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Experiment 26

Geometric Isomerism

Part A: Synthesis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride

Part B: Synthesis of *cis*-Dichlorobis(ethylenediamine)cobalt(III) Chloride

INTRODUCTION The modern era of inorganic chemistry can be said to have begun at the turn of the 20th century with Alfred Werner's pioneering work on metal complex structure and coordination.¹ Werner proved (in 1911) that compounds containing six ligands connected to a central metal atom were indeed octahedral by an elegant resolution of the complex $[\text{Co}(\text{en})_2(\text{NH}_3)\text{X}]^{2+}$. This type of geometry had been theorized earlier (1875) by van't Hoff, who suggested that appropriately substituted octahedral molecules should exhibit geometric isomerism.

Compounds having the same formulas but different structures are isomeric. With geometrical isomers, it is the arrangement of ligands on the central atom that differs. In an octahedral compound of formula MA_4B_2 (M = metal, A and B = ligands), where a central metal is surrounded by four of one type of ligand and two of another, there are two ways to arrange the groups, as shown in Figure 8.6a. In the *cis* isomer, the two B groups are adjacent to each other, while in the *trans* isomer, the two B groups are opposite each other.

Geometrical isomers are totally different compounds, having different physical properties, and often having different colors. In most syntheses, both isomers are obtained. Separation can be a problem, but because of the (usually) different solubilities and reactivities of the isomers, separation is possible. The first geometrical isomers were also identified by Werner, who in 1893 determined the structure of the inorganic geometric isomer pair *cis*- and *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Geometrical isomers frequently contain bidentate ligands, which occupy two coordination sites. Ethylenediamine ($\text{en} = \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$) is such a bidentate ligand. The two geometrical isomers of the compound to be synthesized in this experiment, dichlorobis(ethylenediamine)cobalt(III) chloride, $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, are shown in Figure 8.6b. This pair was also first investigated by Werner. Experiment 27 deals with the separation of optical isomers of this complex. Werner received the Nobel Prize in 1913 for his pioneering work in structural inorganic chemistry.

Numerous complexes of cobalt(III) are known and nearly all have octahedral structures. In solution, these ions undergo ligand substitution reactions rather

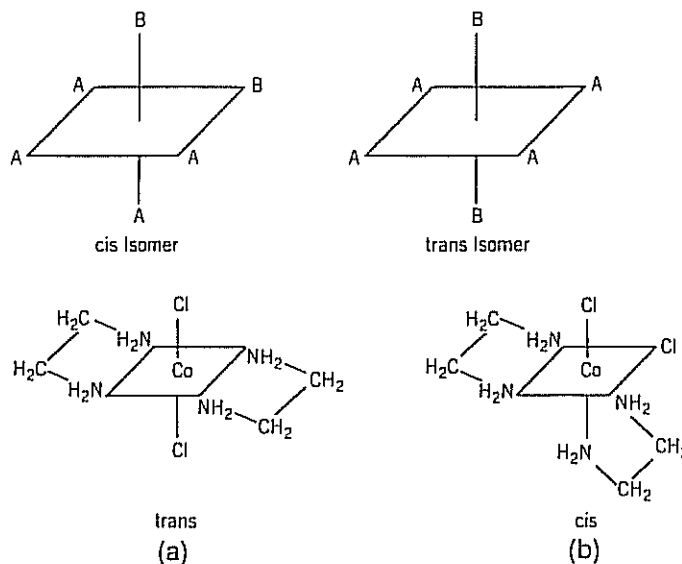
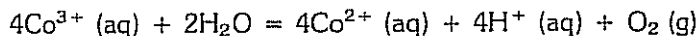


Figure 8.6. a. The cis and trans isomers of MA_4B_2 . b. Geometric isomers of $[Co(en)_2Cl_2]^+$.

slowly compared to the complexes of many other transition metals. Because of this relative stability, they are of particular interest, as they may be easily studied. Indeed, much of our knowledge of and the theory concerning octahedral complexes in general was derived from studies of cobalt(III) species.

