CHEM 122L
General Chemistry Laboratory
Revision 2.0

The Synthesis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride

- To learn about Coordination Compounds and Complex Ions.
- To learn about Isomerism.

In this laboratory exercise, we will synthesize a Coordination Compound of Cobalt, *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride, $[Co(en)_2Cl_2]Cl$, from Cobalt(II) Chloride Hexahydrate, $CoCl_2 \bullet 6H_2O$.

$$4\ CoCl_2 \bullet 6H_2O + O_2 + 4\ HCl + 8\ en \longrightarrow 4\ [Co(en)_2Cl_2]Cl + 26\ H_2O \qquad \text{(Eq. 1)}$$

"en" is short-hand for Ethylenediamine:

$$NH_2\text{-}CH_2CH_2\text{-}NH_2$$

This synthesis involves oxidation of the Cobalt from Co^{+2} to Co^{+3} by Oxygen dissolved in the reaction solution:

$$4\ Co^{2+} + O_2 + 4\ H^+ \longrightarrow 4\ Co^{3+} + 2\ H_2O \qquad \text{(Eq. 2)}$$

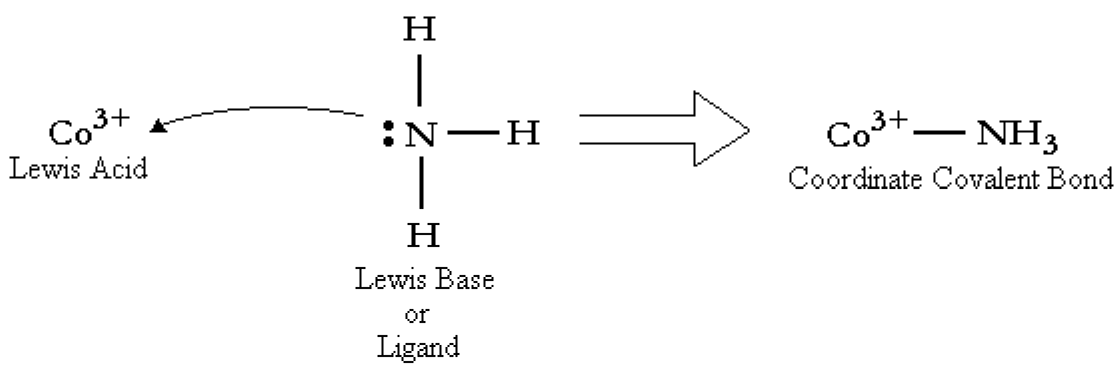
(Here, Oxygen acts as an Oxidizing Agent and is reduced from O^0 to O^{2-}.) However, Co^{3+} is unstable in an aqueous environment, being readily reduced back to Co^{2+}. To prevent this from happening, the resulting Co^{3+} can be stabilized by adding an Ethylenediamine ligand. Hence, if the oxidation is carried out in the presence of Ethylenediamine, the Co^{3+} formed is stabilized and retains the higher oxidation state.

$[Co(en)_2Cl_2]Cl$ is a Coordination Compound. **Coordination Compounds** are substances that contain at least one **Complex Ion**, a species containing a central metal cation that is bonded to molecules or anions, called **Ligands**. In the present case, the coordination compound $[Co(en)_2Cl_2]Cl$ is formed from the $Co(en)_2Cl_2^+$ complex cation and the Cl^- anion. The Complex itself contains four Ligands; two Cl^-'s and two Ethlyenediamines (en). (Note the [ ]'s around the Complex Ion $Co(en)_2Cl_2^+$ in the chemical formula.) Like other Water soluble compounds, this ionic substance can dissolve in Water according to:

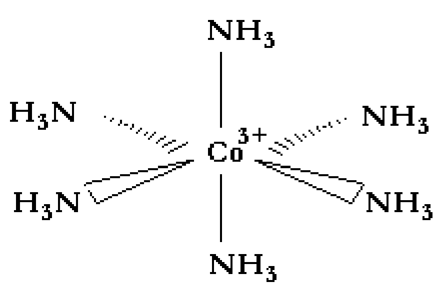
$$[Co(en)_2Cl_2]Cl_{(aq)} \longrightarrow Co(en)_2Cl_2^+{}_{(aq)} + Cl^-{}_{(aq)} \qquad \text{(Eq. 3)}$$

The covalent bonding between the metal ion and its ligands, in our case, between the Co^{3+} and the Cl^{-}'s and en's, is via **Coordinate Covalent Bonds**; the ligands act as Lewis Bases and donate pairs of electrons to the metal, acting as a Lewis Acid.

