(4) Coordination Isomerism

Salts that contain complex cations and anions may exhibit isomerism through the interchange of ligands, between cation and anion. For example, both hexaamminecobalt(III) hexacyanochromate(III), [Co(NH₃)₆][Cr(CN)₆] and its coordination isomer, [Cr(NH₃)₆][Co(CN)₆], are known. Another example is [Cu(NH₃)₄][PtCl₄] and [Pt(NH₃)₄][CuCl₄] in which the isomers differ in color (as a result of the d^o Cu²⁺ chromophore), being violet and green, respectively.

Coordination isomers are obtained when some or all ligands of both the coordination spheres are interchanged with each other. Thus both the complex compounds of each of the following pairs are coordination isomers to each other. In these pairs the central metallic atom in the two coordination spheres may be the same or different.

(i) $[Cr^{3+}(NH_3)_6]^{3+}[Cr^{3+}(CN)_6]^{3-}$ and $[Cr^{3+}(NH_3)_4(CN)_2]^+[Cr^{3+}(CN)_4(NH_3)_2]^-$

(ii) $[Pt^{2+}(NH_3)_4]^{2+} [Pt^{2+}Cl_4]^{2-}$ and $[Pt^{2+}(NH_3)_3Cl]^+ [Pt^{2+}Cl_3(NH_3)]^-$

(iii) $[Co^{3+}(NH_3)_6]^{3+}[Cr^{3+}(CN)_6]^{3-}$ and $[Co^{3+}(CN)_6]^{3-}[Cr(NH_3)_6]^{3+}$

(iv) $[Cr^{3+}(NH_3)_6]^{3+}[Cr^{3+}(SCN)_6]^{3-}$ and $[Cr^{3+}(NH_3)_4(SCN)_2]^+[Cr^{3+}(SCN)_4(NH_3)_2]^-$

(5) Coordination Position Isomerism

This type of isomerism is shown by those complex compounds which contain bridging ligands and arises when the non-bridging ligands are differently placed round the central metal atom. Thus (I) and (II) are coordination position isomers to each other, since NH₃ molecules and Cl ions (non-bridging ligands) are differently placed round the two Co³⁺ ions.

$$\begin{bmatrix} H \\ (NH_3)_4Co^{3+} & O \\ O \\ H \end{bmatrix}^{2+} \\ \begin{bmatrix} Cl(NH_3)_3Co^{3+} & O \\ O \\ H \end{bmatrix}^{2+} \\ \begin{bmatrix} Cl(NH_3)_3Co^{3+} & O \\ O \\ H \end{bmatrix}^{2+} \\ Cl(NH_3)_3Co^{3+} & O \\ H \end{bmatrix}^{2+} \\ Chloro triammine cobalt(III) μ-dihydroxo chloro triammine cobalt(III) μ-dihydroxo chloro triammine cobalt(III) ion. (II) (symmetrical) \\ \end{bmatrix}^{2+}$$

The following binuclear complexes of cobalt also show coordination position isomerism, since the terminal ligands viz. six NH₃ molecules and two Cl ions can be placed in an unsymmetrical and symmetrical manner round the central cobalt ion.

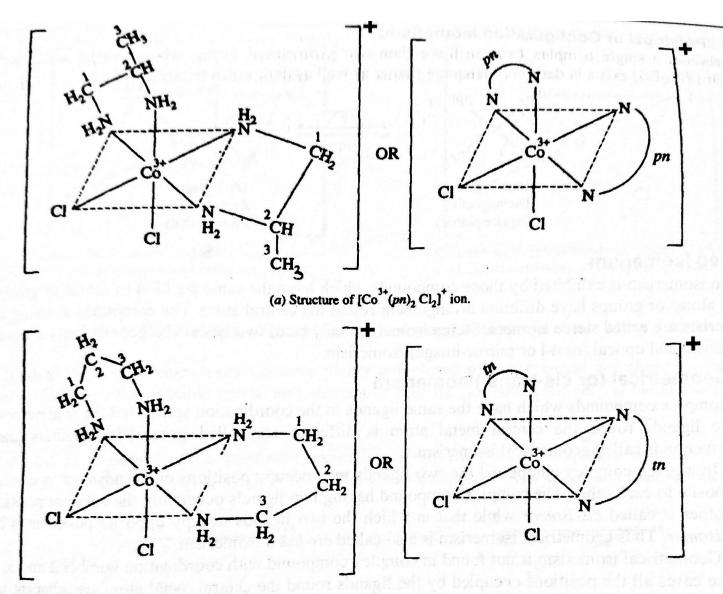
$$\left[(NH_3)_4 Co^{3+} \underbrace{ \begin{pmatrix} NH_2 \\ O_2 \end{pmatrix}}_{\text{(a) unsymmetrical}} Co^{3+} (NH_3)_2 Cl_2 \right]^{2+} \qquad \left[(NH_3)_3 ClCo^{3+} \underbrace{ \begin{pmatrix} NH_2 \\ O_2 \end{pmatrix}}_{\text{(b) symmetrical}} Co^{3+} Cl(NH_3)_3 \right]^{2+}$$

(6) Ligand Isomerism

Since many ligands are organic compounds which have possibilities for isomerism, the resulting complexes can show isomerism from this source. Examples of isomeric ligands are 1,2-diaminopropane ("propylenediamine,"pn) and 1,3-diaminopropane ("trimethylendediamine,"tn) or ortho-, metra- and para toluidine (CH₃C₆H₄NH₂).

Diamine derivatives of propane exist in two isomeric forms which are called 1, 2-diamino propane or propylene diamine (pn) and 1, 3-diamino propane or trimethylene diamine (tn). The structures of propane, pn and tn are given below:

pn and tn both are bidentate (neutral) ligands. When these ligands get coordinated to the metal atom, two isomers are obtained. These are called ligand isomers and the isomerism is called ligand isomerism. Thus $[\mathrm{Co}^{3+}(pn)_2\mathrm{Cl}_2]^+$ and $[\mathrm{Co}^{3+}(tn)_2\mathrm{Cl}_2]^+$ are ligand isomers whose structures are given below. Both these isomers have octahedral geometry.



(b) Structure of $[Co^{3+}(tn)_2 Cl_2]^+$ ion. Structure of $[Co(pn)_2 Cl_2]^+$ and $[Co(tn)_2 Cl_2]^+$ ions.