EXPERIMENT 19   *Ligand Substitution*

Objective

To prepare several transition metal complexes and observe how substituting different ligands influences the spectroscopic absorption.

Introduction

Chemical species like H_2O, NH_3, or Cl^- that have non-bonding electron pairs can form **coordinate covalent bonds** with transition metal cations by sharing an electron pair with the metal. The species that donates the electron pair is called a **ligand** and the resulting compound is called a **complex**. For example, the nitrogen atom in ammonia contains a non-bonding electron pair that can be shared with a transition metal cation such as Ag^+. In this case, the resulting complex is $Ag(NH_3)_2^+$. Transition metal cations form complexes very readily with neutral molecules like H_2O and NH_3, and with anions like Cl^- and CN^-. Consider the transition metal complex ion $[Co(NH_3)_4Cl_2]^+$ in aqueous solution. It is made from one Co^{3+} cation, 4 ammonia molecules, and 2 Cl^- anions. The net charge of the complex ion is the sum of the charges on all of the components: $(+3 -1 -1) = +1$.

The behavior of complex ions is based on their structure; there is a transition metal cation at the center, surrounded by several ionic or neutral chemical groups, the ligands. Transition metal cations, formed by losing electrons from their valence electron shell *s* and *d* orbitals, can share electron-pairs with other chemical species that have non-bonding electron pairs available to donate, forming a coordination bond between the metal cation electron acceptor and the ligand electron donor. Ligands that group around the central cation all have at least one pair of non-bonding electrons that coordinate with unfilled valence orbitals of the cation, to form the complex. Due to the charge on the central cation, coordination bonding frequently is mostly ionic, so that the number of ligands that can coordinate with the cation is determined more by the charge and size of the cation than by the number of valence orbitals.

The number of coordinate bonds that the cation forms is called its **coordination number**, and can vary from 2 to at least 12. The most common coordination numbers are 4 and 6. Only very large, multiply-charged cations form complexes with coordination numbers greater than eight.

In $[Co(NH_3)_4Cl_2]^+$, which has 4 NH_3 and 2 Cl^- ligands, the coordination number for Co^{3+} is six. Each NH_3 group has one non-bonding electron pair and each Cl^- ion has four non-bonding pairs available for coordination. The resulting complex ion has an octahedral symmetry, slightly distorted because the NH_3 and Cl ligands are not equivalent with respect to their sizes and electronegativities.

The complex ion $[Co(NH_3)_6]^{3+}$, where all 6 ligands are completely equivalent, would form a perfect octahedron. As a "rule of thumb" the coordination number often turns out to be 2 times the charge on the cation.

The nature of the cation-ligand bond has a very strong influence on the absorption spectrum of the complex ion, and spectroscopy is an important tool for studying the bonding properties of coordination complexes. The presence of the ligands around the central cation removes the energy degeneracy of the cation d orbitals. With six ligands in octahedral symmetry, (the geometry of the complexes studied in this experiment) two of the d orbitals are raised to a higher energy than the other three (see Figure 19.1 for the splitting diagram). By absorbing light energy, an electron can move from a lower to an upper energy level. (a) in Figure 19.1 represents the uncomplexed Co^{3+}, (b) is the ground state of complexed Co^{3+}, ion and (c) is the excited state of the complexed Co^{3+} ion.

FIGURE 19.1

(a)   (b)   (c)
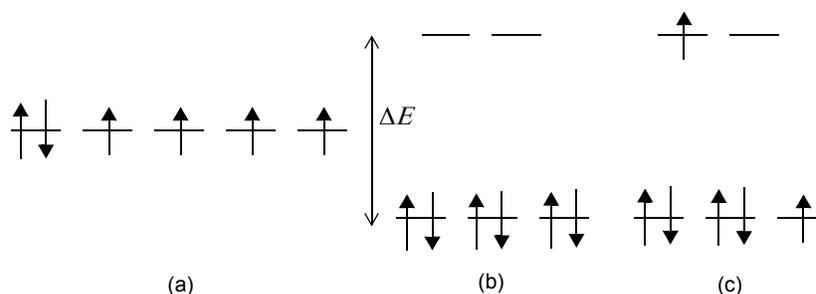
The energy difference between the lower and upper levels is related to the wavelength of light absorbed, as expressed by the equation:

$$\Delta E = \frac{hc}{\lambda}$$

(EQ 19.1)

