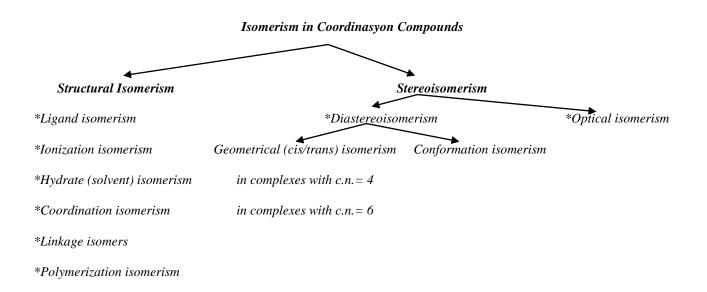
# PROF. DR. SELEN BİLGE KOÇAK

CHM0308 INORGANIC CHEMISTRY II

### **ISOMERISM IN COORDINATION COMPOUNDS**

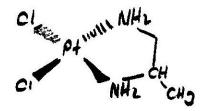


### STRUCTURAL ISOMERISM

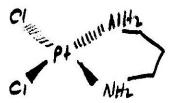
Structural isomers are molecules which have the same molecular formula but have different connectivities.

### Ligand Isomerism

Ligand isomerism is the result of the reflection of the isomerism in the ligand in the complex. The binding of ligands is different, although the isomeric structures all have the same metalligand bonds. For example, complexes  $[PtCl_2(1-methyl-1,2-diaminopropane)]$  and  $[PtCl_2(1,3-diaminopropane)]$  are ligand isomers of each other.



[PtCl<sub>2</sub>(1-methyl-1,2-diaminopropane)]



[PtCl<sub>2</sub>(1,3-diaminopropane)]

### Ionization Isomerism

Ionization isomerism arises from the displacement of ions in the primary valency (outside of the coordination sphere) with ions in the secondary valency (inside of the coordination sphere). Ionization isomers afford different anions and cations in solution. Thus, the ionization isomers can be distinguished from each other easily because they give different ions when dissolved in water. For example,  $[Co(NH_3)_5Br]SO_4$  (red-purple color) and  $[Co(NH_3)_5SO_4]Br$  (red color) are ionization isomers of each other.



[co (NH3); Br] SO4 H10 [Co (NH3); Br]<sup>2+</sup> + SO4<sup>2-</sup> B3C/2 [Co (NH3); Br] C12 + B2SO4(+) [Co (NH3); SO4] Br H20 [Co (NH3); SO4] + Br- A3NO3 [Co (NH3); SO4] NO2 + AgBr(x) 4

Hydrate (Solvent) Isomerism:

Hydrate (solvent) isomerism occurs when water (or other solvent) can appear within the primary or secondary valency (coordination sphere) of a metal ion. That is, in the coordination compound  $H_2O$  may be a ligand or a crystal water.

 $\left[ Cr(H_2O)_6 \right] Cl_3$ violet crystals  $\left[ CrCl(H_2O)_5 \right] Cl_2 \bullet H_2O$ blue-green crystals  $\left[ CrCl_2(H_2O)_{4} \right] Cl \bullet 2H_2O$ 

