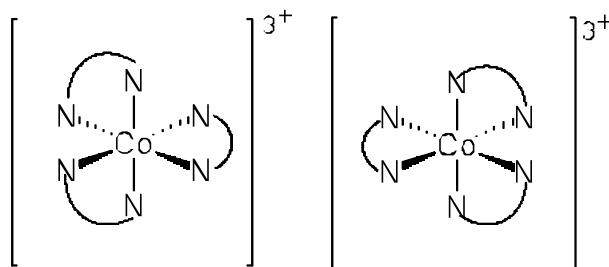
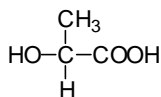
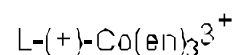


Optical Isomers of $\text{Co}(\text{en})_3^{3+}$

Optical activity is frequently associated with organic molecules containing an asymmetric carbon atom, as for example in lactic acid,



Optical activity, however, is a far more general phenomenon and may be found in any molecule that **Figure 1**



cannot be superimposed upon its mirror image. In

inorganic chemistry, the range of structures that exist as nonsuperimposable mirror images is exceedingly large. While there are many examples of tetrahedral inorganic compounds that have been resolved into their enantiomers, optical activity in octahedral transition metal complexes has been studied far more extensively.

For decades it has been known that certain octahedral complexes of transition metals could be resolved into enantiomers. Some of the earliest work in this area was done in 1912 by Alfred Werner on $\text{Co}(\text{en})_3^{3+}$ (where $\text{en} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$). The enantiomers of $\text{Co}(\text{en})_3^{3+}$ that he resolved were assumed to have the structures shown in Figure 1. One of the isomers rotates plane polarized light toward the right (dextrorotatory) while the other isomer rotates the light by the same amount in the opposite (levorotatory) direction. These



Figure 2

directions are designated (+) and (-) (or sometimes *d* and *l*), respectively. Because of the availability of sodium as a light source, light of 589.3 nm wavelength (the sodium D line) is frequently used in the determination of the rotations. Passing this light through a polarizing prism gives plane polarized light, whose electric field variation is shown in Figure 2.

Optically active materials have the ability to rotate the plane of light to the right or left to a greater or lesser angle depending on the nature of the substance. In order for the rotated polarized light to pass through the analyzer prism, this prism must be rotated, relative to the polarizing prism, to the right or left by an angle that is equal to the rotation caused by the sample. Thus, the direction and number of degrees of rotation may be measured experimentally. As in any form of spectroscopy, the size of the rotation depends not only on the nature of the optically active material but also on the length, ℓ , of the light path through the sample and the concentration, c , of the sample in a solvent. To standardize the units for expressing rotations, 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 having a light path length of 1 decimeter.

$$[\alpha]_{\lambda} = \frac{\alpha}{\ell c} \qquad (1)$$

The wavelength, λ , of light is also specified. Using the sodium D line, the specific rotation is designated $[\alpha]_D$ or $[\alpha]_{589.3}$. In equation (1), α is given in degrees, l in decimeters, and c in grams per mL of solution. A unit that is frequently of more value for comparison between compounds is the molecular rotation, $[M]_\lambda$.

$$[M]_\lambda = \frac{M[\alpha]_\lambda}{100} \quad (2)$$

Since M is the molecular weight of the substance, $[M]_\lambda$ is a relative measure of its rotatory power on a molecular basis.

The rotatory power of a substance varies with the wavelength of the light employed. Thus, it is usually observed that while a molecule may be dextrorotatory toward light of 589.3 nm wavelength, it is levorotatory at other wavelengths. The values of $[M]_\lambda$ as a function of wavelength are shown for in Figure 3. This plot is called an optical rotatory dispersion (ORD) curve.

Since the values of $[M]_\lambda$ for enantiomers at any given wavelength are the same but of opposite sign, the ORD curve of $(-)\text{-Co(en)}_3^{3+}$ may be obtained by rotating the curve for $(+)\text{-Co(en)}_3^{3+}$ by 180° around the 0° line in the figure.

