MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMISTRY

URIECA Chemistry 5.35
Module 2: Synthesis of Coordination Compounds and Kinetics[1]

I. Purpose of the Experiment

This experiment is designed to introduce you to the following:

1. The synthesis of simple coordination compounds;
2. IR and Visible spectroscopy;
3. The kinetics of a chemical reaction by determining its rate and rate law;
4. The determination of activation energy from kinetics data.

This experiment will contribute to improving your skills in the following lab techniques:

- Volumetric and gravimetric measurements
- Crystallization and isolation of metal complexes
- Correct sample preparation and handling of the IR and UV-VIS instruments

II. Safety

1. Concentrated acids, bases and hydrogen peroxide (30%) should be handled only while wearing gloves.
2. Reaction waste should be placed in appropriately labeled bottles.
3. Concentrated ammonia should be used in the hood to avoid breathing its fumes.

III. Introduction

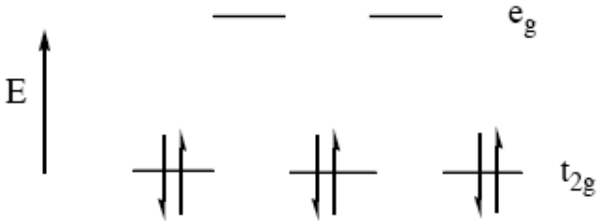
A. Coordination Chemistry

In introductory chemistry you learned that although transition metal salts (e.g., $CoCl_3$) can be obtained in amorphous anhydrous form, they are often obtained as a crystalline hexahydrate. Cobalt(II) nitrate hexahydrate is, in fact

[1] The synthesis and kinetic procedures in this experiment have been adapted from: Angelici, R.J. *Synthesis and Techniques in Inorganic Chemistry*, 2nd Ed.; University Science Books: Mill Valley, 1986; Chapters 1 and 2.

$[Co(H_2O)_6](NO_3)_2$; the six waters are coordinated to cobalt through an electron pair on water (a Lewis base) in an octahedral array around the metal (a cationic Lewis acid). Nitrates are relatively weak ligands and are not coordinated to the metal in this case, although they could coordinate in different circumstances. The coordination environment of the metal can be viewed most simply in electrostatic terms, which is the simplest theory of bonding in transition metal chemistry called Crystal Field Theory (CFT). The lowest energy orbitals in a cationic cobalt complex are the 3d orbitals, followed by the 4s and 4p orbitals. Cobalt is in group 9 in the periodic table, thus Co^{3+} contains six electrons beyond the last inert gas configuration. In an octahedral environment the 3d orbitals are split into two classes based on their energy. The d_{xz}, d_{yz}, and d_{xy} orbitals fall into a class that is called t_{2g} while the d_{x2-y2} and d_{z2} orbitals fall into a class called e_g. (The symbols e_g and t_{2g} denote a doubly degenerate and triply degenerate set of orbitals, respectively, which are *gerade*, i.e., the sign of their wave function does not change upon inversion through the origin.) The orbitals pointing toward the six ligands are higher in energy because the ligands have electron pairs pointing toward the metal. The relative energies of the two classes of d orbitals are shown below:

If six electrons are added such that they are paired up in the t_{2g} set of orbitals (the energy difference between the e_g and t_{2g} orbitals is large with respect to the energy required to pair up the electrons in the t_{2g} orbitals), the metal is said (in CFT) to have the *low spin* d^6 configuration, or more accurately, $(t_{2g})^6(e_g)^0$.



Many octahedral transition metal complexes can be transformed into others by *ligand substitution* reactions, which may be either *associative* or *dissociative* ("S_{N2}" or "S_{N1}", respectively, in terms learned in organic chemistry), or sometimes complex and subtle variations of these basic reactions. The associative reaction would proceed through a seven-coordinate intermediate complex, while the dissociative reaction would proceed through a five-coordinate intermediate

complex. In general low spin octahedral complexes of Co(III) are relatively slow to exchange ligands at the metal because the coordination number is relatively high (six), thereby discouraging formation of a seven-coordinate species for steric reasons. Also the metal electrons are in orbitals that lie *between* the axes (d_{xy}, d_{yz}, d_{xz}), thereby minimizing repulsion between them and the electrons on the six ligands (bases). In contrast, a Co(II) complex (d^7 therefore with electrons in the e_g orbitals) is usually readily substituted. For this reason we begin the synthesis of a Co(III) species with $[Co(H_2O)_6](NO_3)_2$, a high spin d^7 Co(II) species.

