

## The Synthesis and Characterization of Ni(II) Complexes

**Introduction:** The term coordination chemistry is generally applied to transition metal complexes. However, the term “coordination compound” can be extended to any Lewis Acid-Base complex and thus to the vast majority of compounds known in inorganic chemistry. As applied to the transition metals, coordination compounds are among the most extensively investigated areas in the field of inorganic chemistry; and in fact, the first inorganic chemist to win a Nobel Prize, Alfred Werner, won the prize for work on coordination compounds. These compounds exhibit extensive and interesting spectral and magnetic properties in addition to widely varying structures and stoichiometries. In this experiment you will prepare several nickel salts and determine the spectrochemical ordering of several ligands using visible spectroscopy. Magnetic measurements will be made which will aid in the determination of their structure.

### Experimental<sup>1</sup>:

- a. **The preparation of  $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .** Dissolve 6.0g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 3mL of  $\text{H}_2\text{O}$ . A little warming improves the rate of dissolution. Cool the solution in ice while adding 5.0g (5.6 mL) of ethylenediamine. Add the ethylenediamine slowly because the reaction is quite exothermic. Cool. Add 15 mL of cold ethanol to initiate crystallization. Keep cold for 10 min. The collect the product on a Büchner funnel and wash with two 5 mL portions of ethanol. Dry in air. Record the yield.
- b. **The preparation of  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ .** Dissolve 3.0g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 5 mL of warm  $\text{H}_2\text{O}$  in a 125 mL Erlenmeyer flask and add 5.8mL of concentrated  $\text{NH}_4\text{OH}$ . Cool with an ice bath and observe the precipitation of large violet crystals. Add 15 mL of cold ethanol to complete the precipitation. Collect the crystals on a Büchner funnel and wash with two 5 mL portions of ethanol. Dry in air. Record the yield.
- c. **The preparation of  $[\text{Ni}(\text{en})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .** 1.25 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 3.02 g of  $[\text{Ni}(\text{en})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  are gently refluxed in a mixture of 22 mL of methanol and 1.0 mL of  $\text{H}_2\text{O}$  for five minutes. Keep the solution hot and gravity filter

into a 400 mL beaker. Rinse the flask twice with 1.5 mL of hot methanol. In order to initiate crystallization cool the blue solution on ice seed crystals are obtained by the following method: Take 1 mL of the cold solution in a test tube and add 1 or 2 mL of acetone dropwise. Scratch or shake until crystals form. The separation of two layers indicated too much acetone was added. Stir the bulk chilled solution. Add 15 mL of acetone dropwise for about two minutes. Add another 10 mL of acetone and an occasional seed crystal. When the seed crystals no longer dissolve add all of the seed crystals. Continue to stir for about 10 min. after the last acetone addition. Collect the blue crystals using a sintered glass filter. Wash twice with 7-10 mL of acetone and allow to dry. Record the yield.

**Note:** All filtrate may go down the drain.

This crystallization is tricky. **Follow all directions closely**, measure amounts of reagents accurately.

### **Characterization:**

Obtain the visible spectra of the hexaminenickel(II) chloride (in 3M  $\text{NH}_4\text{OH}$ ), the bis- and tris-ethylenediaminenickel(II) chloride (in  $\text{H}_2\text{O}$ ) and the nickel(II) chloride hexahydrate (in  $\text{H}_2\text{O}$ ). From these data you should determine the energy of the three transitions and the spectrochemical ordering of the ligands  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and en. (See Housecroft and Sharpe *Inorganic Chemistry* for a discussion of how this is done and for a general reference on Crystal/Ligand Field Theory).

The magnetic susceptibilities of each compound will be measured using the Johnson and Matthey susceptibility balance (See attachment for instructions).  $[\text{Ni}(\text{en})_2]\text{Cl}_2$  appears to be a 4-coordinate Ni(II) complex (tetrahedral or square planar?) although it could be octahedral with the two chloride ions in the coordination sphere. Show how the magnetic data might permit you to eliminate some of the structural possibilities. Is the structure uniquely defined by the magnetic moment in this case? Why or why not?

**References:**

<sup>1</sup>Figgis, *et al.*, *Prog. Inorg. Chem.* (1964).

Evans, *J. Chem. Soc.*, 2003 (1959). [Evan's Method reference]

**To include in report (besides for the obvious):** Visible Spectra (easies to save Data in Excel and paste the graphs into your Word document) with molar absorptivities and the energies of each transition (there may be more than on observed for some of the complexes, Why?). Include an overlay plot of all the visible spectra. Explain the differences you observe. Magnetic Susceptibilities (include example calculations, values of the gram, molar and corrected molar susceptibilities, the magnetic moment and the calculated number of unpaired electrons). Proposed structures of the complexes including nickel(II) chloride hexahydrate as well as crystal field diagrams with electrons for each complex.