Although its optical activity indicated that $(+)\text{-Co(en)}_3^{3+}$ must have one of the structures shown in Figure 1, the correct structure was not determined until 1954. By a special x-ray technique a Japanese research group established the absolute configuration of $(+)\text{-Co(en)}_3^{3+}$ as being that shown on the left in Figure 1. To show that the absolute configuration is known, the convention of using D to designate this configuration has generally been adopted. Its mirror image, $(-)\text{-Co(en)}_3^{3+}$, must then have the absolute configuration shown on the right of Figure 1. It is labeled L $(-)\text{-Co(en)}_3^{3+}$.

While there must be a relationship between the optical activity of an enantiomer and its absolute configuration, the theory of optical activity is sufficiently complex that calculations of absolute configurations from ORD data are highly unreliable. Empirical correlations of ORD curves of very similar molecules have, however, allowed the assignment of absolute configurations to other metal complexes. Such an assignment has

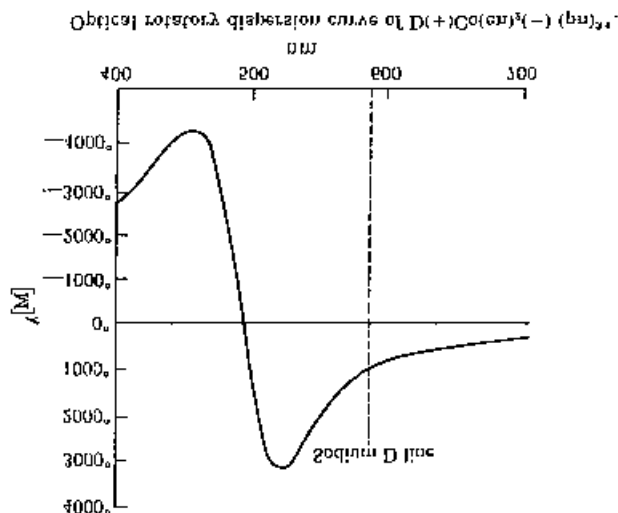


Figure 3

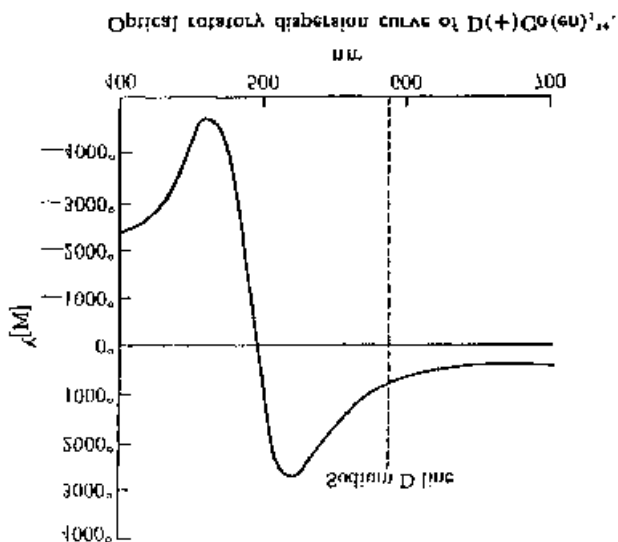


Figure 4

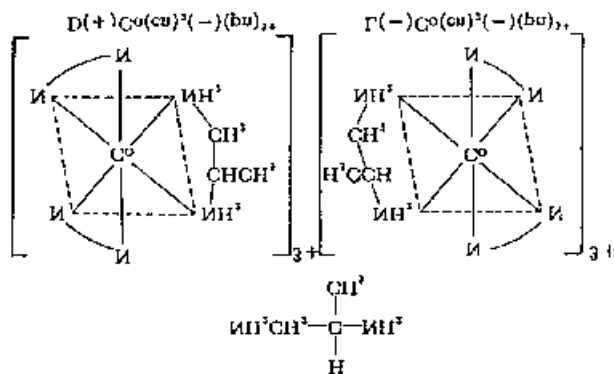
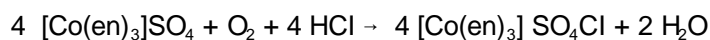
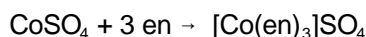