ΔE = energy difference between lower and upper levels h = Planck's constant, c = speed of light, and λ = wavelength of light absorbed in meters

Notice that, since both terms in the numerator of Equation 19.1 are constants, to make ΔE larger, λ must be made smaller. In other words, when ΔE is large, the wavelength of light absorbed is short, and when ΔE is small, a longer wavelength of light is absorbed. The nature of the ligand determines the separation of the energy levels and the magnitude of ΔE.

A listing of ligands, in order of how large an energy level splitting they produce, is called a spectrochemical series. Equation 19.2 gives a spectrochemical series for some common ligands arranged in order of decreasing ΔE:

$$CN^- > NO_2^- > NCS^- > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$$

(EQ 19.2)
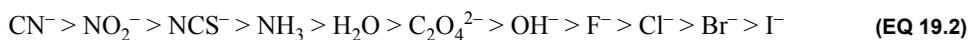
The color of an aqueous solution of a complex ion is determined by which wavelengths of light are absorbed to excite the d electrons. The color observed depends on what wavelengths remain after part of the light has been absorbed. The color that we see is the color of the light that is transmitted

through the sample, not the color of the light absorbed by the sample. In Table 19.1 on page 139, the energies absorbed and colors observed are compared for several complex ions of Co^{3+}. A compound that does not absorb at all in the visible wavelength region will appear to be transparent and colorless; one that absorbs fairly uniformly at all visible wavelengths will be gray or black.

TABLE 19.1

Complex Ion	Color of Solution	Color Absorbed from Incident Light	Wavelength of maximum Absorbance (nm)
$Co(NH_3)_6^{3+}$	yellow	violet	430
$Co(NH_3)NCS^{2+}$	orange	blue	470
$Co(NH_3)_5H_2O^{3+}$	red	blue-green	500
$Co(NH_3)_5Cl^{2+}$	purple	yellow-green	530
trans-$Co(NH_3)_4Cl_2^+$	green	red	680

By measuring how the absorbance spectrum of a complex ion depends on the ligands that are bonded to the central metal cation, we learn about the energy separation between the *d* orbitals in the metal's valence shell and determine the order of ligands in a spectrochemical series. From Table 19.1 on page 139 we see that the wavelength of maximum absorbance for $Co(NH_3)_6^{3+}$ is 430 nm. Therefore the ΔE for the energy splitting of the *d* orbitals is given in Equation 19.3

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.636 \times 10^{-34} \text{J s})(3.00 \times 10^8 \text{m/s})}{430 \times 10^{-9} \text{m}}$$ **(EQ 19.3)**

In Part A, the ligands around an octahedrally complexed Ni^{2+} cation are changed from H_2O to NH_3 and the effect on the absorption spectrum is measured with a spectrophotometer. In Part B, an octahedrally complexed Co^{2+} cation is oxidized to Co^{3+}, its ligands are changed from H_2O to NO_2, and the effect on the spectrum is measured.

You are to do only one of these parts. Your instructor will tell you whether to do Part A or Part B.

In Part C, you use molecular models to study the geometry and isomers of several complex ions.

Procedure

Part A

1. Be certain that the spectrophotometer is turned on so it is warmed up for your measurements.
2. Place 50 mL of concentrated NH_3 solution into a small Erlenmeyer flask or bottle and cool it in an ice bath.
3. On weighing paper, weigh about 6 g of nickel chloride, $[Ni(H_2O)_6]Cl_2$ to 0.1 g. Transfer to a 50 mL beaker and dissolve it in 10 mL H_2O, warming and stirring as needed. If the solution is not clear, centrifuge it rapidly while it is still warm. Then, cool the solution to room temperature.

