There is no interaction between the metal orbital and ligand orbitals.
8. In an isolated metal atom or ion, all d-orbitals have the same energy, i.e., all five d-orbitals are degenerate

Q. 3. Write the formulas for the following coordination compounds:
(i) Tetraamminediaquacobalt(III) chloride
(ii) Potassium tetracyanonickelate(II)
(iii) Tris(ethane−1,2−diamine) chromium(III) chloride
(iv) Amminebromidochloridonitrito-N-platinate(II)
(v) Dichloridobis(ethane−1,2−diamine)platinum(IV) nitrate
(vi) Iron(III) hexacyanoferrate(II)

Ans.

$[CO(H_2O)_2(NH_3)_4]Cl_3$

$K_2[Ni(CN)_4]$

$[Cr(en)_3]Cl_3$

$[Pt(NH)_3BrCl(NO_2)]^-$

$[PtCl_2(en)_2](NO_3)_2$

$Fe_4[Fe(CN)_6]_3$

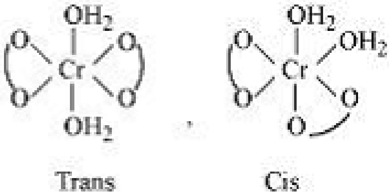
Q. 4. Write the IUPAC names of the following coordination compounds.
(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Co(NH_3)5Cl]Cl_2$
(iii) $K_3[Fe(CN)_6]$
(iv) $K_3[Fe(C_2O_4)_3]$
(v) $K_2[PdCl_4]$
(vi) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$

Ans. (i) Hexaamminecobalt(III) chloride
(ii) Pentaamminechloridocobalt(III) chloride
iii) Potassium hexacyanoferrate(III)
(iv) Potassium trioxalatoferrate(III)
(v) Potassium tetrachloridopalladate(II)
(vi) Diamminechlorido(methylamine)platinum(II) chloride

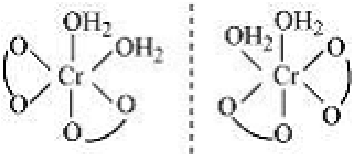
Q. 5. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:
i. $K[Cr(H_2O)_2(C_2O4)_2]$
ii $[Co(en)_3]Cl_3$
iii $[Co(NH_3)5(NO_2)](NO_3)_2$
iv. $[Pt(NH_3)(H_2O)Cl_2]$

Ans.i) Both geometrical (cis-, trans-) isomers for $K[Cr(H_2O)_2(C_2O_4)_2]$ can exist. Also, optical isomers for cis-isomer exist.

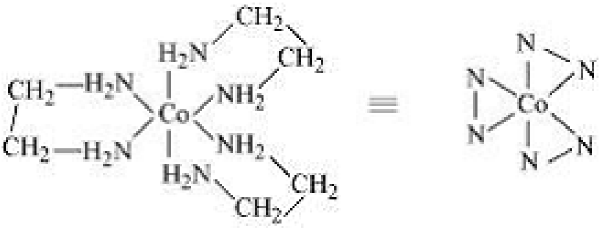
Geometrical isomers



Trans-isomer is optically inactive. On the other hand, cis-isomer is optically active.



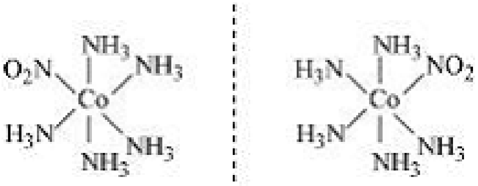
(ii) Two optical isomers for $\left[CO(en)_3\right]Cl_3$ exist.



Two optical isomers are possible for this structure.

(iii) $\left[CO(NH_3)_5(NO_2)\right](NO_3)_2$

A pair of optical isomers:



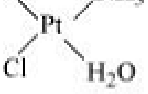
It can also show linkage isomerism.

$\left[CO(NH_3)_5(NO_2)\right](NO_3)_2$ and $\left[CO(NH_3)_5(ONO)\right](NO_3)_2$

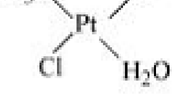
It can also show ionization isomerism.

