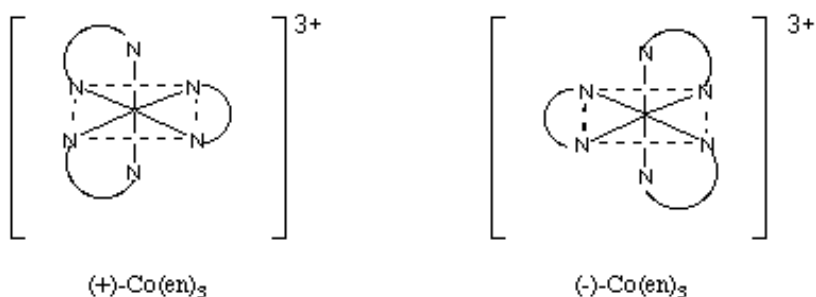


Chem 151L, Spring 2012

Expt. 5. Optical Isomers of Tris(ethylenediamine)Cobalt(III)

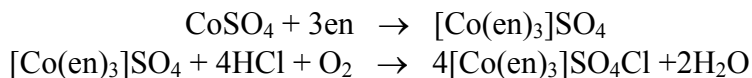
In 1912, Alfred Werner put an end to the controversy which had troubled the world of coordination chemistry by resolving the enantiomers of $(\pm)\text{Co}(\text{en})_3^{3+}$. Werner's work on cobalt enantiomers proved conclusively that coordination number six had octahedral geometry (as opposed to Jørgensen's proposed trigonal prismatic geometry), earning him the 1913 Nobel Prize in Chemistry.

The two enantiomers differ by the manner in which the ligand is wrapped around the metal center. These types of complexes can be treated as three-bladed propellers by looking at the molecules *down the three-fold axis*. The complexes are either right-handed propellers (clockwise rotation) or left-handed propellers (counterclockwise rotation).

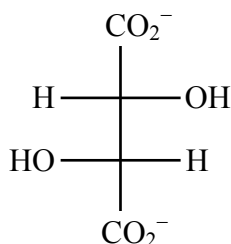


Chiral molecules have the ability to rotate polarized light, the latter produced by passing the light through a prism. Optically active materials have the ability to rotate the plane of light to the right or left, with the angle depending on the nature of the substance. One of the isomers rotates the plane polarized light to the right (+) while the other rotates to the left (-); the two enantiomers are therefore referred to as the “+” or “-” complex. The direction and degree of rotation can be measured experimentally using a polarimeter. As in any form of spectroscopy, the size of the rotation depends on the sample's path length, l , and concentration in the solvent, c . To standardize the units for expressing rotation, the specific rotation, $[\alpha]_\lambda$, has been defined as the rotation produced by a solution containing 1 g of solute per mL of solution and a path length of 1 decimeter ($[\alpha]_\lambda = \alpha / lc$). If the sodium D line is used, it is represented as $[\alpha]_D$.

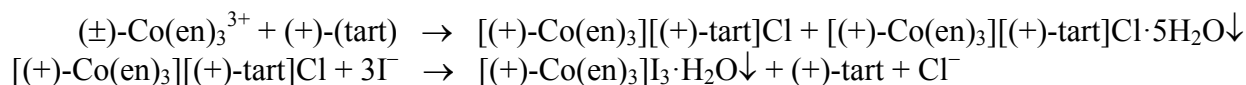
The preparation, resolution and characterization of the optical isomers of $\text{Co}(\text{en})_3^{3+}$ are the objects of this experiment. The preparation of the complex is very similar to the first experiment, preparation of hexamminecobalt(III) chloride. A solution of Co(II) is oxidized by air in the presence of ethylenediamine and activated charcoal:



The resultant $[\text{Co}(\text{en})_3]\text{SO}_4\text{Cl}$ is not isolated from solution, but is immediately resolved by diastereomer formation with optically active d-tartarate, (+)-tart:



Diastereomers have differing solubility; thus it is possible to fractionally crystallize one diastereomer, leaving the other in solution. In this case, [(+)-Co(en)₃][(+) - tart]Cl is the least soluble diastereomer and preferentially crystallizes from solution as the pentahydrate. [(+)-Co(en)₃][(+) - tart]Cl is then converted to [(+)-Co(en)₃]₃·H₂O by reaction with I⁻. The [α]_D of the product is +89°.



The other isomer, [(-)-Co(en)₃]₃·H₂O, is obtained by adding I⁻ to the solution from which the (+) isomer was previously precipitated. The solid that precipitates with I⁻ is a mixture of crystals of the racemate [(±)-Co(en)₃]₃·H₂O and pure [(-)-Co(en)₃]₃·H₂O. The latter is much more soluble in warm water than the racemate and may be extracted into solution. On cooling, the desired enantiomer [(-)-Co(en)₃]₃·H₂O reprecipitates with [α]_D -89°. The optical purity of the isolated enantiomers are evaluated by measuring their specific rotations. The resolved complex can be racemized by boiling an aqueous solution of one of the enantiomers in the presence of activated charcoal.