Figure 5

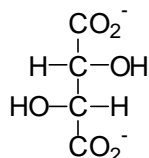
been attempted for $\text{Co(en)}_2(-)(\text{pn})^{3+}$ (Figure 5), where $(-)\text{pn}$ is levorotatory 1,2-diaminopropane. That the ORD curve (Figure 4) of $(+)\text{-Co(en)}_2(-)(\text{pn})^{3+}$ is virtually the same as that of $\text{D-}(+)\text{Co(en)}_3^{3+}$ suggests that the arrangement of the ligands is the same in $(+)\text{-Co(en)}_2(-)(\text{pn})^{3+}$ as in $\text{D-}(+)\text{Co(en)}_3^{3+}$. Hence, its absolute configuration is presumed to be that on the left in Figure 5.

The use of ORD to establish absolute configurations becomes less reliable as the difference between the electronic state of the standard $\text{D-}(+)\text{Co(en)}_3^{3+}$ and the unknown becomes greater. Thus, while the basic shape of the ORD curve of $(+)\text{-cis-Co(en)}_2(\text{NH}_3)_2^{3+}$ is very similar to that of $\text{D-}(+)\text{-Co(en)}_3^{3+}$, the values of $[\text{M}]_\lambda$ are in general much smaller. The discrepancy in curves becomes even larger for $(+)\text{-cis-Co(en)}_2\text{Cl}_2^+$. The question arises as to how similar the curves must be in order to indicate the same absolute configuration. Too few absolute configurations have been established by x-ray methods to permit one to answer this question. Of the vast number of metal complexes that have been resolved into enantiomers, relatively few absolute configurations have been determined, but there is little doubt that this will be an area of active research in the future.

The preparation, resolution, and characterization of the optical isomers of Co(en)_3^{3+} are the objects of this experiment. The preparation of the complex is very similar to that used in the preparation of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ in Experiment 1. A solution of Co(II) is oxidized by air in the presence of ethylenediamine, en, and activated charcoal. The activated charcoal catalyzes, by an unknown mechanism, the oxidation of the rapidly formed Co(II) complex, Co(en)_3^{2+} , to Co(en)_3^{3+} .

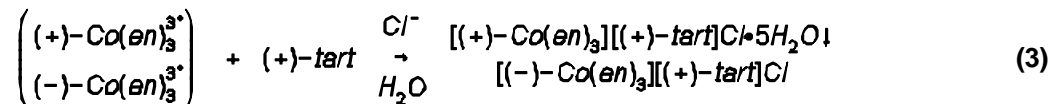


The resulting $[\text{Co(en)}_3] \text{SO}_4\text{Cl}$ is not isolated from solution but is immediately resolved by diastereomer-formation with optically active d-tartrate, $(+)\text{-tart}$,



Diastereomers have differing solubility properties, and with a proper choice of resolving agent it is possible to fractionally crystallize one diastereomer, leaving the other in solution. In this case $[(+)\text{-Co(en)}_3^{3+}][(+)\text{-tart}]\text{Cl}$ is the least soluble diastereomer and preferentially crystallizes from solution as the

pentahydrate.



The $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}$ is converted to $[\text{Co(en)}_3]\text{I}_3\cdot\text{H}_2\text{O}$ by reaction with I^- . The $[\alpha]_D$ of the product is $+89^\circ$.



The other optical isomer, $[(-)\text{Co(en)}_3]^{3+}\text{I}_3$, is obtained by adding I^- to the solution from which $[(+)\text{-Co(en)}_3]^{3+}[(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ was previously precipitated. The solid that precipitates with I^- is a mixture of crystals of the racemate, $(+)$ and $(-)[\text{Co(en)}_3]^{3+}\text{I}_3\cdot\text{H}_2\text{O}$, and crystals of pure $[(-)\text{Co(en)}_3]^{3+}\text{I}_3\cdot\text{H}_2\text{O}$. The $[(-)\text{Co(en)}_3]^{3+}\text{I}_3\cdot\text{H}_2\text{O}$ is much more soluble in warm water than the racemate and may be extracted into solution, which on cooling precipitates the desired enantiomer, $[(-)\text{Co(en)}_3]^{3+}\text{I}_3\cdot\text{H}_2\text{O}$, whose $[\alpha]_D = -89^\circ$. The optical purities of the isolated $(+)$ and $(-)$ enantiomers are to be evaluated by measuring their specific rotations.