$\left[Co(NH_3)_5(NO_2)\right](NO_3)_2$ $\left[CO(NH_3)_5(NO_3)\right](NO_3)(NO_2)$

(iv) Geometrical (cis-, trans-) isomers of $\left[Pt(NH_3)(H_2O)Cl_2\right]$ can exist.



Cis



Trans

Q. 6. Give evidence that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5SO_4]Cl$ are ionization isomers.

Ans. When ionization isomers are dissolved in water, they ionize to give different ions. These ions then react differently with different reagents to give different products.

$$\left[CO(NH_3)_5Cl\right]SO_4 + Ba^{2+} \longrightarrow \underset{\text{White precipitate}}{BaSO_4\downarrow}$$

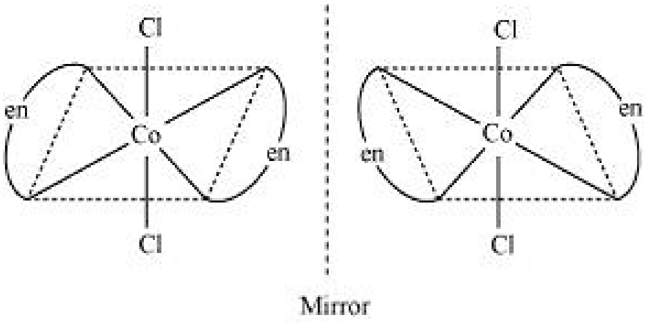
$$\left[CO(NH_3)_5Cl\right]SO_4 + Ag^{+} \longrightarrow \text{No reaction}$$

$$\left[CO(NH_3)_5SO_4\right]Cl + Ba^{2+} \longrightarrow \text{No reaction}$$

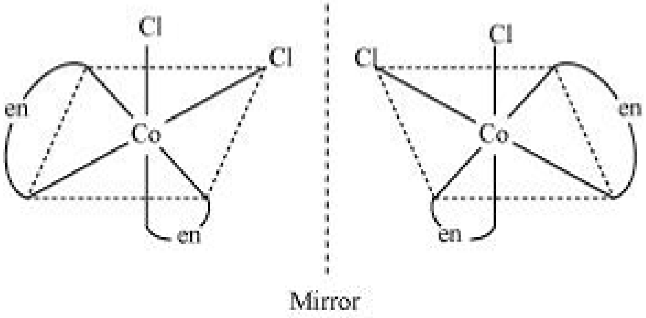
$$\left[CO(NH_3)_5SO_4\right]Cl + Ag^{+} \longrightarrow \underset{\text{White precipitate}}{AgCl\downarrow}$$

Q. 7. Draw all the isomers (geometrical and optical) of:
(i) $[CoCl_2(en)_2]+$
(ii) $[Co(NH_3)Cl(en)_2]_{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]+$

Ans.
1. $[CoCl_2(en)_2]+$



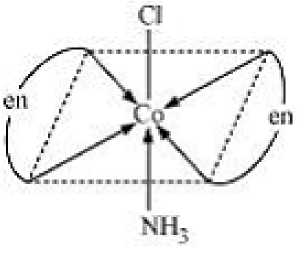
Trans $[CoCl_2(en)_2]^+$ isomer-optically inactive
(Superimposable mirror images)



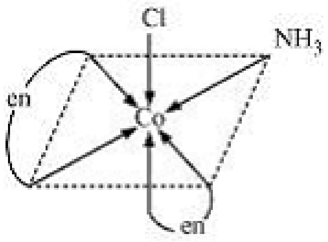
Cis $[CoCl_2(en)_2]^+$ isomer-optically active
(Non-superimposable mirror images)

In total, three isomers are possible.

