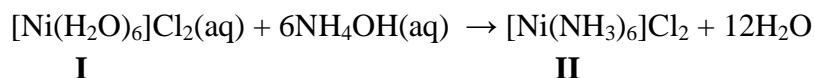


## Lab 8: Ligand Substitution in Transition Metal Complexes

Purpose: In this lab the student will synthesize  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  from  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  by performing a ligand substitution reaction.



Both  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  are complex ions with an octahedral arrangement of donor ligands involved in coordinate covalent bonding around  $\text{Ni}^{2+}$ .

Crystal Field theory suggests that donor electrons from a ligand impose a field on the inner d orbitals of  $\text{Ni}^{2+}$ , such that the energy required for an electron to occupy these orbitals is higher than for an ionic compound with no donor ligands. In the absence of this field, all d orbitals within a principle quantum number are degenerate.

However, since the electron clouds for d-orbitals are directional, some of the orbitals exhibit a higher energy change than others due to the presence of ligands. Specifically, the two orbitals which lie directly on the x, y, and z axis (the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals) are located at octahedral positions relative to the center. They feel a larger effect from neighboring electron donor ligands in an octahedral complex, and hence have a higher energy than the remaining d orbitals ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals).

The energy difference between the three low-energy d orbitals, and the two higher energy d orbitals is, small, but significant enough to be measured, as it represents an energy with a wavelength in the visible region. In fact, this is why many octahedral transition metals complexes exhibit color. The energy difference is referred to as the Crystal Field Splitting Energy Difference, and is given the symbol  $\Delta$ .

Since Crystal Field Splitting Energy,  $\Delta$ , is imposed by the presence of donor ligands, it stands to reason that the identity of a ligand will determine the magnitude of  $\Delta$ . In fact studies have produced a sequence known as the Spectrochemical Series, which orders donor ligands according to their effect on  $\Delta$ . There is a trend for more electronegative donor atoms to exhibit lower  $\Delta$ , placing them lower in the Spectrochemical Series, while less electronegative donor atoms are higher in the Spectrochemical Series, but there are exceptions to this generalization.

You will perform a spectrophotometric analysis of both starting material and product of your ligand substitution reaction to reveal relative effects of ligands  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\Delta$  for  $\text{Ni}^{2+}$ . This information will be used to establish relative positions of these two ligands in the Spectrochemical Series, which you can then confirm by checking your textbook for the accepted Spectrochemical Series. The wavelength of absorption for each complex will be used to determine the crystal field splitting energy according to  $E = (hc/\lambda)(N_A)$ ; where  $h$  = Planck's constant,  $c$  = speed of light,  $\lambda$  = measured wavelength, and  $N_A$  = Avogadro's number.

**Procedure:**

Pour 50 mL  $\text{NH}_4\text{OH}$  solution provided into 250 mL Erlenmeyer and chill on ice.

Measure approximately (RECORD EXACT AMOUNT) 6 g of  $[\text{Ni}(\text{H}_2\text{O})_6] \text{Cl}_2$  and place in a clean 50 mL beaker. Add precisely 10.0 mL  $\text{H}_2\text{O}$  and heat while swirling until the solid dissolves. Remove 1.00 mL solution and set aside in a clean test tube (or small beaker) to dilute and use for spectrophotometric scan of visible wavelength region.

Add 12 mL chilled  $\text{NH}_4\text{OH}$  solution to the remaining 9 mL solution of  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ . Make a note of any observed color changes. Chill this solution for 10 minutes while crystals form.

As solution chills, you may record an absorption scan of your starting material. Your instructor will demonstrate how to operate the spectrophotometer. Please do not attempt to use this instrument in any other way.

Collect crystalline product on filter paper using Buchner funnel and vacuum. Rinse the crystals 3 times with small amounts of chilled  $\text{NH}_4\text{OH}$  and 3 times with small amounts of acetone.

Weigh the crystals (record the weight), and dissolve them in 10 mL  $\text{H}_2\text{O}$ , using mild heating if necessary. Remove 1 mL and dilute as done previously with starting material, to obtain a spectrophotometric scan of the visible wavelength region.

Take an absorption scan of the product, noting maximum wavelength of absorption.

**Data**

Reactant:  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  : Grams \_\_\_\_\_  $M_m$  \_\_\_\_\_ moles \_\_\_\_\_

Observed color \_\_\_\_\_

Product:  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  Grams \_\_\_\_\_  $M_m$  \_\_\_\_\_ moles \_\_\_\_\_

Observed color \_\_\_\_\_

% yield:

Spectrophotometric results:

**Attach and label your absorption scans.**

Maximum  $\lambda$  absorption for  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  \_\_\_\_\_

Corresponds to reflected color of: \_\_\_\_\_ (opposite of color of visible absorption!).

Maximum  $\lambda$  absorption for  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  \_\_\_\_\_

Corresponds to reflected color of: \_\_\_\_\_ (opposite of color of visible absorption!).

In calculating  $\Delta$  below, pay careful attention to units of distance. The units for the speed of light are commonly reported in m (meters) what are the units of  $\lambda$  in your measurements? \_\_\_\_\_

Calculated  $\Delta$  (crystal field splitting energy) for  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ : \_\_\_\_\_

Calculated  $\Delta$  (crystal field splitting energy) for  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ : \_\_\_\_\_

**Lab 8 Post lab questions:**

What are the relative positions of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on the spectrophotochemical series, according to your results? \_\_\_\_\_

Does this agree with the Spectrochemical series listed in your text? \_\_\_\_\_

Does this agree with what you would predict based on electronegativity of the two different ligand donor atoms (why or why not)?

Give possible reasons for your % yield being lower than 100%



**Lab 8 Pre-lab Questions**

1.) Rewrite the equation for the synthesis you will perform for this lab, and calculate the theoretical yield, assuming you will start with 5.00 g of  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ . Note that your work-up will involve dissolving all 5.00 g of  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$  in 10 mL of water, but 1 mL is removed for spectrophotometric analysis and the remaining 9 mL are used in the synthesis of  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ . Thus the actual starting amount is not the moles in 5.00g, but the moles in  $(0.90)(5.00\text{g})$ .

2.) Which d orbital lies directly on the x and y axis? \_\_\_\_\_

Which d orbital lies directly on the z axis? \_\_\_\_\_

Which d orbitals lie in a plane between the x and y axis? \_\_\_\_\_

Which d orbitals lie in a plane between the x and z axis? \_\_\_\_\_

Which d orbitals lie in a plane between the y and z axis? \_\_\_\_\_

Which of the above orbitals would potentially overlap an incoming ligand located directly along any of the axes? \_\_\_\_\_ and \_\_\_\_\_

3.) Draw a Crystal Field Splitting energy diagram for an octahedral transition metal complex, labeling each orbital represented by a space on the diagram:

4.) Why (and how) is the Crystal Field Splitting energy diagram for a square planar transition metal complex different than that for an octahedral complex?

5.) Calculate the value for Crystal Field Splitting Energy,  $\Delta$ , for a particular complex where the measured maximum absorbance in the visible region was 635 nm.