Compounds with the same formula, but different structures are called isomers, of which two types can be classified. These include structural isomer and stereoisomer. One type of structural isomerism that may arise when a ligand has more than one chemically distinct donor atom is linkage isomerism. Co(NH$_3$)$_5$(NO$_2$)$_2^+$ and Co(NH$_3$)$_5$(ONO)$_2^+$ can exemplify the case. It may be noteworthy here that the linkage isomers frequently adopt different names for different coordination modes.

\[
\begin{array}{c}
\text{(NH}_3\text{)}_5\text{Co} \quad \text{(NH}_3\text{)}_5\text{Co} \\
\text{N} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{N} \quad \text{O}
\end{array}
\]

pentaamminenitro cobalt (III)  pentaamminenitrito cobalt (III)

The other structural isomerism finding importance in coordination chemistry is coordination sphere isomerism, e.g.

\[
\begin{align*}
\text{[Cr(H}_2\text{O})_6]\text{Cl}_3 & \quad \text{violet} \\
\text{[Cr(H}_2\text{O})_5\text{Cl}]\text{Cl}_2\text{H}_2\text{O} & \quad \text{green} \\
\text{[Cr(H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2\text{H}_2\text{O} & \quad \text{green}
\end{align*}
\]

Stereoisomerism is the most common and most important class of isomerism, including geometrical isomerism, used to distinguish the phenomena that the same ligand binds to different sites on the metal. There are several types of geometrical isomer, namely cis and trans, fac- and mer-. Facial (fac) isomerism describes 3 of the same ligands lying on one face of an octahedron while meridional (mer) isomerism refers to 3 of the same ligands lying on a plane passing through the center of the complex (a meridian).
In this experiment, the geometrical isomerism will be studied. The ligand of interest is iminodiacetic acid (H$_2$IDA)

Name: Iminodiacetic acid
Synonyms: N-(Carboxymethyl)-glycine
Molecular Formula: (NH(CH$_2$COOH)$_2$)$_2$, C$_{4}$H$_{7}$N$_{4}$O$_{4}$
Molecular Weight: 133.10
When the ligand is coordinated to the metal ion, it becomes a tridentate ligand and its stereochemistry is of five membered amino acid ring. Coordinated to the Co$^{III}$ ion with give the coordination compound with the formula [Co(IDA)$_2$]$^-$, with three possible isomers.

The cobalt$^{III}$ system is chosen due to the highly colored isomers, i.e. purple and brown, both of which can be prepared at different temperatures. According to the possible straining of the C-N-C bond angle in the IDA$^-$ ligand, the trans(mer) isomer can be expected to be rather unstable and a reasonable assignment for the trans compound will be of trans(fac) geometrical configuration. It is also apparent that solubility of the trans isomer is considerably less than that of the corresponding cis isomer. This may be due to a possible intermolecular hydrogen bonds in the trans crystal, formed between the amine protons on one molecule and the carboxyl group on a neighboring molecule.

To identify the isomers, we would normally use molecular models, proton magnetic resonance (PMR) and visible absorption spectra. However in this experiment we will only use visible absorption spectra. On the basis of pmr experiment, the brown isomer can be assigned as the trans(fac) and therefore the purple isomer as the cis isomer. From the respective visible absorption spectra, a discussion of the expected splitting patterns of the $^1A_{1g} \rightarrow ^1T_{1g}$ (O$_h$) and $^1A_{1g} \rightarrow ^1T_{2g}$ (O$_h$) d-d transitions of the low-spin Co$^{III}$
(d⁶) complexes under the lower C₂ᵥ or D₄h symmetries of the isomers can be used to interpret the band profiles in the visible absorption spectra.

**Materials**

1. Solid potassium hydroxides
2. Iminodiacetic acid
3. Cobaltous chloride hexahydrate
4. Hydrogen peroxide (15% and 30%)

**Preparation of purple isomer of cis-K[Co(IDA)₂].2.5H₂O**

Dissolve 1.6 g of KOH using 6.5 ml of water in a 100 ml beaker. After completely dissolve KOH, dissolve further 2.0 g of iminodiacetic acid (H₂IDA), and then 1.7 g of CoCl₂.6H₂O in to a solution. Cool the solution to approximately 12°C using an ice bath. Then, add 5.0 ml of 15% H₂O₂ into a cool solution over a period of 2-3 min with stirring. While maintaining a temperature at about 12°C for 2-3 hour, the mixture should be stirred periodically. The purple crystalline product is finally collected using a Buchner funnel, washed first with one 4-5 ml portion of ice cold water, and then with a 10 ml portion of ethanol. Allow the solid product to dry at 80°C in an air-oven for one day. (1.5-2 g of solid should be obtained)

**Preparation of brown isomer of trans-K[Co(IDA)₂].2H₂O**

Dissolve KOH 1.6 g using 28 ml of water in a 100 ml beaker. Then dissolve 2.0 g of iminodiacetic acid and 1.7 g of CoCl₂.6H₂O, respectively, into the solution. After completely dissolve the reactants, heat the solution using a water bath to 80°C, before slowly adding 1 ml of 30% H₂O₂. (CAUTION! The reaction is vigorous.) After the reaction has ceased, cover the beaker with a watch glass and continue heating the solution for approximately 45 minutes. Place the beaker and cover in dark locker until the next laboratory period (for about a week). After a specified duration, collect the brown crystals by filtration using a Buchner funnel, wash first with a 5 ml portion of ice cold water, and then with a 10 ml portion of ethanol. Allow the crystals to dry at 80°C in an air-oven for one day. (Approximately 1.0 g of solid should be obtained)

**Collect visible absorption spectra**

Dissolve each isomer in water to the fix concentration of 0.01M for the purple isomer, \([\text{cis-K[Co(IDA)₂].2.5H₂O}]\), and 0.025M for the brown isomer, \([\text{trans-K[Co(IDA)₂].2H₂O}]\), using 25 ml
volumetric flasks. Collect the visible absorption spectra of each isomer in a 800-320 nm range using 1 cm glass cells. After this, submit the remained crystals to the instructor.

**Answer the following questions:**

1. Based on the experimental results, calculate the mole ratio between the metal and the ligand.
2. Draw all possible isomers for Ma₂bcd assuming a square pyramidal coordination.

**References**