C. ISOMERISM

Introduction:
The word *isomer* literally means, “having equal parts”, so compounds are isomers if they have the same number and types of parts—in this case *atoms*, but different properties. Isomers can be subdivided into two major categories: 1) *Stereoisomers* (with the same numbers and types of chemical bonds but differing in the spatial arrangement of those bonds), and 2) *Structural isomers* (with the differing numbers and types of chemical bonds).

1) Stereoisomers
These differ in the spatial arrangements of their bonds. If the spatial arrangements result in different geometries, they are defined as *geometric isomers*. The nomenclature of these isomers most often distinguishes between the possible geometric arrangements by appending a descriptive prefix such as *cis*, *trans*, *fac* or *mer* before the name of the compound. The second type of stereoisomer, *optical isomers or enantiomers*, occurs in molecules that have the property of chirality (a word comes from the Greek *cheir*, meaning “the hand”). Chirality can be explained that hands, as we all know, come in two forms, left-handed and right-handed, that are non-superimposable mirror images of each other.

2) Structural isomers
These are defined as the molecules with the same molecular formula having atoms bonded together in different orders, as opposed to stereoisomerism. Many different names have been given to a variety of these isomers but only three different types are included in this section: *coordination, ionization*, and *linkage* isomers.

*Coordination isomers* are those characterized by an interchange of ligands among coordination spheres. One set of example compounds is $[\text{Pt}^{II}(\text{NH}_3)_4][\text{Pt}^{IV}\text{Cl}_6]$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}][\text{Pt}(\text{NH}_3)\text{Cl}_3]$.

*Ionization isomers* are those characterized by an interchange of groups between the coordination sphere and the counter-ions. For example, given the $[\text{Co(en)}_2(\text{NO}_2)\text{SCN}]\text{Cl}$, the thiocyanate counter-ion can be exchanged with either a chloride or nitrite ligand in the coordination sphere to produce and the $[\text{CoCl(en)}_2\text{SCN}]\text{NO}_2$ and the $[\text{CoCl(en)}_2(\text{NO}_2)]\text{SCN}$,
respectively. Very similar to ionization isomerism is hydrate isomerism, in which arises when one of the ligands is water.

**Linkage isomers** are those that result when ambidentate ligand switches its coordinating atom. The first identified instance of linkage isomerism involved the nitrite ion, NO$_2^−$. The Lewis structure of this anion involves the resonance structures, including π-electron density spread out among the three atoms of the anion. Therefore, The ligand can make a bond either via nitrogen atom (in this case the ligand is called nitro), or via oxygen (in this case the ligand is called nitrito). Another example can be the complexes with thiocyanate (SCN$^−$) and/or isothiocyanate (NCS$^−$). Hence, if the ligand makes a bond by using sulfur atom, the ligand will be thiocyanate or if it makes a bond by using nitrogen atom, then it will be called isothiocyanate ligand, and the chemical nature and nomenclature of complex will be different.

**Experiment 4: Linkage Isomerism:**

**Synthesis of [Co(NH$_3$)$_5$ONO]$^{2+}$ and [Co(NH$_3$)$_5$NO$_2$]$^{2+}$**

**Introduction**

Divalent cobalt is more stable than trivalent cobalt for simple salts of cobalt, with only a few salts of Co(III) known (e.g. CoF$_3$). Formation of a coordination complex stabilizes a higher oxidation state as evidenced by a number of octahedral coordinated complexes.

In this experiment, you will prepare two linkage isomer compounds, [Co(NH$_3$)$_5$ONO]Cl$_2$ and [Co(NH$_3$)$_5$NO$_2$]Cl$_2$.

The synthesis of [Co(NH$_3$)$_5$Cl]$^{2+}$ involves the following unbalanced equation,

\[
\text{Co}^{2+} + \text{NH}_3(\text{aq}) + \text{NH}_4^+ + \text{H}_2\text{O}_2 \rightarrow [\text{Co(NH}_3)_5(\text{H}_2\text{O})]^3^+ \\
[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^3^+ + \text{Cl}^- + \text{SO}_4^{2^-} \rightarrow [\text{Co(NH}_3)_5\text{Cl}]\text{Cl}_2 + \text{SO}_4^{2^-}
\]