B. IR and Visible spectroscopy

Infrared Spectroscopy is a powerful tool for simply and quickly learning something about many organic and inorganic species. IR spectroscopy measures the absorption of infrared radiation due to the vibrations of a molecule as a function of their energy.. The specific number of vibrations can be determined through a *normal coordinate* analysis of the possible vibrations in the molecule (for example, a non linear molecule has 3N-6 vibrational modes where N is the number of atoms in the molecule). An IR spectrum can be acquired on a gaseous, liquid, or solid sample. For inorganic samples where only a qualitative spectrum is desired it is often easiest to grind the sample in a relatively non-IR-absorbing material such as solid KBr crystals which are subsequently placed under high pressure to form a thin window, or an oil such as Nujol® (a mineral oil that consists of C_{20}-C_{30} alkanes) or Krytox® (fluorolube, a grease made from polytetrafluoroethylene) to yield a paste, which is either applied to a microporous polymeric film (such as polytetrafluoroethylene or polyethylene) in a thin layer or squeezed gently between two solid salt plates(typically single crystals of NaCl). It is important that these materials do not
absorb IR radiation in the regions of interest. This technique effectively provides a spectrum of a solid, unless the sample happens to dissolve in the grinding material. In the often complex IR spectrum there are frequently strong vibrational modes that are relatively characteristic of a given type of bond, e.g., the C=O stretch in a ketone, or in carbonate (CO_3^{2-}) or the N=O stretch in nitrate (NO_3^-). Visible spectroscopy employs visible light, which is higher energy than infra-red light. Absorption of visible light by a sample (again in the gas, solution, or solid phase) promotes electronic transitions. Absorption of visible light gives rise to the colors of many transition metal complexes and some organic compounds (most organic compounds are colorless or nearly so). According to the Lambert-Beer law (or sometimes simply "Beer's Law"), the amount of light transmitted (T) by an absorbing sample (I/I_o, I = intensity) is given by

$$\% T = I/I_0 = e^{-A} = e^{-\varepsilon cl} \qquad (3.1)$$

where the absorbance A is proportional to the concentration (c, in mol/L) of the solute, the length of the path the light travels through the sample (l, in cm), and

the constant of proportionality, ε, called molar absorptivity coefficient (units M^{-1} cm^{-1}) or molar extinction coefficient, which is characteristic of the sample and the electronic transition (vibrational if using infra-red radiation) in question. Therefore $A = \varepsilon cl$. Since the absorbance is directly proportional to concentration, both IR and visible spectroscopy can be employed to follow changes in the concentration of an absorbing species involved in a reaction.

C. Kinetic studies

In this experiment you will follow the conversion of one compound into another by
measuring the visible spectrum of the compound being consumed at a specified temperature as a function of time. The reaction rate can be measured as the change in concentration of a reactant (x) per unit of time Δt. The change in concentration of a reactant (or alternatively a product) is followed. Therefore

$$\text{Rate} = \frac{[\mathbf{x}]_{t2} - [\mathbf{x}]_{t1}}{t_2 - t_1} = \frac{\Delta[\mathbf{x}]}{\Delta t} \qquad (3.2)$$

As a differential, the rate would be written as d[x]/dt. Therefore in a reaction in which reagent x is consumed, we might find that the rate depends upon the concentration of x, as shown in equation 3.3, where k is the *observed rate constant* for the reaction in question under the conditions employed. In general, however, the rate might depend in a more complex fashion upon [x], and also upon the concentration of other species, such as a catalyst y, which is not consumed in the reaction (equation 3.4). If a = 1, then the reaction is said to be *first order* in [x].