dark green crystals

 $\left[ CrCl_3(H_2O)_3 \right] \bullet 3H_2O$ 

yellow-green crystals

 $\begin{bmatrix} Cr(H_{10})_{6} \end{bmatrix} Cl_{3} & \xrightarrow{H_{2}IO_{4}} \\ \begin{bmatrix} Cr(H_{10})_{5}CI \end{bmatrix} Cl_{2} - H_{10} & \xrightarrow{H_{1}SO_{4}} \\ \begin{bmatrix} CH_{2}O^{+} \end{pmatrix}_{+} (H_{SO_{4}}) \end{bmatrix} + \begin{bmatrix} Cr(H_{2}O)_{5}CI \end{bmatrix} Cl_{2} \\ \begin{bmatrix} Cr(H_{1}O)_{4}CI_{2} \end{bmatrix} Cl_{2} + 2H_{10} & \xrightarrow{H_{1}O_{4}} \\ 2 \end{bmatrix} \begin{bmatrix} CH_{2}O^{+} \end{pmatrix}_{+} (H_{3}O_{5}) \end{bmatrix} + \begin{bmatrix} Cr(H_{10})_{5}CI_{2} \end{bmatrix} Cl_{2} \\ \begin{bmatrix} Cr(H_{10})_{4} \end{bmatrix} Cl_{3} + 2H_{10} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{6} \end{bmatrix} Cl_{3} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{6} \end{bmatrix} Cl_{3} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{6} \end{bmatrix} Cl_{3} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{6} \end{bmatrix} Cl_{3} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{5}CI \end{bmatrix} Cl_{1} & H_{10} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{5}CI \end{bmatrix} Cl_{1} & H_{10} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{5}CI \end{bmatrix} Cl_{3} + 2H_{7}O_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(H_{10})_{4}Cl_{2} \end{bmatrix}^{2} + NO_{7}^{-} + 2H_{7}CI(L_{7}) \\ \begin{bmatrix} Cr(H_{10})_{5}Cl_{3} \end{bmatrix} 2H_{10} + H_{7}NO_{3} & \xrightarrow{H_{1}O} \\ \begin{bmatrix} Cr(CH_{10})_{4}Cl_{2} \end{bmatrix}^{2} + NO_{7}^{-} + H_{7}CI(L_{7}) \\ \end{bmatrix} Cl_{3} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}NO_{3} & \xrightarrow{H_{1}O} \\ \end{bmatrix} Cr(H_{10})_{5}Cl_{3} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}NO_{7} & \xrightarrow{H_{1}O} \\ \end{bmatrix} Cr(H_{10})_{4}Cl_{2} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cr(H_{10})_{5}Cl_{3} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cr(H_{10})_{5}Cl_{3} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cr(H_{10})_{5}Cl_{3} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cr(H_{10})_{5}Cl_{3} \end{bmatrix} Cl_{3} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cr(H_{10})_{7} \\ \end{bmatrix} Cl_{7} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cl_{7} \\ \end{bmatrix} Cl_{7} \\ \end{bmatrix} Cl_{7} + H_{1}O + H_{7}O_{7} \\ \end{bmatrix} Cl_{7}  

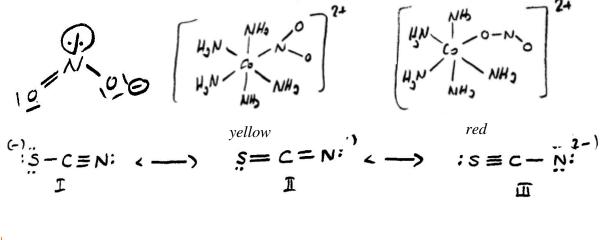
### Coordination Isomerism

In the coordination compounds that both anion and cation are complex ions, coordination isomerism occurs when ligands can be distributed differently between two or more metals. It is available in complexes containing two or more metal ions. For example, complexes  $[Co(NH_3)_6][Cr(CN)_6]$  and  $[Co(CN)_6][Cr(NH_3)_6]$  are coordination isomers of each other. It is also readily apparent that the 6 isomers of this system will be taken into consideration when the ligands are partially displaced.

[co (NH3)6] [cr (cN)6] (co (NH3)5 (CN)] [cr (CN)5 NH3] [co (NH3)4 (CN)2] [cr (CN)4 (NH3)2] [co (NH3)2 (CN)2] [cr (CN)3 (NH3)2] [co (NH3)2 (CN)2] [cr (CN)2 (NH3)4] [co (NH3)2 (CN)2] [cr (CN)2 (NH3)4] [co (NH3) (CN)2] [cr (CN)2 (NH3)3] [co (CN)6] [cr (NH3)6]

### Linkage Isomerism

Linkage isomerism occurs when a ligand can bind in different ways to a metal. It is seen in complexes containing ligands which can be connected to the central atom by two different atoms. The most common examples are  $SCN^{-}$  (thiosionate) and  $NO_{2}^{-}$  (nitrite) ions.



Polymerization Isomerism

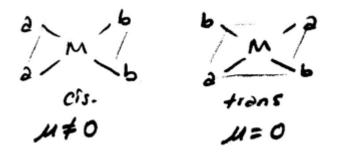
Although complexes have the same empirical formula, the formula masses of them are different from each other and the ratio of formula mass to empirical mass is 2,3,4,...