Synthesis of [Co(NH$_3$)$_5$ONO]Cl$_2$ and [Co(NH$_3$)$_5$NO$_2$]Cl$_2$ involves the following:

\[
[\text{Co(NH}_3)_5\text{Cl}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3)_5(\text{H}_2\text{O})]^3^+ + \text{Cl}^- \\
[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^3^+ + \text{NO}_2 \rightarrow [\text{Co(NH}_3)_5\text{ONO}]^{2+} + \text{H}_2\text{O} \\
[\text{Co(NH}_3)_5\text{ONO}]^{2+} \rightarrow [\text{Co(NH}_3)_5\text{NO}_2]^{2+}
\]

The product [Co(NH$_3$)$_5$ONO]Cl$_2$ will isomerize to [Co(NH$_3$)$_5$NO$_2$]Cl$_2$ at room temperature given sufficient time. This isomerization may also be facilitated by heating.
Procedure Exp 4a:

Part I: Synthesis of [Co(NH₃)₅Cl]SO₄

1) Dissolve 10 g of ammonium chloride in 60 ml of concentrated aqueous ammonia in a 500 ml erlenmeyer flask.

2) While continuously agitating the solution with a stirrer, add 19.3 g of finely powdered cobalt (II) sulfate 7-hydrate in small portions.

3) With continuous stirring of the resulting brown slurry, slowly add 16 ml of 30 % hydrogen peroxide with a dropper. (Caution: Reaction is vigorous. This step should be done very carefully since the yield of the reaction strongly depends on this step.)

4) When the effervescence has ceased, add slowly 60 ml of concentrated HCl. (Caution: The addition should be done in small portions and as slowly as possible. Work very carefully with the concentrated acid.)

5) Continue stirring holding the temperature at about 85°C for 20 minutes.

6) Cool the mixture to room temperature and filter the precipitate [Co(NH₃)₅Cl]SO₄ by suction filtration.

7) Wash the precipitate with 40 ml of cold water in several portions.

8) Then, wash 40 ml of cold 6 M HCl.

9) Finally, wash with 10-15 ml ethanol.

10) Dry the product in an oven at 100°C for 30 minutes.

11) Calculate the yield.

Part II: Synthesis of [Co(NH₃)₅ONO]SO₄

1) Dissolve 5.0 g of previously prepared [Co(NH₃)₅Cl]SO₄ in a solution of 30 ml of concentrated aqueous ammonia in 65 ml of water while stirring and heating (avoid boiling during the heating process).

2) Make sure that all of the starting material is dissolved and cool the solution to about 10°C.

3) Neutralize the solution with continued cooling with conc. HCl until it is just neutral.

4) Dissolve 10.0 g of sodium nitrile (NaNO₂) in the above solution.

5) Place the solution in ice bath and add about 8 ml of conc. HCl very slowly. Observe the precipitate formation.

6) Wait a while for the crystallization to be complete and then filter the crystals of [Co(NH₃)₅ONO]Cl₂ with suction.

7) Wash with 10 ml cold water, followed by 25 ml ethanol, dry the product at room temperature (Caution: Do not put into oven).

8) Calculate the yield.
Procedure Exp 4b:

Part III: Synthesis of $[\text{Co} (\text{NH}_3)_5 \text{NO}_2] \text{SO}_4$

1) Dissolve 2 g of previously prepared $[\text{Co} (\text{NH}_3)_5 \text{ONO}] \text{Cl}_2$ in 20 ml of hot water containing 2.5 ml of ammonia while heating the solution. Add enough ammonia until complete solution is obtained. Note the amount of ammonia used. (Caution: While heating, the temperature should not be raised above 60 °C).
2) While cooling under tap water, add conc. HCl depending on the amount of ammonia used in the previous step. Check the neutrality of the solution with a litmus paper.
3) Cool the solution thoroughly and filter the product by suction filtration.
4) Wash the product with 15 ml ethanol.

Part IV: IR Spectroscopy Analysis of both $[\text{Co} (\text{NH}_3)_5 \text{ONO}] \text{Cl}_2$ and $[\text{Co} (\text{NH}_3)_5 \text{NO}_2] \text{SO}_4$

1) Prepare two different dry KBr pellets one containing $[\text{Co} (\text{NH}_3)_5 \text{ONO}] \text{Cl}_2$ and another one containing $[\text{Co} (\text{NH}_3)_5 \text{ONO}] \text{Cl}_2$ with the help of your lab assistants.
2) Get the IR spectra of these two KBr pellets containing your samples with the help of your lab assistants.