

## Experiment 14

# PREPARATION AND CHARACTERIZATION OF COBALT COMPLEXES

### Objective

The purpose of this experiment is to synthesize the metal complex *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride; to observe the *trans*-to-*cis* isomerization of this complex; and to explain the UV-vis spectrum of the complex using the crystal field theory.

### Lab techniques

- Weighing chemicals.
- Performing synthesis and separation by crystallization
- Operating suction filtration, stirrer/hot plate, and spectrophotometer.

### Introduction

Complexes, also known as coordination compounds, usually consist of a central metal cation/atom and several ligands, where a ligand can be a molecule, such as ammonia ( $\text{NH}_3$ ), or an anion, such as chloride ion ( $\text{Cl}^-$ ) with lone pair electrons. The coordination number of the central metal can range from two to more than ten, among which six and four are the most common. The geometry of four-coordinated complexes can either be square planar or tetrahedral, while six-coordinated complexes are mostly octahedral (Fig. 14-1).

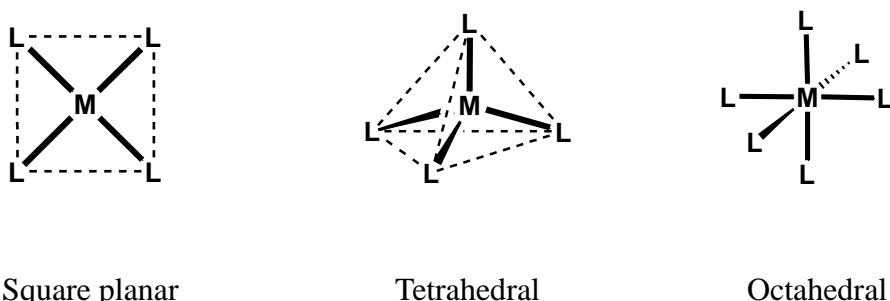


Figure 14-1 Geometry of complexes

Coordination compounds usually have various colors and different magnetic properties. Several theories have been developed to explain this phenomenon. One of

them is the crystal field theory. In the crystal field model, the donor atom of the ligand (which donates the electron-pair) is assumed to be a negative point of charge. In the ground state, the central metal has five degenerate  $d$ -orbitals; i.e., these orbitals have the same energy levels. Since orbital is the space where electrons are most likely to be found around an atom,  $d$ -orbitals are considered to be negatively charged. When the ligands approach the  $d$ -orbitals from different orientations, the five  $d$ -orbitals are subjected to different degrees of repulsion. As a result, the energy level of the  $d$  orbitals increases accordingly. In an octahedral six-coordinated complex, the five  $d$  orbitals split into two energy levels. The  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals pointing directly at the ligands experience greater repulsion. Thus, these two orbitals have a higher energy level. The other three orbitals,  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ , experience relatively less repulsion and thus have a lower energy level. The energy difference (splitting energy,  $\Delta$ ) between these two levels depends on the ligands and the metal center that are bonded together. The metal is considered to experience a strong field if a large energy difference is produced, and a weak field if a small difference is produced. In a strong-field complex, the electrons will not fill  $d$ -orbitals at the higher energy level before  $d$ -orbitals in the lower energy level are completely filled. Such a complex is said to be in a low spin state. On the other hand, the electrons in a weak-field complex follow Hund's rule; they are arranged according to the configurations yielding maximum total spin states. Such a complex is said to be in a high spin state, as shown in Fig. 14-2.