4. Transfer 1 mL of the clear solution to a clean graduated cylinder and dilute it to 10 mL with distilled water. Save the concentrated portion for Step 8.

5. Using the diluted portion, rinse a spectrophotometer cell twice with small portions of the solution. Then, fill the cell with the diluted portion of the nickel chloride solution. To remove bubbles on the cell walls, press a piece of parafilm over the top of the cell with your finger to seal it, and slowly invert and rotate the cell to bring all the bubbles to the liquid surface.

6. Insert the sample cell into the spectrometer and measure its absorption spectrum. Scan over the entire wavelength range, measuring at 20 nm intervals. Record the measured absorbance values on the Data Sheet.
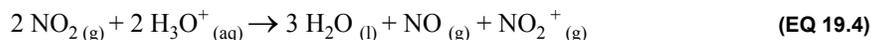
> **Be sure to reset (zero and 100%) your spectrophotometer after each frequency change**.

7. Repeat the scanning procedure with a distilled water blank. Rinse the cell 2 or 3 times with distilled water before measuring. Record the measured absorbance values on the Data Sheet.

8. In a hood, add 12 mL of chilled, concentrated NH_3 solution to the 9 mL of concentrated nickel chloride solution remaining from Step 4, while stirring. Cool the mixture by placing the beaker on ice. Crystals of $[Ni(NH_3)_6]Cl_2$ should form within about 15 minutes. Add more NH_3 if crystallization does not occur.

9. Vacuum filter the crystals. If the filtered crystals are clumped together, spread them out on the filter with a spatula. With suction on, wash the crystals twice, using 2 mL of cold concentrated NH_3 solution each time.

10. Now, wash the crystals 3 times, using 2 mL portions of acetone each time, to remove water. Keep the suction on to draw air through the filter until the crystals are dry.

11. Weigh your product and record the mass in your notebook.

12. Dissolve the $[Ni(NH_3)_6]Cl_2$ crystals in 9 mL 6 M NH_3 and repeat steps 4-6 **(dilute with concentrated NH_3 rather than water)** to measure the absorption spectrum of the solution. It is not necessary to run another water blank.

Part B

1. On weighing paper, weigh about 5 g of cobalt(II) nitrate, $[Co(H_2O)_6](NO_3)_2$ to 0.1 g and record the mass. Transfer the sample to a 100 mL beaker and dissolve it in 15 mL H_2O.

2. Remove 1 mL, of the solution, dilute it to 10 mL with distilled water and measure its absorbance spectrum as in steps 5-6 of Part A.

3. Repeat the scanning procedure with a distilled water blank. Rinse the cell 2 or 3 times with distilled water before measuring. Record the measured absorbance values on the Data sheet.

4. Dissolve 15 g sodium nitrite, $NaNO_2$, into the remaining 9 mL of concentrated cobalt nitrate solution, warming and stirring as needed until dissolved.

5. Cool the solution to 50 °C in a cold water bath.

6. In a hood, add to the solution drop by drop 5 mL of 50% acetic acid solution, while stirring continuously but gently. You want to dissolve the reactants without unnecessary agitation.

7. Transfer the solution to a large test tube (25 × 200 mm). Pour it slowly down the side of the test tube to avoid agitation. The reaction rate in the cool un-agitated solution is very slow.

8. Connect the test tube to an aspirator as in the set-up on the instructor's bench, and turn on the aspirator. Be sure the long tube in the trapping bottle is under the water surface. Air bubbles rising through the reaction solution mixes and warms the reactants. Draw air through the reactants for about 30 minutes. The reaction that occurs is:

$$2 \text{ NO}_{2\,(g)} + 2 \text{ H}_3\text{O}^+{}_{(aq)} \rightarrow 3 \text{ H}_2\text{O}_{(l)} + \text{NO}_{(g)} + \text{NO}_2{}^+{}_{(g)} \qquad \textbf{(EQ 19.4)}$$

One product of this reaction is the corrosive gas nitrogen dioxide, NO_2. Nitrogen dioxide is very soluble in water and dissolves in the water trap bottle. If any NO_2 escapes the water trap, it is entrained and dissolved in the aspirator flow and carried down the drain.

