

The synthesis and optical resolution of Co(en)_3^{3+} isomers essay sample

[Literature](#), [Russian Literature](#)



The tris(ethylenediamine)cobalt ion is an optically active compound. The enantiomers can be separated and distinguished from each other. This is done first through the synthesis of $[\text{Co}(\text{en})_3]^{3+}$ and then the deprotonation from this complex. The separation results with $[\text{Co}(\text{en})_3]^{3+}$ and $(-)-[\text{Co}(\text{en})_3]^{3+}$. The two are distinguished from each other by using a polarimeter and obtaining the optical angle of rotation. From this further calculations are done to further identify and determine if the enantiomers were separated and isolated synthetically. The results found that the isomers were separated and a great deal was recovered according to the theoretical yield that was calculated. It was also proven that the complex can be racemized by boiling and the presence of an activated carbon.

Introduction:

The purpose of this experiment is to synthesize and learn about $[\text{Co}(\text{en})_3]^{3+}$ optical isomers. The tris(ethylenediamine)cobalt ion is an optically active compound. Werner in 1912 was the first to do the resolution of tris(ethylenediamine)cobalt ion. He did this through Second-order Asymmetric Induction. Second-order Asymmetric Induction is when one of the enantiomers can react with a chiral ion. This changes the solubility properties of the one enantiomer making it more soluble than the other.

The other enantiomer then crystallizes out first, making it easy to filter one from the other. (2, 3) The $[\text{Co}(\text{en})_3]^{3+}$ is first synthesized and then is converted to $[\text{Co}(\text{en})_3]^{3+} \cdot 5\text{H}_2\text{O}$ by reaction with NaI . The other optical isomer, $[\text{Co}(\text{en})_3]^{3+}$, is obtained by adding NaI to the filtrate from which $[\text{Co}(\text{en})_3]^{3+} \cdot 5\text{H}_2\text{O}$ was previously precipitated. The solid

that precipitates with NaI is a mixture of crystals of the racemate, (+) and (-)-13 H₂O, and crystals of pure 13 H₂O.

The 13 H₂O is much more soluble in warm water than the racemate and may be extracted into solution, which on cooling precipitates the desired enantiomer, 13 H₂O. The optical purities of the isolated (+) and (-) enantiomers are to be evaluated by measuring their specific rotations from a polarimeter. Finally, it will be shown that the resolved compound may be racemized by boiling an aqueous solution of one of the enantiomers in the presence of activated charcoal.

Experimental:

Tris(ethylenediamine)cobalt(III) Chloride, Cl₃*1/2 NaCl*3H₂O

In a small beaker, dissolve 6.00g (6.02g) (25.0mmol) of CoCl₂·6H₂O and 13.3g (13.3g) (100. mmol) of ethylenediamine dihydrochloride in 25 mL water. Stir for one minute or so to dissolve the cobalt salt. Note that the color should be cloudy pink. Add 8.00g (8.02g) (200. mmol) of NaOH pellets and stir. The solution should be cloudy orange/brownish red. Stir until the NaOH is dissolved. Carefully, a little at a time, add 20mL (20mmol) of 3% H₂O₂ with swirling. The solution should thicken and darken upon the addition of the peroxide. Dilute the mixture to 50.0 mL if it is not already around that volume.

Heat to a boil for a few minutes to remove the cloudiness from the solution.

Place beaker in an ice bath for 30 minutes to cool. Using a suction filter,

collect the orange to yellow/orange needles that have formed. Wash the crystals with 50.0 mL of 95.0% ethanol and 20.0 mL of diethyl ether. Pull air through the crystals until they have dried and warmed to room temperature. The yield recorded was 5.52g of $\text{Cl}_3 \cdot \frac{1}{2} \text{NaCl} \cdot 3\text{H}_2\text{O}$. The filtrate is discarded.