Cobalt(III) exhibits a particular tendency to coordinate with ligands containing nitrogen. A majority of these complexes have ammonia, amines, or nitrogen bonded NCS^- groups. Several of these compounds have cis and trans isomers and one of them, dichlorobis(ethylenediamine)cobalt(III) chloride, is particularly appropriate for demonstrating geometric isomerism in transition metal complexes (Parts 26.A and B). It is of further interest to realize that the cis-isomer of this geometric pair exists as an enantiomeric (optically active) pair of isomers. The racemic mixture is obtained when the cis-isomer is prepared (Part 26.B), but the mixture can be resolved and one of the enantiomers separated (Experiment 27).

The *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, shown in Figure 8.6b, is prepared² by the air oxidation of an aqueous solution of cobalt(II) chloride hexahydrate and ethylenediamine, followed by the addition of concentrated hydrochloric acid. The synthesis uses a Co^{2+} species rather than a Co^{3+} salt, because the cobaltic ion reacts with water and is therefore unstable in the presence of moisture.



Once Co^{3+} has coordinated with ethylenediamine and chloride ligands, it shows little or no tendency to oxidize water.

Prior Reading and Techniques

Section 5.D.3: Isolation of Crystalline Products (Suction Filtration)

Section 5.F.2: Evaporation Techniques

Section 6.C: Infrared Spectroscopy

Related Experiments

Cobalt Chemistry: Experiments 7B, 17, 27, 30, 35, and 47B
 Isomerism: Experiments 27, 37, 46, and 49

EXPERIMENTAL SECTION

Part A: Synthesis of *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride
Safety Recommendations

Cobalt(II) chloride hexahydrate (CAS No. 7791-13-1): This compound is harmful if swallowed, inhaled, or absorbed through the skin. ORL-RAT LD50: 766 mg/kg.

Ethylenediamine (CAS No. 107-15-3): This compound is harmful if swallowed, inhaled, or absorbed through the skin. ORL-RAT LD50: 500 mg/kg. It has an irritating ammonia odor (vapor pressure is 10 mm at 20 °C), so it should only be used in the **HOOD**.

CHEMICAL DATA

Compound	FW	Amount	mmol	bp (°C)	mp (°C)	Density
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	237.85	300 mg	1.26		87	1.920
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	60.10	1 mL/10% solution	1.50	118	8.5	0.899

Required Equipment

Side arm test tube, Pasteur pipets, magnetic stirring hot plate, water aspirator, ice bath, Hirsch funnel, watch glass.

Time Required for Experiment: 1.5 h.

EXPERIMENTAL PROCEDURE^{2,3}

NOTE: If Experiment 27 is to be performed, double all quantities in Part 26.A. Alternatively, combine the product from two students to have enough *trans* product for Experiment 27.

In a side arm test tube equipped with an air inlet (Fig. 8.7), place 300 mg (1.26 mmol) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 2 mL of water (graduated cylinder), and 1.0 mL of 10% ethylenediamine (automatic delivery pipet, **HOOD**!).

Clamp the reaction tube in a hot water bath (90–95 °C) and connect the side arm to a water aspirator through a water trap. Turn on the aspirator so as to draw air through the solution at a slow but steady rate. The reacting system, which is purple in color, is maintained under these conditions for a period of 1.0 h. From time to time, add additional water to the reaction flask (down the air inlet tube) to maintain the water volume. After the 1.0-h heating time, disconnect the aspirator and remove the reaction tube from the water bath.

NOTE: Do not turn off the aspirator until the tube is disconnected. This will prevent any water from being sucked back into the reaction tube due to the change in pressure. This is a good practice to follow even though the water trap is used.

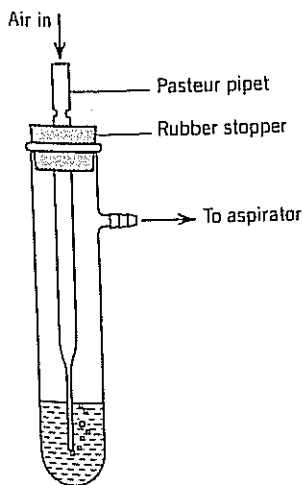


Figure 8.7. Side arm test tube apparatus.

Allow the tube to cool to approximately 50–60 °C. Using a Pasteur pipet, slowly add 600 μL of concentrated HCl down the inlet tube. Swirl the reaction assembly by hand for several minutes and place it back into the hot water bath. Reconnect the aspirator and adjust it so that a steady stream of air is once again pulled through the solution. This procedure is continued until the volume of the solution is decreased to the point that crystals of the product are evident in the tube.