When NO_2 dissolves in cold water, a dilute mixture of nitrous and nitric acids is produced by the reaction:

$$2 \text{ NO}_{2\,(g)} + 3 \text{ H}_2\text{O}_{(l)} \rightarrow 2 \text{ H}_3\text{O}^+{}_{(aq)} + \text{NO}_{2\,(g)} + \text{NO}_3{}^-{}_{(aq)} \qquad \textbf{(EQ 19.5)}$$

This solution can safely be disposed of by pouring it down the sink drain.

9. When the reaction in the test tube is complete, pour the solution through an ordinary filter without suction into a beaker. Cool the beaker in an ice bath. While the beaker is in the ice bath, add dropwise to the cold filtered solution (Use a buret or graduated cylinder) 25 mL ethyl alcohol, C_2H_5OH, while stirring continuously. A crystalline precipitate of sodium hexanitrocobaltate, $Na_3[Co(NO_2)_6]$, should form.

10. Filter out the crystals with suction. Wash the crystals with 3 small portions of ethanol. Continue to draw air through the filter until the ethanol has evaporated. Then transfer the crystals to an evaporating dish or watch glass and dry in an oven at about 115 °C for 15 min.

11. Weigh the crystals and record their mass in your notebook. Calculate and record the percent yield.

12. Dissolve about 1 g of your crystal product in 100 mL of distilled water. Fill a clean spectrometer cell with this solution and measure its absorbance spectrum as in steps 5-6 of Part A. It is not necessary to run another water blank.

Part C

Models of the following complexes are to be constructed by you from atom models in which the sphere representing the central metal cation has holes arranged in an octahedral configuration. Make all sketches in your notebook.

1. Sketch all the possible isomers (geometric and optical) of $[Cr(NH_3)_2(H_2O)_2Br_2]^+$. Label the stereoisomers and diastereoisomers.

2. $[Co(NH_3)_4Cl_2]^+$: Use a single sphere to represent NH_3. How many isomers are possible? Make a sketch of each isomer.

3. $Pt(NH_3)_2Cl_2$: This is a square planar complex. Show that two isomers are possible and sketch their structures.

4. $Pt(NH_3)ClBrI$: This is a hypothetical square planar complex. Show that three isomers are possible and sketch their structures.

Data Treatment

Part A

1. Plot the absorbance for each of the complexes (aqua and ammine).

2. Determine the wavelength of maximum absorbance for each complex and calculate ΔE.

3. Discuss the differences in the colors, wavelength, ΔE and how this relates to the electron configuration in each complex and to whether NH_3 or H_2O is the ligand.

4. Calculate the percent yield of the NH_3 complex.
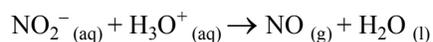
Part C

1. Discuss, briefly, the geometry of each complex for which you built a model.

Post Lab Questions

1. Balance the half reaction for the oxidation of $[Co(H_2O)_6]^{2+}$ to $[Co(NO_2)_6]^{3-}$ and insert the correct number of electrons on the proper side:

$$Co(H_2O)_6^{2+}{}_{(aq)} + NO_2^-{}_{(aq)} \rightarrow Co(NO_2)_6^{3-}{}_{(aq)} + 6\ H_2O_{(l)}$$
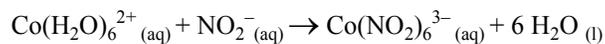
2. Balance the half reaction for the reduction of NO_2^- to NO

$$NO_2^-{}_{(aq)} + H_3O^+{}_{(aq)} \rightarrow NO_{(g)} + H_2O_{(l)}$$

3. Write the balanced equation for the overall redox reaction, both in ionic and in molecular form.

4. Use the molecular equation from 3 above to calculate the mass of $NaNO_2$ needed to react with 5 g of $[Co(H_2O)_6](NO_3)_2$.

5. Calculate the mass of $Na_3Co(NO_2)_6$ that can be produced from 5 g of $[Co(H_2O)_6](NO_3)_2$.