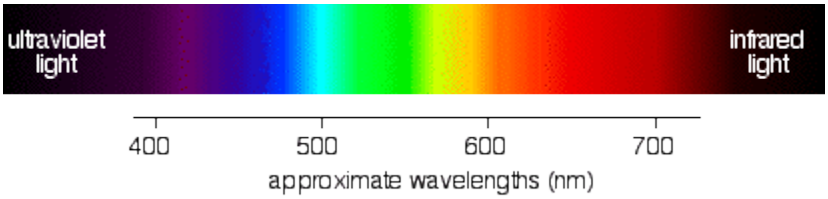
Coordination Complexes

Experiment **9**

Part I (Day 1) – **Synthesis and Analysis of Coordination Complexes**

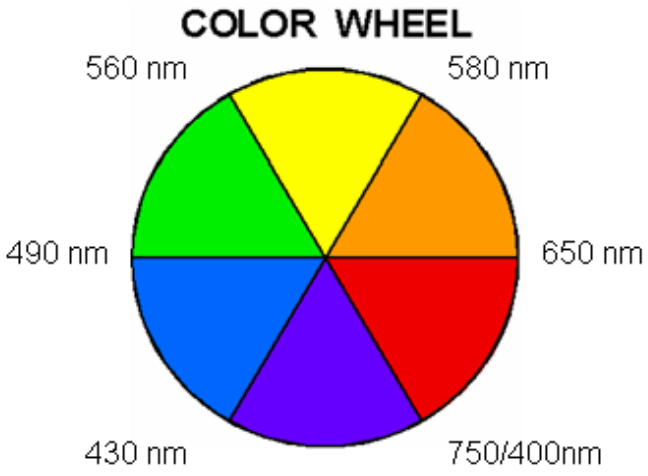
Coordination complexes are formed between a metal ion (Lewis acid) and ligands (Lewis base). The splitting of the d-orbitals (crystal field splitting) and the distribution of the d electrons of the central transition metal ion is dependent upon the ligands that bind to the metal center. The separation of the d-orbitals is called the crystal field splitting energy and is within the visible region of the electromagnetic spectrum (400 nm – 750 nm).



Transition metal complexes have a very wide range of colors within the visible spectrum thus they are commonly found as ingredients in colored paint. A transition metal complex will absorb a photon of light which will excite an electron into a higher energy orbit. The electron then returns to the ground-state emitting a photon within the visible region of the electromagnetic spectrum. The energy of the absorbed light may be calculated as follows:

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

Spectroscopy is a method of analysis based on measuring the energy of light absorbed by a substance and relating that energy to structural characteristics. When a complex absorbs white light, the light left over is the observed color or complementary color of the coordination complex. A color wheel may be used to determine complementary colors.



In this experiment, you will work in groups to synthesize various cobalt complexes in solution. The instructor will assign each group a complex to prepare. The the colors of the complexes may be used to compare the excitation energies when different ligands are present.

Note observations for all those complexes made in the lab class. In each case, Co(II) is oxidized to Co(III) which is stable only when coordinated with the ligand bonds such as the ones formed in this experiment. All complexes will be octahedral (6-coordinate). If less than 6 ligands are shown below, H_2O will be the remaining ligand.

Materials and Equipment (Day 1)
(Reagents needed: 12 to 18 preparations for one lab class.)

Saturated solutions, 250 ml each. Set out jars of the solids in the lab also.

$NaHCO_3$	NH_4NO_3
$(NH_4)_2CO_3$	NaCl

200ml each of these solutions:

3% $Co(NO_3)_2$ or 0.20 M $Co(NO_3)_2$	10% EDTA (disodium salt)
3% H_2O_2	10% ethylene diamine

250ml each of these:

concentrated HCl, 12 M	
concentrated NH_3, 15M	dilute NH_3, 6 M

Solids.

Decolorizing carbon	NH_4NO_3
$NaHCO_3$	NaCl
$(NH_4)_2CO_3$	

Additional equipment

Hot plate in the fume hood
Qualitative filter paper
Filter funnels, 5 or 6

Procedure: (Day 1)
GroupA

Place 2 scoops of the appropriate solid in a 50 ml beaker, then add 15 ml saturated solution of the same solid. Add 1 ml $Co(NO_3)_2$ and 1 ml 3% H_2O_2, mix thoroughly and transfer to a 7" test tube. Be sure to transfer some of the solid too.

Desired Complex	Solid and Saturated Solution to be used:
1. $Co(CO_3)_3^{3-}$	$NaHCO_3$
2. $Co(NH_3)_2(CO_3)_2^-$	$(NH_4)_2CO_3$

3. $Co(NH_3)_5(OH)^{2+}$	NH_4NO_3 Also add 8 ml 6 N NH_3
4. $CoCl_6^{3-}$	NaCl. To this mixture add 15 ml concentrated NH_3 and 1 scoop charcoal. Place the beaker on a hotplate in the fume hood. Evaporate almost to dryness, cool, then add 15 ml concentrated HCl cautiously. Filter into a 7" test tube.

