EXPERIMENT 4

COORDINATION COMPLEXES - COBALT(III) AMINE COMPLEXES

1. Preliminary Exercises

(a) Read the appropriate pages of, for example, Cotton and Wilkinson on cobalt(II) and cobalt(III) complexes.

(b) The book *Synthesis and Technique in Inorganic Chemistry* by R. J. Angelici has some useful information on this experiment.

2. Preparation of Tetraaminecarbonatocobalt(III) Nitrate $[Co(NH_3)_4CO_3]NO_3$

Dissolve 20 g of ammonium carbonate in 60 ml of water and add 60 ml concentrated aqueous NH_3 (solution A). Dissolve 15 g of cobalt(II) nitrate hexahydrate in 30 ml of water (solution B). Mix solution A with solution B and add 8.0 ml of 30% hydrogen peroxide solution (slowly), stirring continuously. Pour this solution into an evaporating dish and concentrate to about 90 ml on a hot plate. During the evaporation add in small portions, a total of 5 g of ammonium carbonate. Filter the hot solution and cool the filtrate in an ice-water bath. When crystallization is complete, filter off the red crystals under suction, and wash with 2-3 ml of water then two or three times with 10 ml of ethanol. Preserve some sample for conductance measurements and use 5 g for the next preparation.

3. Preparation of Pentaaminechlorocobalt(III) Chloride $[CO(NH_3)_5Cl]Cl_2$

Dissolve 5 g of the prepared tetraaminecarbonato complex in 50 ml of water, and add 10 ml of concentrated hydrochloric acid. Neutralize the solution with concentrated aqueous ammonia, and add 5 ml in excess. Heat in an evaporating dish on the steam bath for 20 mins., and then cool slightly and add 75 ml of conc. HCl. Re-heat on the steam bath for a further 10 mins. and then cool. Filter and wash the purple crystals with 5 ml of ice-cold water, *(on a Büchner funnel)*, then with two portions of 15 ml of ethanol, followed by two 15 ml portions of acetone. Allow to dry and record the yield. Calculate a theoretical yield and a percentage yield for **each** of the cobalt(III) complexes.

4. Measurement of Electrical Conductance

The number of ions constituting a given compound can, in favorable cases, be determined by measuring the electrical conductance in solution.

A number of definitions are necessary:

Specific resistance ρ = the resistance in ohms of a solution in a cell which has two 1 cm^2 electrodes separated by 1 cm.

Specific conductance $L = \frac{1}{\rho}$

Resistance of a non-standard cell, $R = k\rho$ (k = conversion factor the cell constant)

Thus $R = \frac{k}{L}$

Thus, one first calibrates a cell using a standard solution of electrolyte. Using a solution whose specific conductance (L) is known enables the constant k to be determined. Then knowing k, the value of R for any solution will enable L to be calculated. The **Molar Conductance** Λ can then be calculated.

$$\text{Molar Conductance } \Lambda = \frac{1000\,L}{M} \quad (M = \text{Molarity of solution})$$

For some known cases, typical values of Λ are:

Number of Ions	Λ
2	118 - 130
3	235 - 275
4	408 - 435
5	~ 550

5. Experimental Procedure

Consult your Demonstrator before using the Conductance Bridge.

(a) Prepare a 0.0200 M solution of KCl in distilled water and use it to calculate the cell constant k. Specific conductance at 25° C is 2.768 x 10^{-3} ohm^{-1}.

(b) Prepare 0.001 M solutions of (A) and (B) and measure the conductance of these. Calculate Λ values and compare them with the above. Be sure to rinse the cell with distilled water before and after use.

Post-lab Questions

1. Draw the structure of the tetraaminecarbonatocobalt(III) cation.
2. What can you determine about the structure of a coordination complex by measuring its conductance in a solution of known concentration?
3. Predict how many ions would be produced per formula unit of the compound $Co(NH_3)_4(NO_2)_3$, assuming it is monomeric, and contains an octahedrally coordinated cobalt?
4. Write a balanced equation for the oxidation of Co(II) to Co(III) by hydrogen peroxide. Why is this oxidation process assisted by the presence of ammonia?
5. Nitrate and carbonate are isoelectronic and isostructural anions. How could you try to show that the real formulation of tetraminecarbonatocobalt(III) nitrate is as written, rather than its ionization isomer?