Disconnect the tube from the aspirator, remove it from the water bath and place it in an ice bath to cool. Scrape the resulting solid from the tube and collect it by suction filtration using a Hirsch funnel. Wash the crystals with two 2-mL portions of cold methanol, which is added to the reaction flask to assist in the removal of additional crystalline product. This is followed by washing with two 2-mL portions of cold diethyl ether. The beautiful green crystals that form are actually the hydrochloride salt of the desired product. To obtain the *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride, place the crystals on a small watch glass, and heat them in an oven at 110 °C for 1.5 h.

Characterization of Product

Record the IR spectrum (KBr pellet) of the compound for comparison with the *cis* isomer prepared in Part 26.B of this experiment. The Visible spectrum may also be obtained and compared.

Part B: Synthesis of *cis*-Dichlorobis(ethylenediamine)cobalt(III) Chloride

Safety Recommendations: See Part 26.A

Required Equipment

Hot water bath, 5-cm watch glass, 10-mL beaker, magnetic stirring hot plate, magnetic stirring bar.

Time Required for Experiment: 45 min.

EXPERIMENT PROCEDURE

NOTE: If Experiment 27 is to be performed, increase the amounts used in Part 26.B by a factor of 7–8.

Place 10 mg (0.06 mmol) of the green *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride on a 5-cm watch glass. Dissolve this solid material in 300 μL of water (automatic delivery pipet) and allow the solution to stand for about 10 min at room temperature. Place the watch glass on a hot water bath prepared from a 10-mL beaker containing a magnetic stirring bar filled with boiling water. The beaker is previously positioned in a sand bath on a magnetic stirring hot plate. Heat the green solution and concentrate it to dryness. A deep violet, glassy material is formed on the watch glass.

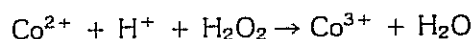
Isolation of Product

Cool the product and carefully scrape it from the glass surface (**Caution**—the glassy product tends to scatter). Weigh the material and calculate the percentage yield. A quantitative yield is usually obtained.

Characterization of Product

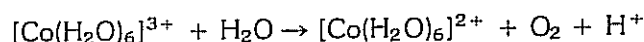
Obtain the IR spectrum of the material (KBr pellet) and compare it to that of the *trans* isomer prepared in Part 26.A. The Visible spectrum may also be obtained and compared.

- QUESTIONS**
1. How many isomers exist of the complex having formula MA_3B_3 ? Draw and name them.
 2. It was stated that Co^{3+} complexes are very stable and the ligands in such complexes are not labile. Define labile and explain the relative inertness of Co^{3+} complexes.
 3. Define the symmetry elements of the trans and cis isomers prepared in this experiment and assign the isomers to symmetry point groups.
 4. In place of oxygen as the oxidizing agent, hydrogen peroxide may be used in this reaction. Balance the following oxidation–reduction reaction using this reagent.



Which species is the reducing agent in this reaction?

5. In the absence of the ethylenediamine ligands, the hexaaquacobalt(III) ion reacts rapidly with water according to the following scheme.



Balance the equation and determine which species is the reducing agent.

6. Today, chemists take for granted the octahedral configuration of most transition metal complexes. It should be known, however, that this was no easy matter to prove. One of the great chemical literature debates took place between S. M. Jørgensen and Alfred Werner about the true structure of cobalt amine complexes. Describe both men's arguments and detail how Werner's views eventually won out. There is also an interesting analogy between the lives of Werner and August Kekulé (of benzene fame). See the following for details: Kauffman, G. B. *J. Chem. Educ.* **1976**, *53*, 445. George Kauffman has written extensively about chemical history.

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Experiment 27

Optical Isomers: Separation of an Optical Isomer of *cis*-Dichlorobis(ethylenediamine) cobalt(III) Chloride

- INTRODUCTION** The cis isomer of $[Co(en)_2Cl_2]Cl$ (see Experiment 26 for the synthesis of this isomer) actually consists of two isomers that are mirror images of each other.

