Isomerism in Coordination Complexes

Isomers are compounds having the same number and kinds of atoms arranged differently. The phenomena of existence of isomers is called *isomerism*. Since their structural arrangements are different, the properties of isomers are also different. Isomers can be broadly classified into two types, each type having further sub-classifications.

Isomerism

- **Structural Isomerism**
  1. Ionization isomerism
  2. Hydrate isomerism
  3. Linkage isomerism
  4. Coordination isomerism
  5. Coordination position isomerism
  6. Ligand isomerism
  7. Polymerisation isomerism
- **Stereoisomerism**
  1. Geometrical isomerism
  2. Optical isomerism

Structural Isomerism

Structural isomers are those which contain different atom-to-atom bonding sequences. These involve either more than one coordination sphere or different donor atoms of the same ligand in the same coordination sphere.

(1) Ionization Isomerism

The isomers which involve exchange of ligands between coordination sphere and ionization sphere are called ionization isomers. Ionisation isomers show different properties. For example,

(a) $[Co(NH_3)_5Cl]SO_4$ and
pentamminechlorocobalt(III) sulfate
$[Co(NH_3)_5SO_4]Cl$
pentamminesulfatocobalt(III) chloride

In pentamminechlorocobalt(III) sulfate complex, the chloro ligand is in the coordination sphere, while the sulfate group is in the ionization sphere. An aqueous solution of this complex, on treatment with barium chloride, yields white precipitates of barium sulfate.

$$[Co(NH_3)_5Cl]SO_4 + BaCl_2 \longrightarrow [Co(NH_3)_5Cl]Cl_2 + \underset{\text{White ppt}}{BaSO_4}\downarrow$$

In pentamminesulfatocobalt(III) chloride complex, the sulfato ligand is in the coordination sphere, whi the chloride group is in the ionization sphere. With silver nitrate, an aqueous solution of this comple yields white precipitates of silver chloride.

$$[Co(NH_3)_5SO_4]Cl + AgNO_3 \longrightarrow [Co(NH_3)_5SO_4](NO_3) + \underset{\text{White}}{AgCl}\downarrow$$

(b) $[Co(NH_3)_5Br]SO_4$ is red violet. An aqueous solution of this compound gives a white ppt. of $BaSO_4$ with $BaCl_2$ solution. Thus confirming the presence of free SO_4^{2-} ions. In contrast $[Co(NH_3)_5(SO_4)]Br$ is red. A solution of this complex does not give a positive test of SO_4^{2-} with $BaCl_2$. It does give a cream coloured ppt. of AgBr with $AgNO_3$ solution, thus confirming the presence of free Br^- ions.

$$\underset{(I)}{[Co(NH_3)_5Br]SO_4} + \underset{(Solution)}{BaCl_2} \longrightarrow \underset{White\ ppt.}{BaSO_4} + [Co(NH_3)_5Br]Cl_2$$

$$\underset{(I)}{[Co(NH_3)_5Br]SO_4} + \underset{(Solution)}{AgNO_3} \longrightarrow \text{No Reaction}$$

$$\underset{(II)}{[Co(NH_3)_5SO_4]Br} + \underset{(Solution)}{BaCl_2} \longrightarrow \text{No Reaction}$$

$$\underset{(I)}{[Co(NH_3)_5SO_4]Br} + \underset{(Solution)}{AgNO_3} \longrightarrow \underset{Yellow\ ppt.}{AgBr} + [Co(NH_3)_5SO_4]NO_3$$

Other examples of ionisation isomers are:

(a) $[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4Cl(NO_2)]Cl$

(b) $[Pt(NH_3)_4Cl_2]Br_2$ and
tetramminedichloroplatinum(IV) bromide
$[Pt(NH_3)_4Br_2]Cl_2$
tetramminedibromoplatinum(IV) chloride

(c) $[Co(en)_2NO_2Cl]SCN$
chlorobis(ethylene diamine)nitrocobalt(III) thiocyanate

$[Co(en)_2NO_2SCN]Cl$ and
bis(ethylene diamine)nitrothiocyanato-Scobalt(III) chloride

$[Co(en)_2SCNCl]NO_2$
chlorobis(ethylene diamine)thiocyanato-S cobalt(III) nitrite