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 PROCEDURE

Preparation of the Resolving Agent, Barium d-Tartrate

Prepare solutions of BaCl_2 and of d-tartaric acid by dissolving 12.2 g (50 mmoles) of $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ in a minimum amount of water and 7.5 g (50 mmoles) of d-tartaric acid in water. After heating these solutions to 90°C , mix them and add the base ethylenediamine until the solution is neutral. Allow the solution to cool to room temperature. Filter the precipitate and wash with warm water.

Preparation and Resolution of Co(en)_3^{3+}

Prepare in a filter flask a solution containing 10.3 g (170 mmoles, 11.5 mL) of ethylenediamine (en) in 25 mL of water. After cooling the solution in an ice bath, add 5 mL of concentrated (12 M) HCl, 14 g (50 mmoles) of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ dissolved in 25 mL of cold water, and 2 g of activated charcoal. Bubble a rapid stream of air through this solution for 4 hours by pulling water-aspirator vacuum on the filter flask as shown in Figure 6.

Then add dilute HCl or ethylenediamine, as required, until its pH is 7.0-7.5. Heat the mixture in an evaporating dish on a steam bath for 15 minutes. Cool the solution to room temperature, filter off the charcoal,

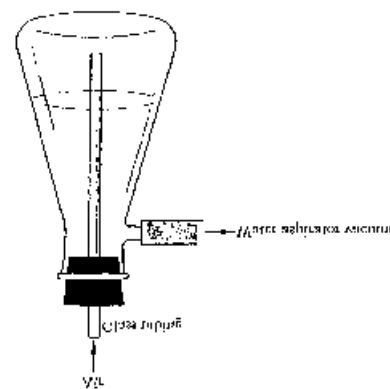


Figure 6

and wash with 10 mL of water on the filter. Add the wash to the filtrate.

To the Co(en)_3^{3+} solution just prepared, add all of the barium d-tartrate prepared previously. After heating the mixture on a steam bath for 30 minutes with vigorous stirring, filter off the precipitated BaSO_4 and wash with a small amount of hot water. Evaporate the solution on a hot plate or with a burner to 50 mL, and allow the crystals of $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ to precipitate overnight. Filter off the crystals and save the filtrate for later isolation of the $(-)\text{-Co(en)}_3^{3+}$ enantiomer. Wash the crystals with a 40% (by volume) ethanol-water solution, and recrystallize the product by dissolving it in 15 mL of hot water followed by cooling in ice. Wash the crystals with 40 percent ethanol-water and then with absolute ethanol. Air-dry and determine the yield of $[(+)\text{-Co(en)}_3^{3+}][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$.

To determine the specific rotation of this compound, dilute approximately, 0.05 g of the sample to a solution volume of 10 mL. Introduce this solution into a 1 cm cylindrical spectropolarimeter cell making certain to remove any air bubbles from the light path. Following the instrument operating instructions, measure the circular dichroism over the range 600-200 nm. Present the data in units of molecular ellipticity.

To convert the diastereomer to $[(+)\text{-Co(en)}_3^{3+}]_3\cdot\text{H}_2\text{O}$, dissolve the $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$ in 15 mL of hot water and add 0.25 mL of concentrated ammonia (15 M) solution. With stirring, add a solution of 17 g (113 mmoles) of NaI dissolved in 7 mL of hot water. After cooling in an ice bath, suction filter and wash the crystals with an ice cold solution of 3 g of NaI in 10 mL of water to remove the tartrate. After washing with ethanol and finally with acetone, allow the $[(+)\text{-Co(en)}_3]_3\cdot\text{H}_2\text{O}$ to air-dry and determine the yield. Measure its CD using a solution of approximately 0.05 g of sample in 10 mL of water.