#### STEREOISOMERISM

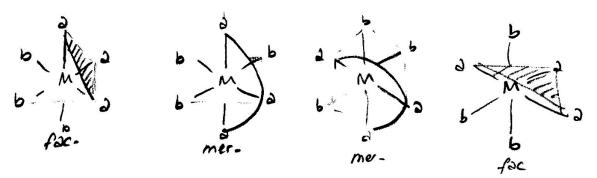
Stereoisomers are the compounds in which closed formulas and chemical bonds are the same as the order of bonding of the atoms according to each other, but the arrangement of the atoms in space is different in each isomer, and this phenomenon is called stereoisomerism. The two main types of stereoisomerism are: Diastereomerism (including cis/trans isomerism) and Optical isomerism (also known as enantiomerism and chirality)

#### Geometrical Isomerism

The ligands may originate from different configurations around the central atom (Square planar, tetrahedral), but they originate from the different order of the ligands (cis, trans) in the same geometrical shape. The compounds in which the geometric isomerism is observed are complexes with the coordination numbers 4 and 6. The geometrical isomerism is not observed in tetrahedral complexes since the ligands are adjacent and equivalent. The geometrical isomerism is seen in square planar complexes. In the cis-isomer, groups are on the same sade. In trans-isomers, grorups are on opposite sides.

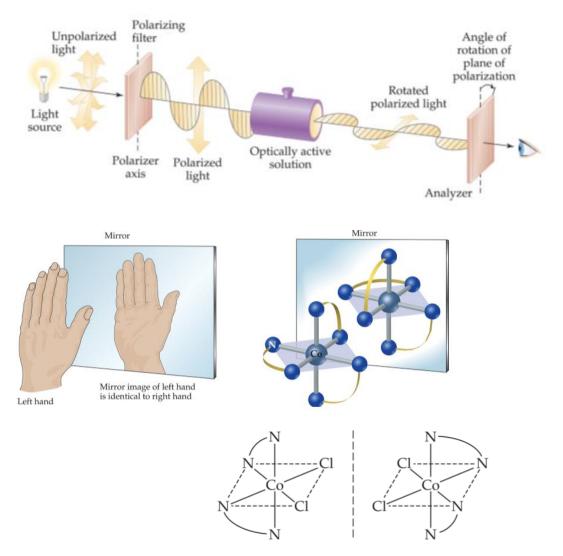


The complexes in the  $Ma_3b_3$  structure have two different isomers called fac (facial) and mer (meridional).

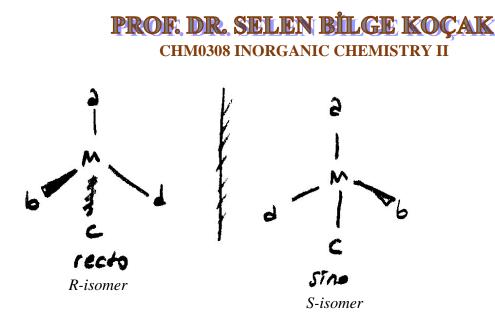


#### **Optical Isomerism**

Isomers that convert the vibration plane of the polarized light in different directions (right or left) are called optical isomers. Physical properties of optical isomers are identical (boiling point, freezing point, density, etc.) except the interaction of optical isomers with plane polarized light. Optical isomers are called enantiomers. Optical isomers or enantiomers, are mirror images of each other, such as the right and left hand, and cannot be superimposed on each other.



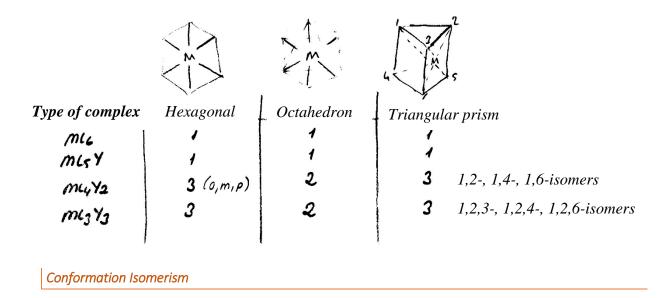
In a tetrahedral complex, there are enantiomers if the groups bound to the central atom are different from each other.



Non-superimposable mirror images

There are no optical isomers because there is a mirror or a symmetry plane in square plane structures.

Isomerism in complexes with coordination number 6



It is a rare diastereoisomerism in complexes. When a part of a molecule is rotated around a bond axis relative to the remainder of the molecule, the isomeric structures turning into each other are called the conformational isomer.