

# Synthesis, characterization, and resolution of enantiomers of tris(ethylenediamine)cobalt(III) chloride

## Introduction:

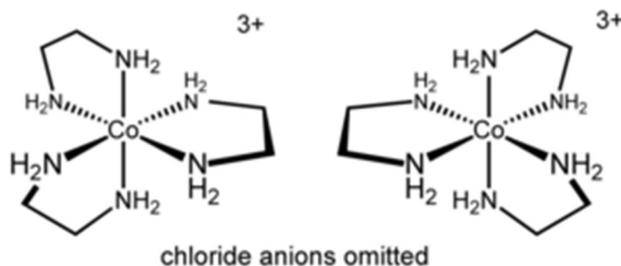
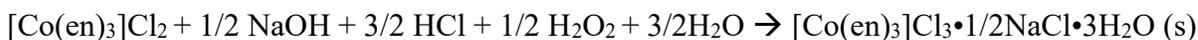
The development of coordination chemistry prior to 1950 involved the synthesis and characterization of metal complexes with monodentate ligands (e.g.  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NH}_3$ ) and bidentate ligands [e.g. ethylenediamine (en)  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , oxalate  $-\text{O}_2\text{CCO}_2^-$ , glycine ( $\text{H}_2\text{NHCH}_2\text{CO}_2^-$ ), and  $\text{CO}_3^{2-}$ ]. Modern inorganic chemistry has greatly expanded the variety and complexity of ligands.

Coordination complexes of Co(III) and Cr(III) have been of particular interest because the complexes undergo slow ligand substitution reactions compared to complexes of many other transition metal complexes [1-6]. Many inorganic metal coordination compounds have a coordination number of six. There is the potential for the formation of isomers, provided the coordination compound lacks an internal mirror plane. The enantiomers formed in this experiment are isomers that are mirror images of one another. In such cases, the compound may also react differently with achiral reagents.

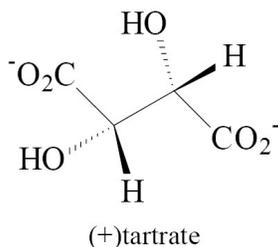
In this lab experiment, you will synthesize several salts based on the  $\text{Co(en)}_3^{3+}$  ion and resolve (separate) their enantiomers. The synthesis involves the oxidation of a cobalt (II) salt,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . A Co(II) complex is initially made by reaction of the  $\text{CoCl}_2$  with ethylenediamine dihydrochloride ( $\text{en} \cdot 2\text{HCl}$ ) as shown below.



Next, the acidic solution is neutralized and  $\text{Co}^{2+}$  is oxidized by hydrogen peroxide.



The mixture of enantiomers is resolved by *slow and careful* crystallization in the presence of the optically active dianion (+)tartrate [abbreviated as (+)tart]:



In this experiment,  $[(+)\text{Co(en)}_3][(+)\text{tart}]\text{Cl}$  is much less soluble than its (-) enantiomer salt and it preferentially crystallizes out of aqueous solution, as the pentahydrate, leaving the (-) isomer in solution as shown in the following unbalanced equation.



## Experimental Section: Safety

Investigate the properties and briefly list in your lab notebook any special hazards associated with each of the following reagents: cobalt(II) chloride hexahydrate  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ , concentrated aqueous ammonia (ammonium hydroxide), hydrogen peroxide  $\text{H}_2\text{O}_2$ , ethylenediamine dihydrochloride ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$ ).

## Experimental Procedures

### Part I: Preparation of racemic tris(ethylenediamine)cobalt(III) chloride:

Add 25 mmol of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 100 mmol of ethylenediamine dihydrochloride ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$ ) and a stir bar in a 250-mL beaker with approximately 25 mL  $\text{H}_2\text{O}$ . Stir for a couple of minutes until the cobalt salt is dissolved completely. The mixture will appear a cloudy pink. Add 200 mmol of sodium hydroxide pellets and stir. A cloudy orange solution is formed. Continue stir for a few minutes until the sodium hydroxide is completely dissolved. Add 20 mL of 3%  $\text{H}_2\text{O}_2$  (adjust amounts if a different concentration of hydrogen peroxide is used). The solution should darken upon addition of the peroxide. If needed, slightly dilute the mixture slightly and heat just below boiling for a few minutes on a stirring hot plate until the cloudiness disappears. Allow a few mL to evaporate during the near boiling step to concentrate the solution, then cool slightly and remove the stir bar from the hot solution with a stir bar retriever. Place the beaker in ice bath and cool for approximately 30 minutes. With a suction filtration apparatus and filter paper, collect the fine orange to yellow-orange needles that have formed. Make sure to filter the solution while it is cold. *Before rinsing the crystals, transfer the filtrate back to the beaker* and, if needed, recover additional product from the filtrate by reducing its volume and re-cooling. Impurities will also eventually precipitate, for example NaCl with solubility of 0.36 g/mL in water.[7] Do not recrystallize and combine products unless the first yield is poor.

Press the solid flat and even on the filter paper and wash it with small portions of a total of 50 mL of 95% ethanol and then small portions of 20 mL of diethyl ether. Pull air through the crystals until dry. Weigh the collected sample and record the yield. Discard the filtrate wash solution in the in the appropriate waste containers in the fume hood.

*Note:* Save some of the product (at least 0.4-0.5 g) for UV-Vis and IR spectroscopic analyses in lab session 1 and proceed to the resolution of the tris(ethylenediamine)cobalt(III) ion.