As a general example of this type of bonding, consider the formation of the $Co(NH_3)_6^{3+}$ complex ion. The NH_3 ligand has one lone pair of electrons which can coordinate covalent bond to the Co^{3+} metal center:



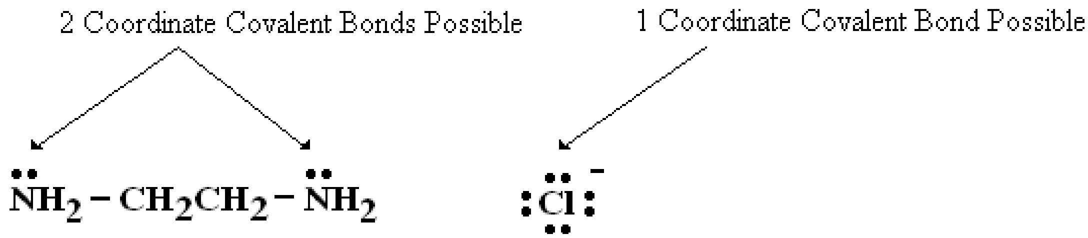
Since this example complex contains six NH_3 ligands, it has six coordinate covalent bonds arranged octahedrally about the metal center:



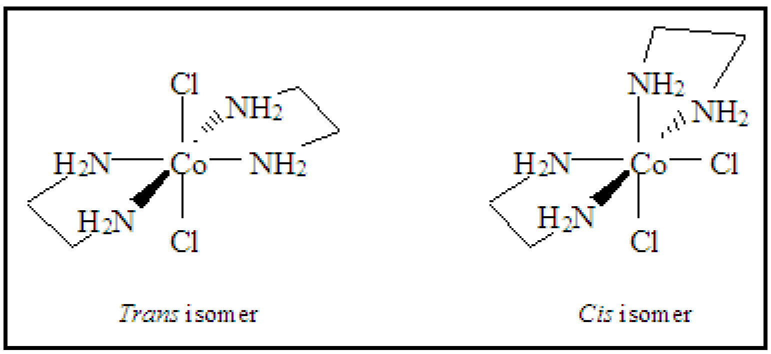
The number of coordinate covalent bonds formed is referred to as the Coordination Number of the complex. In the above example, the coordination number is six. The coordination number determines the geometry of the complex. Typical coordination geometries are:

Coordination Number	Geometry
2	Linear
4	Square Planar or Tetrahedral
6	Octahedral

For our complex ion, $Co(en)_2Cl_2^+$, the coordination number is also six. 2 electron pairs are donated to the Co^{3+} ion by each chloride ion, Cl^-, ligand. The remaining 4 electron pairs are donated by the two Ethylenediamine ligands, the Ethylenediamine ligand being bidentate; forming two bonds to the metal per "en".



Because each "en" ligand in our Complex is bidentate, two different Isomers of our Complex are possible; a *cis* form and a *trans* form. These are pictured below:



We will be synthesizing the *trans* isomer (Green) of this complex, although some of the *cis* isomer (Purple) will be formed as an impurity.

Isomers are substances that have the same chemical formula, but are different compounds; *i.e.*, each has its own set of physical and chemical properties. Each of the above pictured isomers has the chemical formula $CoCl_2C_4H_{16}N_4^+$ and yet the *trans* form is distinctly different than the *cis* form, as can be seen from the fact that the former is a Green color and the later is a Purple color.

A more obvious example is the isomerism exhibited by compounds with the chemical formula C_2H_6O. Two isomers with this formula are:

Dimethyl Ether	$C\ H_3\text{-}O\text{-}CH_3$
Ethanol	$CH_3CH_2\text{-}OH$

These two Structural Isomers have the same chemical formula C_2H_6O, but the bonding between the atoms is distinctly different. (In Dimethyl Ether the Oxygen is bound to two Carbons; C-O-C. In Ethanol, the Oxygen is bound to a Carbon and a Hydrogen; C-O-H.) These bonding differences manifest themselves in differences in the Physical and Chemical Properties of the two substances.

Dimethyl Ether

Boiling Pt.	$-23^{o}C$
Melting Pt.	$-138.5^{o}C$
Density	1.59 g/L

Ethanol

Boiling Pt.	78.4^{o}
Melting Pt.	$-114.3^{o}C$
Density	0.789 g/mL

Transition metal complex ions exhibit a number of different types of isomerism:

Coordination Isomers

The composition of the complex ion changes, but not that of the compound.

Ex: Compounds with the formula $CoCrC_6H_{18}N_{12}$

Cmpd 1: $[Co(NH_3)_6][Cr(CN)_6]$
Cmpd 2: $[Cr(NH_3)_6][Co(CN)_6]$

Note the metal center of each complex has switched.