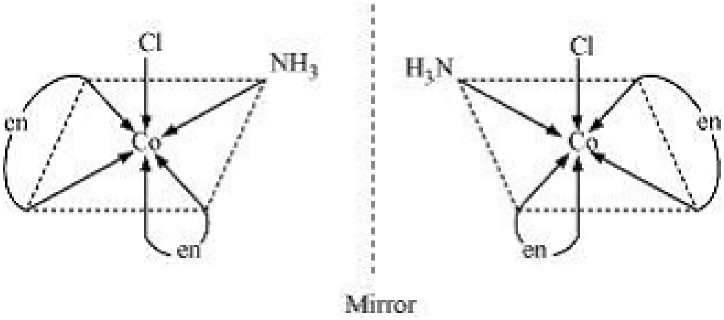
2. $[Co(NH_3)Cl(en)_2]_{2+}$



Trans



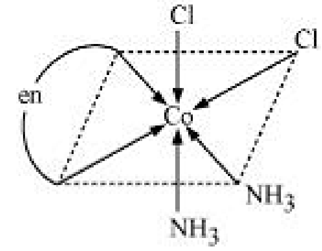
Cis

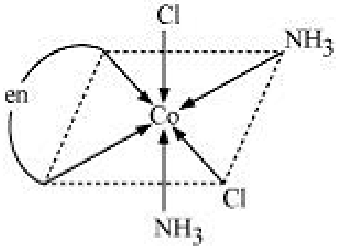


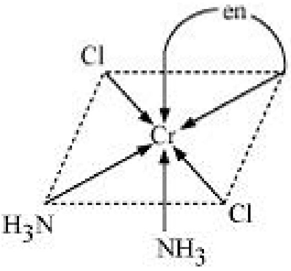
Trans-isomers are optically inactive.

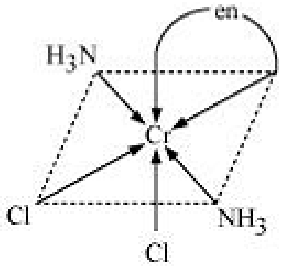
Cis-isomers are optically active.

3. $[Co(NH_3)_2Cl_2(en)]+$



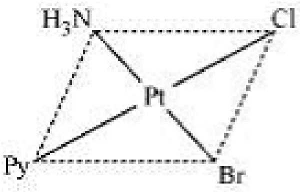


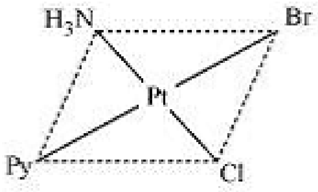


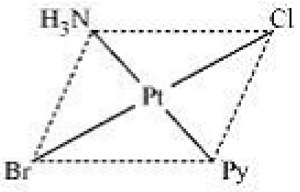


Q. 8**.** Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

Ans. $[Pt(NH_3)(Br)(Cl)(py)$







From the above isomers, none will exhibit optical isomers. Tetrahedral complexes rarely show optical isomerization. They do so only in the presence of unsymmetrical chelating agents.

Q. 9. Aqueous copper sulphate solution (blue in colour) gives:
(i) a green precipitate with aqueous potassium fluoride, and }
(ii) a bright green solution with aqueous potassium chloride Explain these experimental results.

Ans. Aqueous $CuSO_4$ exists as [Cu(H2O)$_4$]SO_4. It is blue in colour due to the presence of
[Cu[H_2O)$_2$+ ions.
(i) When KF is added:

$$\left[Cu(H_2O)_4\right]^{2+} + 4F^- \longrightarrow \underset{(green)}{\left[Cu(F)_4\right]^{2-}} + 4H_2O$$

(ii) When KCl is added:

$$\left[Cu(H_2O)_4\right]^{2+} + 4Cl^- \longrightarrow \underset{(bright\ green)}{\left[CuCl_4\right]^{2-}} + 4H_2O$$

In both these cases, the weak field ligand water is replaced by the F− and Cl− ions.

Q. 10**.** What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when$_2$S(g) is passed through this solution?

Ans.

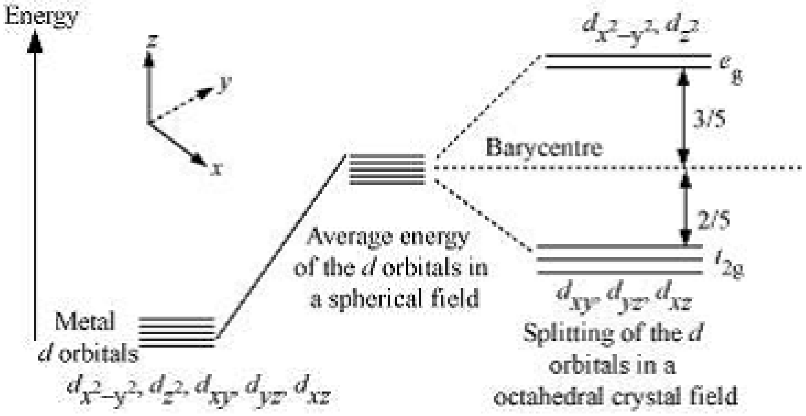
$$CuSO_{4(aq)} + 4KCN_{(aq)} \longrightarrow K_2\left[Cu(CN)_4\right]_{(aq)} + K_2SO_{4(aq)}$$

i.e $\left[Cu(H_2O)_4\right]^{2+} + 4CN^- \longrightarrow \left[Cu(CN)_4\right]^{2-} + 4H_2O$