$$\frac{d[\mathbf{x}]}{dt} = -k[\mathbf{x}] \qquad (3.3)$$

$$\frac{d[\mathbf{x}]}{dt} = -k[\mathbf{x}]^a[y]^b \ldots \qquad (3.4)$$

If b = -1/2, then the reaction is *inverse 1/2 order* in [y], and so forth. The observed rate law will be consistent with the *mechanism* of the reaction, i.e., a series of *elementary reactions.* (An example of an elementary reaction is a simple collision between two species.) It is often possible to think of several elementary reactions (each with its own "absolute" rate constant) that taken together would yield the observed rate law with the observed rate constant. The units of the rate of a reaction in solution are mol l^{-1} s^{-1} or M s^{-1}. The rate of a reaction generally is limited by a relatively slow elementary reaction. Relatively fast elementary reactions that occur before or after a relatively slow reaction are not observable, i.e., are not part of the observed law. In a given solvent (e.g., water) generally it cannot be determined to what extent the solvent itself is involved in the reaction since its concentration is constant. Therefore a rate constant is given for a specific solvent at a specific temperature. The Nobel Prize in chemistry in 1903 was awarded to Svante Arrhenius, who proposed that the rate constant for a

reaction depended upon temperature according to equation 3.5,

$$k = \mathbf{A}\, e^{-\left(\frac{E_a}{RT}\right)} \qquad (3.5)$$

the Arrhenius equation, where k is the rate constant, **A** is the "pre-exponential factor", R is the universal gas constant (1.99 cal deg^{-1} mol^{-1} or 8.31 joules deg^{-1} mol^{-1}), T is the temperature in Kelvin, and Ea (in kcal mol^{-1} or kJ mol^{-1}) is the a*ctivation energy* for the reaction (units must fully agree to cancel). The activation energy is the energy required by molecules reacting with one another to pass through a *transition state* and yield a product or products. If a reaction is well behaved in a given temperature range a plot of ln(k) versus 1/T will produce a straight line with slope $-E_a/R$ and intercept ln(**A**). Rate constants (and therefore reaction rates) usually are found to increase by a factor of 2 - 3 with every 10 degree increase in temperature. Later and more advanced treatments in physical chemistry courses will reveal more details about **A**, but the simple treatment shown in equation 3.5 is still correct and will suffice for now.

IV. General References

a. Reading

General Spectroscopy: Skoog, D.A. et al. *Fundamentals of Analytical Chemistry* 8th Ed. Part V Spectrochemical Methods: Chapter 24 Introduction to Spectrochemical Methods and Chapter 25 Instruments for Optical Spectrometry.

UV-VIS Spectroscopy: Skoog, D.A. et al. *Fundamentals of Analytical Chemistry* 8th Ed. Part V Spectrochemical Methods: Chapter 26 Molecular Absorption Spectrometry.

IR Spectroscopy: Mohrig J.R. et al. *Techniques in Organic Chemistry* 2nd Ed. Technique 18.

Kinetics: Skoog, D.A. et al. *Fundamentals of Analytical Chemistry* 8th Ed. Chapter 29 Kinetic Methods of Analysis. (See also your general chemistry textbook's section on kinetics)

Coordination Chemistry: See your general chemistry textbook's section on coordination compounds/transition metal chemistry. (For more advanced treatments of coordination chemistry see Miessler, Gary and Tarr, Donald. *Inorganic Chemistry* 2nd Edition)

b. TA Demonstrations

How to use balances
How to use a volumetric flask
FT-IR spectrometer
UV-Vis spectrometer

c. Digital Laboratory Techniques Manual

1. Volumetric Techniques
7. Filtration
11. Balances

V. Procedure

You will first prepare two cobalt compounds, $[Co(NH_3)_4(CO_3)]NO_3$ and $[Co(NH_3)_5Cl]Cl_2$. These reactions may be carried out in air. However, they should be performed in a fume hood. Each member of a pair of researchers will individually synthesize $[Co(NH_3)_4(CO_3)]NO_3$. As part of the pre-lab calculate the

molar quantities of each reactant required for the two syntheses. For each synthesis specify the limiting reagent.

Day 1 - Synthesis of $[Co(NH_3)_4(CO_3)]NO_3$

In a 50 or 100mL beaker containing a half inch magnetic stir bar set on a magnetic stir/hot plate in a fume hood dissolve 4.0 g of $[Co(H_2O)_6](NO_3)_2$ in 10 mL of water (Helpful hint: note how this volume appears in the beaker, see below).

