Experiment 2
Geometrical Isomers: Cis & Trans Isomers of
Dichloro*bis*(ethylenediamine)cobalt(III) Chloride

Introduction

Geometrical isomers are metal complexes in which the coordinating ligands are present in the same proportion but vary in the arrangement of the ligands around the central metal atom. Despite always having identical chemical formulas, geometrical isomers often have widely different properties, such as magnetic moments, colors, bond strengths, and reactivities.
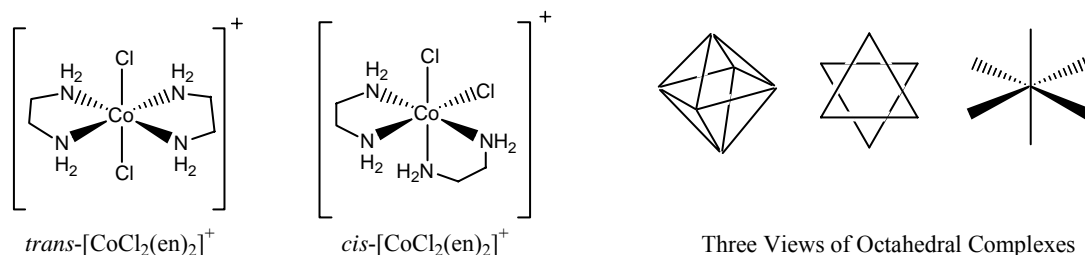

trans-[CoCl$_2$(en)$_2$]$^+$ *cis*-[CoCl$_2$(en)$_2$]$^+$ Three Views of Octahedral Complexes

Figure 1. Geometrical isomers from octahedral coordination complexes.

The cobalt complexes that we will investigate are both six coordinate. There are six ligands bound to the central metal atom in an octahedral structure. An octahedron is a geometrical solid with six vertices, each vertex being at 90 degrees to its four nearest neighbors and 180 degrees from the remaining vertex. When viewed as a polyhedron, it can be seen that an octahedron has eight triangular faces. In a perfect octahedron the faces are all identical equilateral triangles. Because we have a mixed ligand set [chloride and ethylenediamine (en), where en is a bidentate ligand that has two metal binding sites], our molecules will have a distorted octahedral structure.

Complexes of cobalt(III) undergo ligand substitution reactions relatively slowly and tend to be stable even when solvated. This allows us to isolate metastable species by crystallizing them before they can convert to the most thermodynamically stable form. Despite the benign chemistry of cobalt(III) complexes, the Co(III) ion is not stable in water due to the hydrolysis reaction below.

Figure 8.7. Side arm test tube apparatus.

$$4\ Co^{3+}\ (aq) + 2\ H_2O\ (aq) \rightarrow 4\ Co^{2+}\ (aq) + 4\ H^+\ (aq) + O_2\ (g)$$

We could ensure a constant (if small) supply of Co^{3+} during our reaction by bubbling air through our reaction solution using the apparatus shown on the right. Instead, we will use the stronger oxidizer, hydrogen peroxide (H$_2$O$_2$), to oxidize cobalt. Once Co^{3+} has been coordinated by the (en) and Cl ligands, it is stable against reduction.
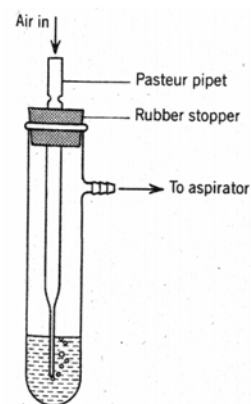
Throughout these preparations, note any color changes in your laboratory notebook. These changes are indicators of changes in the coordination sphere around the cobalt ion.

Preparation of *trans*-[Co(en)$_2$Cl$_2$]Cl

Start by dissolving 1.2 g of cobalt(II) chloride hexahydrate in 9.5 ml of deionized water in a sidearm test tube equipped with an air inlet (a Pasteur pipette inserted through a rubber stopper, as diagrammed in the introduction) but DO NOT connect this tube to an aspirator. Insert a magnetic stirbar and stir the solution during the following additions. First add 2.5 ml of a 16% ethylenediamine solution to the test tube. Then slowly add 1.2 ml of 30% H$_2$O$_2$ solution (dropwise) – this should take about 5 minutes. Finally, add 2.4 ml of concentrated HCl dropwise to the reaction mixture.

Next, heat the test tube over a steam bath while using your aspirator to pull air through the Pasteur pipette. This removes water. Allow the solution to evaporate until the volume is reduced to roughly 2 ml – green crystals will be apparent. Cool the solution in an ice bath, and then filter to recover the crystals. This deep green product is *trans*-[Co(en)$_2$Cl$_2$]Cl•HCl•2H$_2$O. Wash twice with 8 ml portions of methanol, and then two 8 ml portions of diethyl ether – this usually removes the HCl co-solvate.   Spread crystals and air dry. Assume for this lab that your washed crystals are *trans*-[Co(en)$_2$Cl$_2$]Cl•2H$_2$O. After determining your yield, prepare a solution of your product for uv-vis spectroscopy (see analysis section below).

Preparation of *cis*-[Co(en)$_2$Cl$_2$]Cl

Dissolve 80 mg of *trans*-[Co(en)$_2$Cl$_2$]Cl (actually, *trans*-[Co(en)$_2$Cl$_2$]Cl•2H$_2$O) in a minimum amount of deionized water on a watch glass. Let the solution stand for 5-10 min before moving it to a steam bath and evaporating it to dryness. The product should be uniformly violet in color. If not the evaporation procedure must be repeated. Scrape the solid onto a small funnel, and wash with three drops of ice water. Violet crystals should remain, which you should assume are the anhydrous *cis*-[Co(en)$_2$Cl$_2$]Cl.

If you are unable to isolate the violet solid, instead make 5 ml of a 0.015 M aqueous solution of the *trans* isomer. Heat this green solution over a steam bath – it should turn violet. Cool the solution in ice and observe what happens; reheat the solution if necessary. Use this solution to collect a uv-vis absorbance spectrum.

Analysis of the Cobalt Complexes

Collect a uv-vis absorbance spectrum for each complex. Use a 0.0150 M aqueous solution for the visible region of the spectrum (300 nm - 900 nm) – *you should calculate the masses needed for this in your prelab*. Make note of the wavelength of maximum absorbance or peak positions. Calculate the molar extinction coefficient at each absorbance peak in your spectra. You cannot accurately calculate a molar extinction coefficient if you do not know the precise molarity of your solution. Refer to the web links or your lecture notes for additional information on the Beer-Lambert law and molar extinction coefficients.

Questions

1. How many isomers exist for complexes of the general formula MA_3B_3? Draw and name each of them.

2. Is the *cis* isomer the enantiomer of the *trans* isomer? Justify with a drawing.

3. Write the balanced redox reaction between cobalt and H_2O_2 that occurred during your preparation.

4. What was done differently in the two steps of the procedure to prepare the two different geometric isomers? What chemical species was used to favor one isomer over the other?

5. Co(III) exhibits a strong tendency to coordinate with ligands containing nitrogen. Is this consistent with the hard-soft acid-base (HSAB) concepts that we studied in lab 1?

6. How many *d* electrons are present in Co(II) and Co(III) ion? How do these electron counts affect the ligand lability for octahedral complexes? Draw an energy level diagram to illustrate the d-orbital populations of each? *[The underlined portions do not need to be answered in 2007 since you may have not yet had a lecture on crystal field theory. You should be able to answer that part of the question by the time the lab is handed back].*