Thus, the coordination entity formed in the process is K_2[Cu(CN)$_2$]. $K_2\left[Cu(CN)_4\right]$ is a very stable complex, which does not ionize to give Cu^{2+} ions when added to water. Hence, Cu^{2+} ions are not precipitated when H_2S(g) is passed through the solution.

Q. 11**.** Draw figure to show the splitting of d orbitals in an octahedral crystal field.

Ans.



The splitting of the d orbitals in an octahedral field takes palce in such a way that , experience a rise in energy and form the eg level, while dxy, dyzand dzx experience a fall in energy and form the t2g level.

Q. 12. Discuss briefly giving an example in each case the role of coordination compounds in:
(i) biological system
(ii) medicinal chemistry
(iii) analytical chemistry
(iv) extraction/metallurgy of metals

Ans.
(i) Role of coordination compounds in biological systems.
We know that photosynthesis is made possible by the presence of the chlorophyll pigment. This pigment is a coordination compound of magnesium. In the human biological system, several coordination compounds play important roles. For example, the oxygen-carrier of blood, i.e., haemoglobin, is a coordination compound of iron.
(ii) Role of coordination compounds in medicinal chemistry:
Certain coordination compounds of platinum (for example, cis-platin) are used for inhibiting the growth of tumours.
(iii) Role of coordination compounds in analytical chemistry:
During salt analysis, a number of basic radicals are detected with the help of the colour changes they exhibit with different reagents. These colour changes are a result of the coordination compounds or complexes that the basic radicals form with different ligands.
(iii) Role of coordination compounds in extraction or metallurgy of metals:
The process of extraction of some of the metals from their ores involves the formation of complexes. For example, in aqueous solution, gold combines with cyanide ions to form $[Au(CN)_2]$. From this solution, gold is later extracted by the addition of zinc metal.

Q. 13. How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?
(i) 6

(ii) 4

(iii) 3

(iv) 2

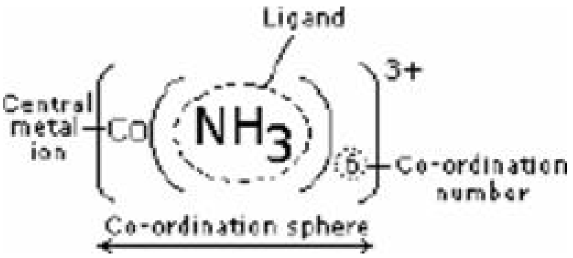
Ans.
(iii) The given complex can be written as $[Co(NH_3)_6]Cl_2$.
Thus, $[Co(NH_3)_6]$+ along with two Cl− ions are produced.

Q. 14. The oxidation number of cobalt in $K[Co(CO)_4]$ is
(i) +1
(ii) +3
(iii) −1
(iv) −3

Ans. We know that CO is a neutral ligand and K carries a charge of +1. Therefore, the complex can be written as K+[Co(CO)4]−. Therefore, the oxidation number of Co in the given complex is −1. Hence, option
(iii) is correct.

Q. 15. (a) What are co-ordinate compounds, define (i) Complexes (ii) Ligand (iii) Chelating agent (iv) Co-ordination number (v) Charge on a complexion. (b) What are various rules for the nomenclature of a complex compound?