In a small beaker dissolve 5 g of $(NH_4)_2CO_3$ in 10 mL of water and add 15 mL of concentrated ammonia in water. Add the $(NH_4)_2CO_3$ solution slowly with stirring to the cobalt solution. Observe the color change. While stirring, add 2 mL of 30% H_2O_2 dropwise over a period of about 1 minute.

While heating and stirring, concentrate the solution by allowing the temperature of the
solution (measure it with a thermometer) to reach but go no higher than 75-80°C. Add a total of 1 g of $(NH_4)_2CO_3$ in several small portions during the process of reducing the volume to ~10 mL. (A small final volume ensures that more of the product will crystallize out.) Let stand undisturbed for 15 minutes, then place the beaker in an ice bath for 15 minutes. (Disturbing the solution will cause rapid formation of fine crystals that are not as easy to filter off.)

Filter off the purple-pink crystals using a 30-50 mL medium glass frit and wash once with 3 mL of ice water, then twice with 3 mL of ethanol. (Helpful hint: turn off the vacuum to add the wash solution, and then turn the vacuum back on) Dry *in vacuo* (if possible) by placing a rubber stopper over the top of the funnel and pulling a vacuum through the end of the funnel. Release by shutting off the vacuum, holding the stopper, and removing the tube to the vacuum. Record the weight, repeating the drying process until the weight no longer changes (Helpful hint: use two cork rings stacked to support the glass frit on the balance). Store the product in your desiccators. (Helpful hint: be sure the desiccant is dry i.e., free-flowing) Alternatively you may simply let the product air dry until the next class period. Calculate your theoretical yield (based on the actual quantity of limiting reagent used) and your percent yield, which should be in the range 35-65%. Clean the glass frit by running dilute hydrochloric acid followed by water through the frit.

Obtain IR spectra, following the procedure demonstrated by your TA, of the product, $[Co(NH_3)_4(CO_3)]NO_3$, $CaCO_3$ (chalk) and $[Co(H_2O)_6](NO_3)_2$. Be sure to also obtain spectra of the materials used to prepare the sample for analysis. Compare the spectra obtained. Identify the absorptions above 1300 cm^{-1} that can be assigned to ammonia, carbonate, water, and nitrate.

Question: You can readily identify the peak due to free or uncoordinated carbonate in the
$CaCO_3$ spectrum. Without consulting the literature, how can you determine which peak is due to nitrate's NO stretch and which are due to carbonate's CO stretches in $[Co(NH_3)_4(CO_3)]NO_3$? Justify you answer.

Day 2 - Synthesis of $[Co(NH_3)_5Cl]Cl_2$

Partners should combine their products in order to perform the second synthesis.

In a 100 mL Erlenmeyer on a stir/hot plate dissolve 2 g of $[Co(NH_3)_4(CO_3)]NO_3$ in 15 mL of water and add ~3 mL of concentrated HCl dropwise until no more CO_2 is expelled. Neutralize with concentrated aqueous ammonia (use pH paper to indicate neutrality – to avoid contamination of the cobalt solution, use a glass stir rod to transfer a drop of solution to the paper), and then add 2 mL of concentrated aqueous ammonia. Heat at 75-85°C for 20 minutes.

Cool the solution to about 50°C. Add 20 mL of concentrated HCl slowly while gently swirling the mixture. Reheat the mixture for 20 to 30 minutes to 75-85°C; observe the color change. Cool the solution to 5 °C in an ice bath. Collect the fine purple-red crystals of $[Co(NH_3)_5Cl]Cl_2$ by filtration using a medium glass frit and wash twice with 3 mL of ice-cold distilled water, filtering each time. Wash twice with 3 mL of ethanol and filter. Dry in an oven at 100-120°C for one hour, cool, weigh, and calculate the percent yield. **Transfer your product to a vial and return the glass frit to the Stockroom.** Typical yields vary between 50 and 75%.

Obtain an IR spectrum of the product and compare it with the spectra obtained above.

Question: Where are the IR absorptions for bound ammonia?

Aquation of $[Co(NH_3)_5Cl]^{2+}$ to yield $[Co(NH_3)_5(H_2O)]^{3+}$

A. The Lambert-Beer equation and determination of ε for $[Co(NH_3)_5Cl]Cl_2$

Goals

- Become familiar with the Cary 100 spectrometer by recording the UV-VIS spectrum (λ = 350-700 nm) of each of 4-6 solutions. Determine the λ_{max} for $[Co(NH_3)_5Cl]Cl_2$ in 0.5 M nitric acid, HNO_3 solution.