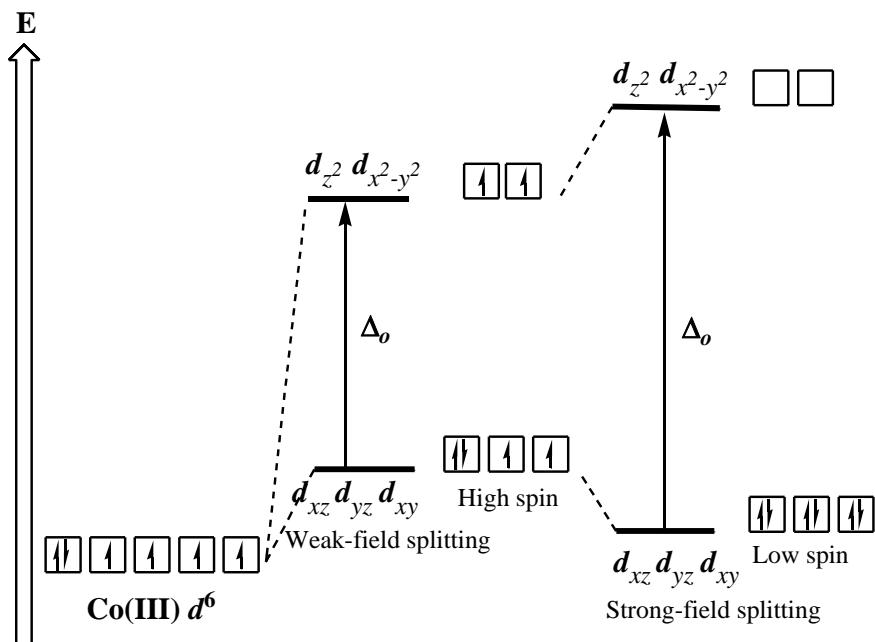


Figure 14-2 Electron configurations for the strong-field and weak-field cases in an octahedral crystal field model

The splitting energy of *d*-orbitals in metal complexes usually corresponds to the energy of visible light and the ultraviolet range. Electrons occupying orbitals in the lower energy level can absorb different wavelengths of light and jump to the higher energy level. Hence, complexes are a group of substances that show a rich variety of colors. By analyzing the absorption spectra of different complexes, we can determine the influence of the ligands on the splitting energy of the complexes. Weak-field ligands produce smaller splitting, associated with long wavelengths; while strong-field ligands produce larger splitting, associated with shorter wavelengths. Chemists have deduced a “spectrochemical series” based on this relationship in order of increasing field strength:

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{pyridine} \doteq \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$   
where en is the abbreviation of ethylenediamine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ). Each of the two nitrogen atoms in the en molecule can form a coordinate covalent bond with the same central metal; thus, ethylenediamine belongs to the bidentate ligand.

The purpose of this experiment is to synthesize and identify the *trans*- and *cis*- forms of dichlorobis(ethylenediamine)cobalt(III) chloride ( $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ ). This complex consists of a cobalt(III) ion with two chloride ions and two en molecules acting as ligands, forming an octahedral structure. The chloride ions can occupy either adjacent positions on the octahedron (*cis*), or the two vertices (*trans*). The result is geometric isomerism (Fig. 14-3). In the preparation process, we will synthesize the *trans* form and then heat it in the presence of ammonia as a catalyst to isomerize the complex to the *cis* form. The crystal environment of the cobalt ion is different in the two isomers, so they have different colors. The *trans* isomer is green, and the *cis* isomer is purple.

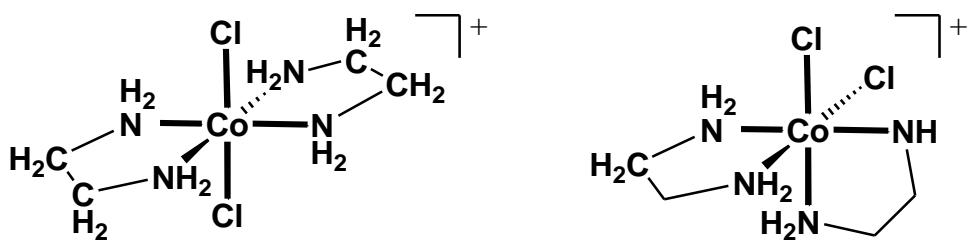


Figure 14-3 Left: *trans*- and right: *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  cations

## Apparatus

Suction pump, suction filtration flask, Hirsch funnel, graduated cylinders (10 mL), evaporating dish (2), magnetic stirring bar, glass rod, spatula, latex gloves, linen gloves, filter paper, Styrofoam cup, spectrophotometer, and cuvettes (3).

## Chemicals

Cobalt(II) chloride hexahydrate,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

Concentrated hydrochloric acid, 12 M  $\text{HCl}(\text{aq})$

Concentrated ammonia water, 15 M  $\text{NH}_3(\text{aq})$

10% Ethylenediamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$

95% Ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$

10% Hydrogen peroxide,  $\text{H}_2\text{O}_2$

## Procedure

- ★ Most of the chemicals used in this experiment are corrosive. Wear latex gloves and perform the experiments in the fume hood as necessary.