Ans . (a) **Co-ordination compounds :** These are the complex substances which contain a central metal atom or ion surrounded by oppositively charged ions or neutral molecules. These are stable in solid state as well as in dissolved state i.e., The constituent is not retained in solutions. For example $NiCl_6$ $4NH_3$ is stable in solid state as well as in aqueous solution. Its aqueous solution does not give test for Ni++ or Cl- and NH_4. It is also defined as a compound which contains a complex ion.
(i) **Complex ion** d-block elements or their ions have valence vacant d-orbitals, high nuclear charge of their atoms or ions, accommodate lone pair of electrons from electron pair donors. These new ions so formed are called complex ions.
(ii) **Ligands :** The cluster of anions or molecules which surround the central metal ion are called ligands or an atom or group of atoms which binds to the central atom through the lone pair of electrons present in the donor atom. Depending on number of pairs donated
(iv) **Chelating ligand :** If a polydentate ligand forms a cyclic complex with central metal ion it is termed as chelating ligand.
(iv) **Co-ordination number or valency :** The total number of ligands surrounding the central atom in co-ordination sphere is the co-ordination number
(v) **Charge on complex ion :** The sum of oxidation number of all atoms/molecules/ions constituting the co-ordination sphere is the charge on the complex for



example

Ans. (b) **Rules for nomenclature are :**

(i) The positive part of a co-ordination compound is named first and is followed by the negative part.

(ii) The ligands are named first followed by the central metal. The prefixes DI-trio-tetra etc. are used to indicate the number of each kind of ligand present. The prefixes is (two ligands) tries (three ligands) etc. are used when the polydentate ligands surround the central atom.

(iii) The ligands are named in _, _, order. Names of anionic ligands end in O, those of cationic in ium. Neutral ligands have their regular names except that H_2O is named as aquo, NH_3as ammine, NO as Nitrosyl and CO as carbonyl.

(iv) The oxidation state of the central metal is indicated in Roman number in Parentheses.

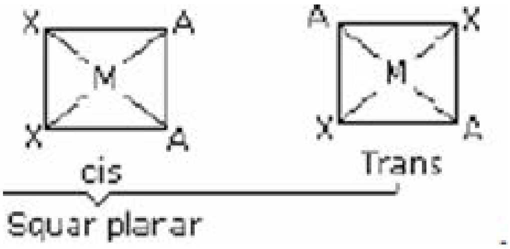
(v) When a complex species has a negative charge, the name of the central metal ends in ate. For some elements, the ion name is based on the Latin name of the metal for example, argentate for silver.

Example : $[Cr(H_2O)_4Cl_2]Cl$ tetraquo dichloro chromium (III) chloride. $[Co(en)_2Cl_2]Cl$, bisethylene diammine dichloro cobalt (III) chloride.

$K_4|Fe(CN)_6|$ potassium hexa cyano Ferrate (II).

Q. 16. Explain geometrical isomerism in Square planar and octahedral complexes..

Ans. (i) **Geometrical isomerism :** Arises when the two identical ligands either occupy adjacent positions to each other (cis) or are opposite to each other (trans). Square planar complexes of the type MA_2X_2, $MABX_2$, MA_3X_3 (where A and Y) are monodendate, show geometrical isomerism



show geometrical isomerism. .

(ii) Apart from these complexes square planar complexes having unsymmetrical ligands can also show geometrical isomers e.g $|Pt(gly)_2]$

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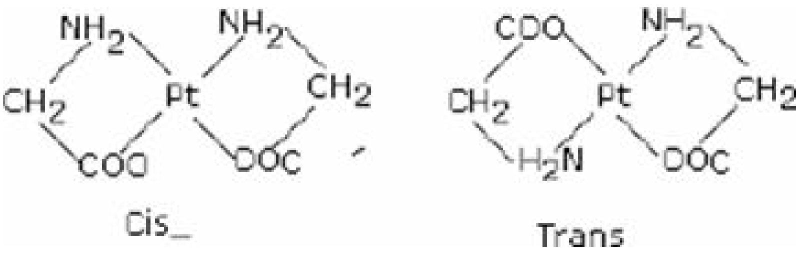

Cis_

Trans

Q. 17**.** What is effective atomic number?

Ans. EAN (Effective atomic number) : EAN is defined as the total number of electrons on the metal atom or ion after the complex formation. For example in a metal carbonyl represented by the formula M(CO)x, the value of x can be given on the basis of EAN. If M is Fe (Z = 26) or Cr(Z = 24), than value of x = 5 and 6 respectively. It is because the sum of atomic number of iron (2 **x** 5) = 10 electron form five Co ligands will be equal to 36 i.e., atomic number of nearest noble gas krypton.