- Determine the validity of Lambert-Beer law **at 550nm** (which is *not* λ_{max}).

Day 3 – Lambert-Beer Study

Prepare four to six solutions (each person should prepare two solutions) of known $[Co(NH_3)_5Cl]Cl_2$ concentration made up in 25 mL volumetric flasks. Weigh out your samples first on weigh paper to approximate the correct mass. Next, tare the flask (zero the balance with the flask in place), then carefully add the weighed quantity of $[Co(NH_3)_5Cl]Cl_2$ and finally weigh the flask with the cobalt complex to 0.1 mg. Rinse any compound adhering to the neck of the flask into the flask and fill to the 25 mL line with 0.5 M HNO_3 (Helpful hints: add part of the acid solution, swirl to mix getting most of the complex in solution, then use a Pasteur pipet to add the nitric acid solution dropwise until the meniscus rests on the calibrated line). Concentrations between 2.5 and 10 mM would be most useful. Why? Be sure to span a range of concentrations. Calculate the mass required for 2.5 and 10 mM solutions as part of the pre-lab.

On the UV-VIS spectrophotometer's computer screen select "General Scanning". Check that the parameter file is set correctly, and then take a background reading using a glass cuvette filled with the 0.5 M nitric acid solution. (Glass cuvettes will be used due to the instability of the plastic cuvettes at the higher temperatures required by the kinetic runs). See Appendix 1 for step-by-step instructions for running the Cary100 spectrometer to obtain a UV-VIS Spectrum. Be sure the outer walls of the cuvette are dry and clean by wiping them with a Kimwipe®. Fill cuvettes with your solutions and measure their absorbance. Manually record the absorbance at 550 nm for each spectrum or transfer your data files to a USB drive for analysis.

Plot absorbance (A) versus concentration (c). Don't forget to include the (0, 0) data point in your calculations. Include the least squares line and correlation coefficient on the plot. If the Lambert-Beer equation is valid over this range of concentrations, a straight line should be obtained whose slope is equal to εl, or in fact to ε if $l = 1$ cm. What is the error in ε? How should ε be reported?

Day 4-5 – Kinetics Measurements @ 60° C

The conversion of $[Co(NH_3)_5Cl]^{2+}$ to $[Co(NH_3)_5(H_2O)]^{3+}$ is accompanied by a change in color from a purplish-pink to a lighter, more orange-pink and a shift of the λ_{max} to higher energies. You will follow the conversion of $[Co(NH_3)_5Cl]^{2+}$ into $[Co(NH_3)_5(H_2O)]^{3+}$ at 550 nm where $\varepsilon = 21\ M^{-1}\ cm^{-1}$ for $[Co(NH_3)_5(H_2O)]^{3+}$. If you know the amount of $[Co(NH_3)_5Cl]^{2+}$ in the sample initially, you can calculate the concentration of $[Co(NH_3)_5(H_2O)]^{3+}$ when the reaction is over (at "infinite" time). The absorption at 550 nm at infinite time, A_∞, is simply the absorption after complete conversion to $[Co(NH_3)_5(H_2O)]^{3+}$. For a first order conversion of $[Co(NH_3)_5Cl]^{2+}$ into $[Co(NH_3)_5(H_2O)]^{3+}$ $\ln(A-A_\infty) = - kt + C_1$ where t is the time, k is the rate constant for the reaction, and C_1 is a constant.

Weigh out two samples of $[Co(NH_3)_5Cl]Cl_2$ accurately (to 0.1 mg) by taring a 25-mL volumetric flask and then reweighing it plus the sample of $[Co(NH_3)_5Cl]Cl_2$. The amounts should be different, for example ~20 mg and ~40 mg. Label both flasks. Dilute to the 25 mL mark with an aqueous solution of 0.5 M HNO_3.