Group B

For each of the follow, place 1 ml $Co(NO_3)_2$ and 1 ml 3% H_2O_2 in the beaker and then add the solution indicated.

5. $Co(NH_3)_6^{3+}$	15 ml concentrated NH_3
6. Co(EDTA)	10 -15 ml EDTA and 1 scoop charcoal. Heat 5 minutes then filter into a 7" test tube.
7. $Co(en)_3^{3+}$	15 ml ethylenediamine (en) and 1 scoop charcoal. Heat 5 minutes then filter into a 7" test tube.

Report:

1. Each group is to record the color of the compound formed on the black board. This is the color of light transmitted by the solution.

2. Using the color wheel, determine the color absorbed by the solution. The color absorbed is the complement of that observed. It may be helpful to note that the complement consists of the primary colors not present in the observed tone. Example: Green is made of the primary colors yellow and blue. Red, the remaining primary, is the complement of green.

3. Use the chart of colors and wavelengths above to estimate the wavelength (nm) of light absorbed by each complex. Calculate the energy of the light absorbed for your complex (kJ/mol). Using the values of Planck's constant ($h = 6.626 \times 10^{-34}$ Js and the speed of light ($c = 3.00 \times 10^8$ m/s) calculate the crystal field splitting energy for your complex.

$$\Delta E = \frac{hc}{\lambda(\frac{10^{-9}nm}{m})} \times \frac{6.02x10^{23}ion/mol}{1000J/kJ} = kJ/mol$$

4. Tabulate your results on the blackboard and copy the class data set.

Part II (Day 2) - **Chromatographic Analysis of Transition-Metal Ions.**

HCl is used to form chloro-complexes of transition metal ions, which are eluted with acetone. The elution rate depends on the relative stability of the different complexes.

Procedure.

1. Obtain 2 pieces of chromatography paper each 10 cm x 1.1 cm. Handle the paper by the edges as much as possible to avoid getting skin oils on it. Draw a pencil line parallel to the 10 cm edge and 1 cm in from the edge. See the diagram. Fold the paper in half lengthwise and then bring the outer edges up to the center fold to give accordion pleats. Crease sharply along the folds.
2. Put a few drops of each test solution on a spot plate. Place the papers under a heat lamp (if available) and add with a toothpick, repeatedly apply spots of each solution to the appropriate place on the paper. Allow the spots to dry between applications so that spots are no more than 1 cm in diameter. Make sure to use a different toothpick for each different sample.

Test solutions are:

1. Fe(III) 2. Co(II) 3. Ni(II) 4. Cu(II)
5. Mixture of all four ions. Samples 6, 7 and 8 are three different unknown mixtures of the ions.

3. Eluting the chromatogram. Pour 35 ml of acetone and 8 ml 6M HCl in the bottom of the 600 ml beaker and mix well. Carefully set in the papers so that they don't touch each other or the walls of the beaker. Cover the beaker with plastic wrap and secure it with a rubber band. Let stand. When the solvent has risen to within 1 to 2 cm from the top of the paper, lift it out and place on toweling under the lamp to dry. Note colors and positions of visible spots on each paper.
4. Developing the spots, NH_3. Pass the chromatogram over a 50 ml beaker containing 15 M NH_3 1 or 2 mm deep. Allow sufficient time for the NH_3 to neutralize the HCl on the paper. Again record colors and positions of all visible spots.
5. Develop the spots, NaSCN in acetone. Spray each paper with a fine mist of NaSCN in acetone. Record colors and positions of visible spots. Compare with a strip of unspotted paper that has been eluted and sprayed. The instructor may prepare the comparison strip.
6. Developing the spots, dimethylglyoxime. Dry the papers under the lamp and spray with a fine mist of 1% dimethylglyoxime solution. Pass the papers over the NH_3 beaker again, if necessary, to develop the pink color of the nickel complex. Record colors and positions of the new spots. Draw the chromatograms in your book and clarify the locations of the various spots.

Conclusions. Calculate R_f values for each of the known metal ions and compare them with the known mixture containing all four ions. The R_f value equal to the distance the spot traveled divided by the distance the solvent traveled. Then identify the ions present in the three unknown samples.

Stockroom materials

Reagents:

50 ml each in glass dropping bottles:

0.1 M $Fe(NO_3)_3$, 0.1 M $Ni(NO_3)_2$, 0.1 M $Cu(NO_3)_2$, 0.1 M $Co(NO_3)_2$

20 ml mixture of all 4 of above, each 0.05 M. Prepare by mixing 5 ml each of 0.2 M solutions of the salts listed above. Label with ion formulas, Fe(III), Ni(II), Cu(II), Co(II).

5 to 10 ml mixture of unknowns. Prepare five to eight mixtures containing 2 or 3 of the ions. Label with Roman numerals.

Acetone, 500 ml per 10 students; 6 M HCl, 200 ml; 15 M NH_3 100 ml.

Spray bottles containing NaSCN/acetone, half the saturation concentration and 1% dimethyl glyoxime.

Other materials: Plastic wrap, rubber bands, capillary tubes, 10 cm x 11 cm chromatography papers, 2 per student