To isolate $(-)\text{-Co(en)}_3^{3+}\cdot\text{H}_2\text{O}$, add 0.25 mL of concentrated 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 (see previous discussion). Heat the solution to 80°C and add with stirring 17 g (113 mmoles) of NaI. Upon cooling in an ice bath, impure $(-)\text{-Co(en)}_3^{3+}\cdot\text{H}_2\text{O}$ precipitates and is filtered and washed with a solution of 3 g of NaI dissolved in 10 mL of water. To purify, dissolve the precipitate, with stirring, in 35 mL of water at 50°C . Filter off the undissolved racemate and add 5 g of NaI to the filtrate. Crystallization of $(-)\text{-Co(en)}_3^{3+}\cdot\text{H}_2\text{O}$ occurs on cooling. Filter the precipitate, wash with ethanol and then with acetone, and finally air-dry. Determine the yield and measure the CD as before.

Racemization of $(+)\text{-Co(en)}_3^{3+}$ or $(-)\text{-Co(en)}_3^{3+}$

Dissolve approximately 1 g of either $[(+)\text{-Co(en)}_3^{3+}]_3\cdot\text{H}_2\text{O}$ or $(-)\text{-Co(en)}_3^{3+}\cdot\text{H}_2\text{O}$ in a minimum volume of warm water. Add a small amount of activated charcoal and boil the solution for approximately 30 minutes. Then filter the solution while hot, and add a few grams of NaI to aid in the precipitation of the racemate. Wash with alcohol and acetone and air-dry. Determine the CD of the racemized $[\text{Co(en)}_3^{3+}]_3\cdot\text{H}_2\text{O}$.

REPORT

Include the following:

1. Percentage yields of $[(+)\text{-Co(en)}_3][(+)\text{-tart}]\text{Cl}\cdot 5\text{H}_2\text{O}$, $[(+)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$, and $[(-)\text{-Co(en)}_3]\cdot \text{H}_2\text{O}$.
2. CD curves for the above complexes.
3. If $[\alpha]_D$ of pure $[(+)\text{-Co(en)}_3]^{3+}\text{I}_3\cdot \text{H}_2\text{O}$ is $+89^\circ$, what percentage of your sample of this compound is actually this enantiomer? Assume that the only impurity is $[(-)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$. Do the same calculation for your sample of $[(-)\text{-Co(en)}_3]\cdot \text{H}_2\text{O}$.
4. $[\alpha]_D$ of the $[\text{Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$, which is isolated from boiling a solution of (+) or (-) Co(en)_3^{3+} with activated charcoal.

QUESTIONS

1. Plot an ORD curve for $(-)\text{-Co(en)}_3^{3+}$ analogous to that given in Figure 8-3 for $(+)\text{-Co(en)}_3^{3+}$.
2. If you were to resolve an unknown complex, M(en)_3 , how would you know whether or not your resolved products were 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. Draw structures of the optical isomers of Co(EDTA)^- , where $\text{EDTA} = (\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2^-)_2$.
6. In the preparation of barium d-tartrate, what was the purpose of adding ethylenediamine?
7. In the purification of both (+) and $(-)[\text{Co(en)}_3^{3+}]\text{I}_3\cdot \text{H}_2\text{O}$, the compounds were washed with water containing NaI. What was the purpose of the NaI?
8. Outline methods for analyzing $[(+)\text{-Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ for its percentage Co and iodine content.

INDEPENDENT STUDIES

- A. Analyze $[\text{Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ for its percentage Co and/or I content.
- B. Confirm the 4-ion nature of $[\text{Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ by measuring its molar conductance.
- C. Measure the proton nmr spectrum of $[\text{Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$ in D_2O solvent. (J. K. Beattie, *Accounts Chem. Res.*, **4**, 253 (1971).)
- D. Prepare and resolve $[\text{Ni}(\text{o-phen})_3](\text{ClO}_4)_2$, where o-phen is 1,10-phenanthroline, into its d and l enantiomers. (G.B. Kauffman and L.T. Takahashi, *Inorganic Syntheses*, Vol. 8, McGraw-Hill, New York, 1966, p. 227.)
- E. Record and compare the ultraviolet-visible spectra of the optical isomers of $[\text{Co(en)}_3]\text{I}_3\cdot \text{H}_2\text{O}$.

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