### (2) Solvate Isomerism or Hydrate Isomerism

When water (solvent) molecules are interchanged between coordination sphere and ionisation sphere, the resulting isomers are called hydrate (or solvate) isomers.
This is a somewhat special case of the above interchange of ligands involving neutral solvate molecules.
The best known example involves isomers of "chromic chloride hydrates" of which three are known:
$[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$. These differ in their reactions:

$$[Cr(H_2O)_6]Cl_3 \xrightarrow{\text{dehydr.over } H_2SO_4} [Cr(H_2O)_6]Cl_3 \text{ (no change)}$$

$$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O \xrightarrow{\text{dehydr.over } H_2SO_4} [Cr(H_2O)_5Cl]Cl + H_2O$$

$$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O \xrightarrow{\text{dehydr.over } H_2SO_4} [Cr(H_2O)_4Cl_2]Cl + 2H_2O$$

$$[Cr(H_2O)_6]Cl_3 \xrightarrow{Ag^+} [Cr(H_2O)_6]^{3+} + 3AgCl(s)$$

$$[Cr(H_2O)_5Cl]Cl_2 \xrightarrow{Ag^+} [Cr(H_2O)_5Cl]^{2+} + 2AgCl(s)$$

$$[Cr(H_2O)_4Cl_2]Cl \xrightarrow{Ag^+} [Cr(H_2O)_4Cl_2]^+ + AgCl(s)$$

## (3) Linkage Isomerism

It deals with ligands having two potentially ligating atoms that are capable of bonding through one type of donor atom in the situation but a different donor atom in another complex.

The first example of this type of isomerism was provided by Jorgense, Werner's contemporary. His method of preparation was as follows:

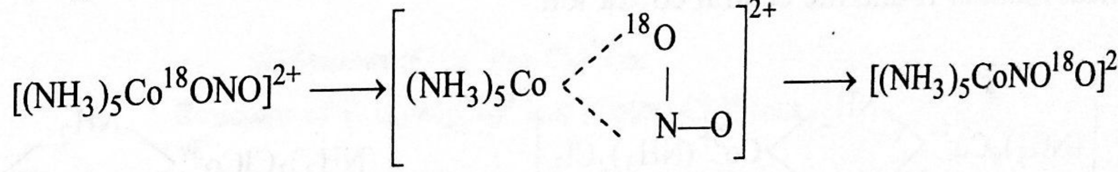
$$[Co(NH_3)_5Cl]Cl_2 \xrightarrow{NH_3} \xrightarrow{HCl} \xrightarrow{NaNO_2} \text{“Solution A”}$$

$$\text{“Solution A”} \xrightarrow{\text{Let stand in cold}} [(NH_3)_5CoONO]Cl_2 \text{ red}$$

$$\text{“Solution A”} \xrightarrow{\text{Heat}} \xrightarrow[\text{Conc. HCl}]{\text{Cool}} [(NH_3)_5CoNO_2]Cl_2 \text{ Yellow}$$

Jorgensen and Werner agreed that the difference between the two isomers resides in the linkage of the $NO_2$ group to the cobalt. The N-bonded (or “nitro”) structure was assigned to the yellow isomer and the O-bonded (or “nitro”) structure to the red isomer on the basis of the color of similar compounds.

Murmann and Taube showed that on $^{18}O$ labeled nitrite complex may be caused to rearrange by heating. In this process no loss of $^{18}O$ is found even in the presence of excess nitrite, confirming that the reaction is an inramolecular rearrangement:



$$[(NH_3)_5Co^{18}ONO]^{2+} \longrightarrow \left[ (NH_3)_5Co \begin{matrix} {}^{18}O \\ | \\ N{-}O \end{matrix} \right]^{2+} \longrightarrow [(NH_3)_5CoNO^{18}O]^{2+}$$

### Electronic Effects

The first thiocyanate linkage isomers were isolated after it was noted that the structures of cis complexes containing thiocyanate and either ammonia or phosphine were S- or N-linked, respectively. The hypothesis provided was that these isomers were more stable than the alternatives (i.e., S-bonded in the phosphine complex, N-bonded in the ammine complex) because of the competition for π bonding orbitals on the metal. The phosphine forms the best π bond and hence tends to monopolize the π bonding *d* orbitals of the platinum, reducing the stability of the weaker sulfur π bond, hence the thiocyanate ion bonds through the nitrogen atom. In the absence of competition for π orbitals (ammonia cannot form a π bond), the sulphur atom is preferentially bonded. Using this hypothesis as a basis, Basolo and coworkers attempted to find complexes in which the π bonding tendencies were balanced, allowing the isolation of both isomers. Examples of the complexes thus isolated are $[(Ph_3As)_2Pd(SCN)_2]$, $[(Ph_3As)_2Pd(NCS)_2]$, and $[(bpy)Pd(SCN)_2]$, $[(bpy)Pd(NCS)_2]$. In both cases, on warming, the S-bonded isomer is converted to the N-bonding isomer, which is presumably slightly more stable.

## (4) Co