### Resolution of the tris(ethylenediamine)cobalt(III) ion

Add 14.0 mmol of  $[\text{Co}(\text{en})_3]\text{Cl}_3$ , 17.4 mmol of (+)tartaric acid, and a stir bar in a 100-mL beaker and add 20 mL of  $\text{H}_2\text{O}$ . Adjust the quantities of both the compounds and solution if you use a different amount of the cobalt starting material. Add 35 mmol of sodium hydroxide and cover the beaker with a watch glass. Gently stir the mixture and heat, without boiling, on a stirring hot plate for a few minutes until the solids completely dissolve, add more  $\text{H}_2\text{O}$  if needed. Remove the stir bar with a stir bar retriever and let the solution cool to room temperature. Cover and store in the inorganic cabinet under a fume hood. Collect the crystals by filtration in the next laboratory session.

### Part II: Resolution of the $(+)\text{Co}(\text{en})_3^{3+}$ ion as the $\text{Co}(\text{en})_3[(+)\text{tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ salt

In the previous laboratory session, the resolution of the tris(ethylenediamine)cobalt(III) ion was initiated by adding (+)tartrate to the mixture of enantiomers (or stereoisomers) of tris(ethylenediamine)cobalt(III)chloride. The  $[(+)\text{Co}(\text{en})_3][(+)\text{tart}]\text{Cl}$  is much less soluble than the (-) enantiomer salt and preferentially crystallizes out of aqueous solution first, as the pentahydrate, leaving the (-) isomer in solution.



Prepare a filtration assembly and obtain your covered beaker from last week that contains the crystallized  $[(+)\text{Co}(\text{en})_3][(+)\text{tart}]\text{Cl}\cdot 5\text{H}_2\text{O}(\text{s})$  and  $(-)\text{Co}(\text{en})_3^{3+}$  in solution. Prepare 20 mL of a 1:1 (vol.) water:acetone solution and a 20 mL portion of pure acetone to rinse the product. Decant the dark orange solution into an Erlenmeyer flask that *should* contain (primarily) your (-)enantiomer and retain this solution for an upcoming step. Isolate the dark orange crystals by filtration. Wash the crystals with the water/acetone solution and then pure acetone. Pull air through the product until it is dry and record the yield.

### Isolation $[(+)\text{Co}(\text{en})_3]\text{I}_3\cdot \text{H}_2\text{O}$

Place 3.9 mmol of  $[(+)\text{Co}(\text{en})_3][(+)\text{tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$  in a 50 mL beaker with 15 mL of water. If necessary, break up large crystals with a spatula. With continuous stirring with a stir bar, add one (1) pellet of NaOH, and heat the solution very gently until all of the solids dissolve. Do **not** boil the solution or heat for more than a few minutes. While the solution is still warm, add 24 mmol of NaI. Continue stirring for one minute and then cool in an ice bath. Vacuum filter the crystals and wash with 10 mL of an ice-cold solution of 0.3 g/mL NaI in water. Wash the crystals with 10 mL of 95 % ethanol and then with 10 mL of acetone. Pull air through the crystals until dry.

### **Isolation of $[-]\text{Co}(\text{en})_3\text{I}_3\cdot\text{H}_2\text{O}$**

Obtain the filtrate solution saved from resolution of the  $(+)\text{Co}(\text{en})_3^{3+}$  ion as the  $\text{Co}(\text{en})_3[(+)\text{tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$  salt and dilute to 30 mL. Add one pellet of NaOH, gently heat and stir the solution until the NaOH dissolves, then add 57 mmol of NaI while stirring. Cool the solution in an ice bath, collect the impure precipitate (it may contain some (+) enantiomer) by filtration, and wash with 0.3 g/mL NaI in water. Discard the filtrate into the waste. Isolate the pure (-) enantiomer by dissolving the precipitate in 35 ml of warm water (50 °C). Filter off the undissolved (+) enantiomer and add 5 g of NaI to the filtrate containing the  $(-)\text{Co}(\text{en})_3^{3+}$ . The  $[-]\text{Co}(\text{en})_3\text{I}_3\cdot\text{H}_2\text{O}$  product should crystallize from the solution on cooling. Collect the precipitate, wash with ethanol and acetone, and air-dry.

### **Racemization of $(+)\text{tris}(\text{ethylenediamine})\text{cobalt (III) iodide}$ , $[(+)\text{Co}(\text{en})_3]\text{I}_3\cdot\text{H}_2\text{O}$ .**

*If instructed*, dissolve 1 g of  $[(+)\text{Co}(\text{en})_3]\text{I}_3\cdot\text{H}_2\text{O}$  in a minimum volume of warm water (50 °C). Add a small amount of activated carbon (charcoal) and boil the solution for approximately 30 minutes. Vacuum filter the solution while hot to remove the charcoal. Discard the filter paper. Add 2 g of NaI to the recovered filtrate to aid in precipitation. Filter again then wash the product with ethanol and acetone, and air-dry.

### **Physical Property Characterization:**

Infrared and ultraviolet-visible spectroscopy should be performed on each of the iodide compounds. Plan experiments in a manner that will minimize waiting time for instrumentation by arranging each of your experiments in a manner that will minimize conflict with others. For example, the isolation of  $[(+)\text{Co}(\text{en})_3]\text{I}_3\cdot\text{H}_2\text{O}$  and the isolation of  $[-]\text{Co}(\text{en})_3\text{I}_3\cdot\text{H}_2\text{O}$  may be done either before, or after the spectroscopic experiments on the other compounds.

### **Supplemental Work:**

Polarimetry: Confirm that the  $(+)\text{tart}$  and  $\text{Co}(\text{en})_3[(+)\text{tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$  is optically active by polarimetry. If time permits, also attempt to determine the optical activity of  $\text{Co}(\text{en})_3[(-)\text{tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ . Approximately 0.05 g/mL in  $\text{H}_2\text{O}$  should be used in the polarimetry experiments.

## References:

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