Linkage Isomers

The composition of the complex ion remains the same, but the binding attachment of the ligand donor atom changes.

Ex: Complexes with the formula $CoN_6H_{15}O_2^{2+}$

Cmpl 1: $Co(NH_3)_5ONO^{2+}$
Cmpl 2: $Co(NH_3)_5NO_2^{2+}$

Note that in Complex 1 the bonding to the NO_2^- ligand is through the O atom, whereas in Complex 2 it is through the N atom.

Geometric Isomers

Atoms or groups of atoms are arranged differently in space relative to the central atom. (*cis-trans* isomerism is an example of this type of isomerism.)

Ex: The *cis-trans* isomers of our Cobalt complex are example of this type of isomerism.

Thus, we will be synthesizing a particular isomer (*trans*) of the coordination compound $[Co(en)_2Cl_2]Cl$ where the complex ion $Co(en)_2Cl_2^+$ adopts an octahedral geometry due to the six coordinate covalent bonds formed with the ligands.

Pre-Lab Questions

1. How many grams of O_2 is consumed during this synthesis? What is the source of this O_2?

2. How many grams of Ethylenediamine (en) is required for this syntheis? How many grams of Ethylenediamine (en) is contained in 15 mL of 10% Ethylenediamine (en)?

3. What should be the color of your Product? What is the color of the *cis* Isomer of this Product, which may contaminate your Product?

Procedure

At some point during the lab, when you are waiting for the reaction to proceed, build models of both the *cis* and the *trans* Dichlorobis(ethylenediamine)cobalt(III) complex.

Perform the following steps in a fume hood.

1. Heat about 300mL of water in a 600mL beaker and maintain at a moderate boil.

2. In an evaporating dish, combine 4.0g of Cobalt (II) Chloride Hexahydrate with 10mL of distilled water. To this, add 15mL of 10% ethylenediamine (en).

   Place the evaporating dish on top of the beaker of boiling water. Stir the mixture over this steam bath for 40 minutes; maintain the volume of the solution at about 20mL by occasionally adding small portions of water. During this process, the Co^{2+} is oxidized to Co^{3+} by the Oxygen in the Air. Good agitation is necessary to promote solvation of the oxygen.

3. Add 12mL of Concentrated 12M HCl. Continue heating and stirring, without addition of water, until a thin slurry of crystals has formed. (*Note: Stopping the evaporation at the right time is critical to the success of the synthesis. Stopping too soon will give a poor yield of the product; stopping too late will give an impure product.)*

   Cool the slurry to Room Temperature by setting the evaporating dish on the lab bench. Stir occasionally for 15 minutes.

4. Filter the mixture using a Buchner funnel with Side-Arm Flask attached to an aspirator.

   When the draining from the Buchner funnel has essentially stopped, add 5mL of 6M HCl to the funnel and gently stir up the mixture with a spatula, taking care not to tear the filter paper. **(Do not use Pure Water to wash your product. If you do, the complex will decompose.)**

   If the product is still brown or blue, repeat the washing process with 6M HCl. If the product is pure green, skip the washing to avoid loss of product.

5. Transfer the moist crystals of the product to a clean watch glass. Dry the material on the steam bath. During the last stages of drying, powder the material on the watch glass by scrapping and pressing with a spatula.

6. Transfer the dried product to a previously weighed 3-dram vial. Label this vial with your Name(s), Product Name, Product Formula, Mass Product Obtained and the Date.

Data Analysis

1. Calculate the Theoretical Yield of your Product.

2. Calculate the Percentage Yield of your Product.

3. Identify the points in the Procedure at which loss of Product is likely.

Post Lab Questions

1. Why is only one pair of electrons on the Cl^- ion available for bonding to the Co^{3+} metal center in the complex ion $Co(en)_2Cl_2^+$?

2. How will the Percentage Yield of your Product be affected if the product is a little damp when weighed?

3. Determine the Oxidation State and the Coordination Number of the Transition Metal Ion in each of the following Complex Ions:

   a) $Ni(H_2O)_6^{2+}$
   b) $Mn(CN)_6^{4-}$
   c) $CuCl_4^{2-}$
   d) $Cr(NH_3)_6^{3+}$

4. Write a chemical equation representing what happens when each of the following water soluble Coordination Compounds dissolves in water.

   a) $[Cr(NH_3)_4Cl_2]Cl$
   b) $K_2[PtCl_4]$
   c) $[Co(en)_3](NO_3)_3$

5. $PdCl_2(NH_3)_2$ occurs as a square planar complex with two different Isomers. Sketch these.