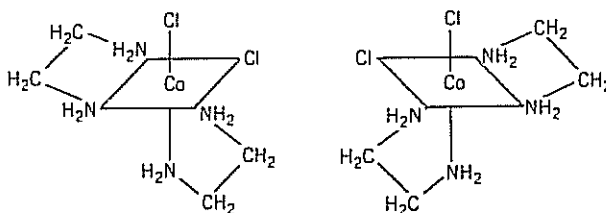
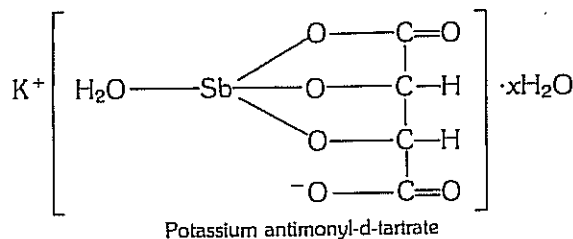


Figure 8.8. Optical isomers of $\text{cis-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$.

Such isomers are termed optical isomers. The two forms are shown in Figure 8.8.

These two forms, much like your right and left hands, cannot be superimposed upon each other. Optical isomers generally have physical properties that are quite similar, and are generally very difficult to separate (resolve). The most common way to resolve optical isomers is by treating the mixture (called a racemic mixture) with another compound that is optically active, with which one of the isomers will form an insoluble salt. In this experiment, the two optical isomers are treated with potassium antimonyl-*d*-tartrate, which selectively precipitates one of the two optical isomers, the *d* isomer. Werner was also active in this area, having reported (in 1912) on several such compounds, including conversions of *levo* (left handed) into *dextro* (right handed) complexes.

By addition of potassium antimonyl-*d*-tartrate, the *d* isomer of cis-dichlorobis(ethylenediamine)cobalt(III) chloride can be selectively precipitated from the racemic mixture of the two optically active isomers.



Prior Reading and Techniques

Section 5.D.3: Isolation of the Crystalline Products (Suction Filtration)

Related Experiments

Cobalt Chemistry: Experiments 7B, 17, 26, 30, 35, and 47B

Isomerism: Experiments 26, 37, 46, and 49

EXPERIMENTAL SECTION Safety Requirements

Potassium antimonyl-*d*-tartrate hydrate (CAS No. none): This compound is harmful if swallowed, inhaled, or absorbed through the skin. ORL-HMN LDLo: 2 mg/kg. ORL-RAT LD50: 115 mg/kg.

CHEMICAL DATA

Compound	FW	Amount	mmol	mp (°C)	Density
cis-Dichlorobis(ethylene-diamine)cobalt(III) chloride	285.45	145 mg	0.50		
Potassium antimonyl-d-tartrate hydrate	333.93	167 mg	0.50		2.607

Required Equipment

Magnetic stirring hot plate, 10-mL Erlenmeyer flask, magnetic stirring bar, water bath, Pasteur filter pipet, 10-mL graduated cylinder, Hirsch funnel, clay tile or filter paper.

Time Required for Experiment: 2 h.**EXPERIMENTAL PROCEDURE^{1,2}**

In a 10-mL Erlenmeyer flask containing a magnetic stirring bar, dissolve 167 mg (0.5 mmol) of potassium antimonyl-d-tartrate hydrate in 2 mL of water (graduated cylinder). Clamp the flask in a water bath set on a magnetic stirring hot plate.

In a 10-mL beaker, dissolve 145 mg (0.5 mmol) of cis-dichlorobis(ethylenediamine)cobalt(III) chloride in 4 mL of water.

Transfer the solution in the beaker, by use of a Pasteur filter pipet, to the solution in the Erlenmeyer flask. Heat the solution in the water bath to 70–80 °C, with stirring, for 45 min. A pale violet precipitate will form over this time period. Cool the flask to room temperature.

Isolation of Product

Collect the crystalline product by suction filtration using a Hirsch funnel. Wash the filter cake with two 0.5-mL portions of chilled water. Dry the product on a clay tile.

Characterization of Product

Determine the specific rotation of the product using a polarimeter. The compound may be dissolved in very hot water, and the specific rotation must be measured immediately, as the product will precipitate upon cooling.

QUESTIONS

1. In order for an organic molecule to be optically active, what configuration must be present?
2. What symmetry elements make a compound optically inactive?
3. What is circular dichroism and how does it relate to optical activity?
4. Once an optically active compound is isolated, how does one know which configuration it has? From the literature, discuss the Cotton Effect in terms of assignment of absolute configuration.

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