### I. *Trans*-dichlorobis(ethylenediamine)cobalt(III) chloride ( $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ )

1. Get a 100 mL beaker and fill it with 70 mL of water. Heat it on the hot plate as the steam bath in later steps. Check the amount of water remaining every 3 minutes and add water as necessary.
2. Weigh 1 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  directly on a clean evaporating dish. Record the exact weight.
3. Add 4 mL of 10% ethylenediamine solution to the evaporating dish. Stir until the solid dissolves completely.
4. In the fume hood, add 2 mL of 10%  $\text{H}_2\text{O}_2$  drop by drop to the evaporating dish and position it on the mouth of the 100 mL beaker prepared in step 1. Heat it on the steam bath and stir for 5~10 min until the solution shows a deep red-brown color.

Note: Co(II) is oxidized to Co(III) in this step. Do not spill  $\text{H}_2\text{O}_2(\text{aq})$  onto skin.

5. Add 3 mL concentrated hydrochloric acid (12 M) drop by drop to the evaporating dish. Continue heating on the steam bath and stirring the reacting solution until a thin layer of crystalline flakes floats on the surface of the solution. Then place the evaporating dish on the bench top inside the fume hood. Let it cool to room temperature. Then put the dish in an ice-water bath to ensure complete crystallization of the product.
6. Use the Hirsch funnel and suction filtration to collect the green solid product. Rinse the product with 1 mL of 95% ethanol. Repeat the rinsing process for three times.

Note: Refer to the experimental skills videos to learn how to perform suction filtration.

7. Dry the product through suction for 10 min. Transfer the product into a clean evaporating dish, and dry it in an oven at 110~120°C for 10 min to remove excess

HCl.

8. Measure the weight of the green *trans* isomer product and calculate the yield.
9. The liquid waste contains heavy metals and should be recycled at the end of the experiment.

## **II. *Cis*-dichlorobis(ethylenediamine)cobalt(III) chloride ( $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ )**

10. Weigh accurately ca. 0.3 g *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  directly onto a clean evaporating dish.

Note: Gather the *trans* complex at the center of the evaporating dish.

11. Add DI water drop by drop to dissolve the solid with the smallest amount of water possible (approx. 15~20 drops). Heat with the steam bath for several min and then add 2~3 drops of concentrated (15 M) ammonia water.

Note 1: If too much water is added, the *trans* isomer may not be able to isomerize to the *cis* form.

Note 2: The water of the steam bath should be boiling to provide high temperature.

12. Keep heating the evaporating dish with the steam bath to evaporate the liquid content. Observe any color changes in the solution. If any of the green *trans* complex still remains on the evaporating dish, use a few drops of concentrated ammonia water to wash it off into the solution. Continue heating until the content of the evaporating dish is completely dried.
13. Scrape off the purple *cis* complex from the evaporating dish and measure its weight. Both the *trans* and the *cis* complexes should be submitted to the lab instructor at the end of the experiment.

## **III. Spectrophotometric analysis of isomers**

14. Turn on the spectrophotometer to warm it up.

Note: Refer to the experimental skills videos to learn how to operate a spectrophotometer.

15. Measure 0.05 g of the green *trans* complex and 0.03 g of the purple *cis* complex obtained in the experiments and transfer them into separate test tubes. Dissolve each sample with 10 mL DI water and place the tubes in an ice-water bath. Obtain the visible light absorption spectrum of each sample solution immediately to prevent water from replacing the ligands.

16. Get three cuvettes and fill one of them with DI water as the reference solution (blank). Fill the other two with *trans* and *cis* sample solutions, respectively.

Note: Rinse the cuvette with portions of sample solution.

17. Set the spectrophotometer to absorbance function and the analytical wavelength

to 400 nm.

18. Adjust and measure the absorbance of the *trans* and *cis* complex sample solutions.

19. Repeat the analysis at various wavelengths, increasing the analyzing wavelength by 20 nm interval from 400 to 700 nm.

Note: Calibrate the spectrophotometer with the blank solution each time when the wavelength is changed.

20. Plot an absorbance vs. wavelength graph for each sample solution.

21. The liquid waste contains heavy metals and should be recycled at the end of the experiment.