Resolution of Tris(ethylenediamine)cobalt(III) Ion

In a small beaker, put 6.00g(14mmol) of $\text{Cl}_3 \cdot \frac{1}{2} \text{NaCl} \cdot 3\text{H}_2\text{O}$, 2.60g (17.4 mmol) of (+)tartaric acid, and a stir bar. Add 20.0mL of water. Then add 1.40g(35mmol) of NaOH and cover the beaker with a watch glass. Stir and heat until the solids completely dissolve. Remove the stirring bar and cool the solution to room temperature overnight.

Collect the dark orange crystals through filtration using a 60.0 mL glass frit. Transfer the filtrate into a medium sized beaker and save the solution, which contains the isomer. After the filtrate is transferred, wash the crystals first with 20.0mL of a 1: 1 ratio of acetone and water and then with 20.0mL of acetone. Pull air through the crystals. $\text{Cl}_3 \cdot 5\text{H}_2\text{O}$ is formed. The yield measured was 2.87g. The theoretical yield was 4.23. The percent yield was 69.7%.

To determine the specific rotation of the compound, dilute approximately 0.50g of the sample to a solution with a volume of 10.0mL. Pipette the solution into a 1-dm polarimeter tube. Tilt the tube so that the air bubble is not in the path of the light. Blank the polarimeter with air so that the angle of rotation is zero. Place the polarimeter tube into the polarimeter. The sign and

magnitude of the rotation was measured. The rotation was +2.73 at a fixed wavelength of 589.3 nm.

To convert the tart salt to (+)-Co(en)₃I₃·H₂O, put 2.00 g (3.90 mmol) of Cl₅H₂O in a 50.0 mL beaker. The crystals were broken up because they were too large. One pellet of NaOH, a stir bar, and 15.0 mL of distilled water was added. The solution was heated on a hot plate while stirred until all the solids dissolved. Heating the solution longer than 5 minutes would cause the cobalt complex to racemize. Added to the solution was 3.60 g (24 mmol) of NaI.

Heating was continued for 1 minute longer and then the solution was cooled in an ice bath to room temperature. The solution was then filtered and washed with 3.00 g of NaI in a 10.0 mL water solution to remove the tartrate. The crystals were washed with 10.0 mL of ethanol and then 10.0 mL of distilled water. The (+)-Co(en)₃I₃·H₂O complex was dried through the filter frit. The mass collected was 2.49 g. The theoretical yield was 2.48 g. The percent yield was 100%. Polarimetry was done on the collected compound.

To isolate the (-)-Co(en)₃I₃·H₂O isomer, the filtrate that was collected and saved from earlier was diluted to 30.0 mL. One pellet of NaOH was added and the solution was heated. With stirring, 8.50 g (57 mmol) of NaI was added. The solution was cooled in an ice bath and then filtered through to collect the impure (-)-Co(en)₃I₃·H₂O. The precipitate was washed with a solution of 3.00 g of NaI dissolved in 10.0 mL of distilled water. To purify the (-)-Co(en)₃I₃·H₂O, the compound was dissolved in 35.0 mL of distilled water at 50 degrees Celsius. The undissolved racemate was filtered off and 5.00 g

of NaI was added to the filtrate. The crystallization of the (-)-Co(en)₃I₃·H₂O occurred with cooling in an ice bath. The precipitate was collected through filtration and then washed with ethanol and acetone. Lastly the complex was air-dried. The mass collected was 2.88g. The theoretical yield was 3.16g. The percent yield was 91.1%. Polarimetry was done on the collected compound.

Racemization of (+)-Co(en)₃³⁺ or (-)-Co(en)₃³⁺

The last thing was to racemize one of the enantiomers. A small amount of I₃·½ H₂O (1.00g) was dissolved in about 10mL of water. Activated carbon, charcoal, was added to the beaker and it was heated for 30 minutes. The hot solution was filtered to get rid of all the activated carbon. About 2 grams of NaI was added to the filtrate and the I₃·½ H₂O precipitated out and was collected by filtration. It was then dried and weighted. The mass collected was 0.33g. Polarimetry was done on the collected compound.