Preparation of the Resolving Agent, Barium d-Tartrate:

Make this during the 2 hour air-bubbling part of the preparation of Co(en)₃²⁺. Prepare separate solutions of 12.2 g of BaCl₂·H₂O (50 mmol) dissolved in a minimum amount of distilled water and 7.5 g of d-tartaric acid (50 mmol; **Care: be sure to use the d- form, not l-tartaric acid!**) dissolved in a minimum amount of distilled water. After heating these solutions to 90 °C, mix and add the base ethylenediamine until the solution is neutral. Allow the solution to cool to room temperature. Filter the precipitate and rinse with warm water.

Preparation and Resolution of Co(en)₃³⁺:

Prepare a solution containing 10.3 g ethylenediamine (170 mmol, 11.5 mL) in 25 mL distilled water in a filter flask. After cooling the solution in an ice bath, add 5 mL conc. HCl (12 M), 14 g (50 mmol) CoSO₄·7H₂O dissolved in 25 mL of cold water, and 2 g of activated charcoal. Bubble a rapid stream of air through this solution for 2 hours by pulling a vacuum on the filter flask (as in Expt. 1).

Then add dilute HCl or ethylenediamine as required to the solution until the pH is 7.0 to 7.5. Heat the mixture in an evaporating dish on a steam bath for 15 min. Cool the solution to room temperature, filter off the charcoal and rinse with 10 mL of water on the filter. Add the rinse to the filtrate.

To the Co(en)₃³⁺ solution just prepared, add all the barium d-tartrate prepared previously. After heating the mixture on a steam bath for 30 min with vigorous stirring, filter off the reprecipitated BaSO₄ and rinse with a small amount of hot water. Evaporate the solution to 50 mL on a hot plate, then allow the crystals of [(+)-Co(en)₃][(+) - tart]Cl·5H₂O to precipitate until next week, covering with parafilm.

Next lab period: filter off the crystals and save the filtrate for isolation of the other enantiomer later. Rinse the crystals with a 40% (by volume) ethanol-water solution, then recrystallize the product by first dissolving in 15 mL of hot water, then cool the solution in an ice

bath. Rinse the crystals with 40% ethanol-water and then absolute ethanol. Air-dry and determine the yield of $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$.

To determine the specific rotation, dissolve approximately 0.5 g of the complex in 10 mL water and consult your TA about using the polarimeter. Calculate the $[\alpha]_D$ for $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$.

To convert the diastereomer to $[(+)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$, dissolve $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ in 15 mL warm water and add 0.25 mL conc. ammonia (15 M) solution. With stirring, add a solution of 17 g (113 mmol) of NaI dissolved in 7 mL hot water. After cooling in an ice bath, suction filter and rinse the crystals with an ice cold solution of 3 g NaI in 10 mL water to remove the tartrate. After rinsing with ethanol and finally acetone, allow the $[(+)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ to air-dry and determine the yield. Measure its $[\alpha]_D$ by dissolving approximately 0.5 g in 10 mL water.

To isolate $[(-)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$, add 0.25 mL conc. NH_3 solution to the filtrate from which $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ was precipitated. Heat the solution to 80 °C and add 17 g NaI (113 mmol) with stirring. Upon cooling in an ice bath, impure $[(-)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ precipitates. Filter and rinse with a solution of 3 g NaI dissolved in 10 mL water. To purify, dissolve the precipitate by stirring in 35 mL water at 50 °C. Filter off the undissolved racemate and add 5 g of NaI to the filtrate. Crystallization of $[(-)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ occurs on cooling. Filter the precipitate, rinse with ethanol, then acetone, and finally air-dry. Determine the yield and $[\alpha]_D$.

Racemization of (+) or (-) Co(en)_3^{3+} :

Dissolve approximately 1 g of either enantiomer in the minimum volume of warm water. Add a small amount of activated charcoal and boil the solution for approximately 30 min. Then filter the solution while hot, adding a few grams of NaI to aid in the precipitation of the racemate. Rinse with alcohol and air-dry. Determine $[\alpha]_D$ of the racemized product.

Questions:

- 1) Determine which enantiomer is delta and which is lambda.
- 2) If you were to resolve an unknown complex, M(en)_3^{3+} , how would you know whether or not your resolved products are optically pure?
- 3) Draw structures of the geometrical and optical isomers of Co(gly)_3 , where $\text{gly} = \text{NH}_2\text{CH}_2\text{COO}^-$.
- 4) Why is it not possible to resolve Co(en)_3^{2+} ?
- 5) In the preparation of barium d-tartrate, what was the purpose of adding ethylenediamine?
- 6) In the purification of both (+) and (-) $[\text{Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$, the compounds were rinsed with water containing NaI. What was the purpose of the NaI?