**Experiment 4: Ligand Replacement Reactions**

**Synthesis of \([\text{Ni(NH}_3\text{)}_6]\text{Cl}_2\) and \([\text{Ni(NH}_3\text{)}_6](\text{BF}_4)_2\)**

**Introduction**

Many transition metals form octahedral complexes with \(\text{H}_2\text{O}\) when in aqueous solution. Examples include pink \([\text{Co(H}_2\text{O)}_6]^{2+}\), green \([\text{Ni(H}_2\text{O)}_6]^{2+}\) and pale-blue \([\text{Cu(H}_2\text{O)}_6]^{2+}\). Addition of ammonia to such solutions results in a series substitution reactions in which the water molecules are replaced by ammonia molecules. For example, when concentrated aqueous ammonia is added to the color changes to the violet color of the ion.

\(\text{NH}_3\) ligand displaces \(\text{H}_2\text{O}\) in a stepwise fashion, and each replacement is accompanied by the evolution of heat. For example, the reaction:

\[
[\text{Ni(H}_2\text{O)}_6]^{2+} + \text{NH}_3 \rightarrow [\text{Ni(H}_2\text{O)}_5(\text{NH}_3)]^{2+} + \text{H}_2\text{O} \quad \Delta H = -17\text{kJ/mol}
\]

is followed by

\[
[\text{Ni(H}_2\text{O)}_5(\text{NH}_3)]^{2+} + \text{NH}_3 \rightarrow [\text{Ni(H}_2\text{O)}_4(\text{NH}_3)_2]^{2+} + \text{H}_2\text{O} \quad \Delta H = -17\text{kJ/mol}
\]

and so on, until all the water molecules are replaced by ammonia.

**Part I: Synthesis of hexaamminenickel(II) chloride: \([\text{Ni(NH}_3\text{)}_6]\text{Cl}_2\)**

1) Dissolve 6 grams of \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) in 10 ml of warm water.
2) Add 12.5 ml of concentrated aqueous ammonia to \(\text{NiCl}_2\cdot6\text{H}_2\text{O}\) solution.
3) Cool the resulting dark violet colored solution on ice. Do scratching to aid the precipitation process.
4) Add 25 ml of ethanol (95%) to the violet solution to complete the precipitation. The liquid above it should be almost colorless.
5) Filter the product by suction filtration and wash it twice with 5 ml of ethanol.
6) Air dry the product.
7) Find the % yield
8) Check the solubility in water.
Part II: Synthesis of hexaamminenickel(II)tetrafluoroborate: $[\text{Ni(NH}_3\text{)}_6](\text{BF}_4)_2$

1) Dissolve 2.9 grams of hexaamminenickel(II) chloride by careful addition of cold water (< 8 ml), added in 0.5 ml portions with continues stirring. Do not hydrolyze the complex with excess water.

2) Filter off any small insoluble residue. Save the filtrate part.

3) Dissolve approximately 2.5 grams of ammoniumtetrafluoroborate in dilute aqueous ammonia (2M).

4) Add this solution into the hexaamminenickel(II) chloride solution.

5) A precipitate of hexaamminenickel(II) tetrafluoroborate will form. Cool this in an ice bath and do scratching.

6) Filter the product with suction filtration.

7) Wash the precipitate with aqueous ammonia until the filtrate is colorless.

8) Wash the final product with acetone and dry the crystals.

9) Check the filtrate for any left over Cl$^-$ ions by adding couple drops of AgNO$_3$.

10) Find the % yield.