Remove a sample from each flask with a clean pipette and transfer to a glass cuvette. Select the scanning kinetics icon on the Cary 100 Spectrophotometer and follow the instructions outlined in Appendix 1, part B. Obtain a baseline spectrum of the 0.5 M nitric acid solution. Place the cuvettes in the sample holder of the Cary 100 Spectrometer and equilibrate for 15 minutes at 60ºC. **IMPORTANT NOTE:** There will be several teams using each instrument, requiring coordination of the start time for the kinetics runs. The spectrometer will record spectra every 20 minutes. Manually record the time and absorbance at 550 nm for each spectrum and record the location of all isosbestic points or transfer your data files to a USB drive for analysis.

Calculate the expected value for A_∞ and construct a table of $\ln(A-A_\infty)$ and time t for the two solutions. Continue to follow the reactions until the value of $A-A_\infty$ is approximately half the value of A_o-A_∞, where A_o is the expected absorption of $[Co(NH_3)_5Cl]Cl_2$ alone at 550 nm, which you know from the quantity you weighed out and ε for $[Co(NH_3)_5Cl]Cl_2$ 550 nm. The time at which $A-A_\infty$ is half the value of A_o-A_∞ is the **half-life** for this first order reaction, i.e., the time required for it to proceed halfway. After five half-lives the reaction is essentially
finished, but you will have time to follow the reaction for approximately only one half-life.

Note carefully the presence of one or more *isosbestic points*. An *isosbestic point* is found at some value of λ where the absorbance of the mixture *does not change* during the reaction. A "clean" set of isosbestic points is characteristic of a simple conversion of one absorbing compound into another.

Day 6-7- Kinetics Measurements @ 40° C and 70° C

****CAUTION** Please ensure that you use the cuvettes with Teflon stoppers for your runs ONLY. Cuvettes do not need to be filled more than ~75% full for accurate readings.**

Each partner will carry out a kinetic study at another temperature, one higher (e.g., 65 °C) and one lower (e.g., 40 °C). It is desirable to have the minimum and maximum temperatures differ by at least 25 °C, but be aware that a temperature that is too high can lead to a reaction that is inconveniently fast to measure, while a temperature that is too low can lead to a reaction that is inconveniently slow to measure during a given lab period. For these runs monitor the reaction progress with the spectrophotometer set to 550 nm. Select the kinetics icon (not scanning)

on the Cary 100 Spectrophotometer and follow the instructions outlined in Appendix 1, part C.

IMPORTANT NOTE: The group will have to come to a consensus on the two temperatures to be studied. One UV-VIS spectrometer will be set to the lower temperature and the other UV-VIS will be set to the higher temperature. Again cooperation will be required, as all teams will need to start their kinetic runs simultaneously. Manually record the time and absorbance at 550 nm for each data point or transfer your data files to a USB drive for analysis.

VI. Kinetics Data Treatment

1. Plot $\ln(A-A_\infty)$ versus t in order to obtain k in each kinetic run. Express k in s^{-1}. Include
the least squares line and correlation coefficient on each plot.

2. Determine the activation energy for the aquation reaction over the temperature range you studied by plotting the various rate constants you obtained at different temperatures
versus 1/T. Include the least squares line and correlation coefficient on the plot.
(Remember that T should be in K and be careful about J versus kJ)

3. Using the value for the activation energy, predict the rate constant for the aquation reaction at 22 °C. How long you would have to monitor the reaction at 22 °C in order to reach one half-life? How much error is generated by room temperature aquation in the experiments in which you determine ε for $[Co(NH_3)_5Cl]^{2+}$ at 550 nm? How much $[Co(NH_3)_5Cl]^{2+}$ is converted into $[Co(NH_3)_5(H_2O)]^{3+}$ during the time required to make up a solution and measure the absorption for $[Co(NH_3)_5Cl]^{2+}$?

4. Calculate the amount of starting material remaining after five half-lives (essentially
"completion") of a first order reaction.

5. Show that plotting $\ln(A-A_\infty)$ versus t is the same as plotting $\ln\{[Co(NH_3)_5Cl]^{2+}\}$ versus t by turning the equation $\ln(A-A_\infty) = - kt + C_1$ into $\ln\{[Co(NH_3)_5Cl]^{2+}\} = - kt + C_2$, where C_1 and C_2 are constants. (C_2 is actually $[Co]_o$, the concentration of $[Co(NH_3)_5Cl]^{2+}$ at time t = 0. What is C_1?)

6. You could have chosen to follow the reaction at a different wavelength. What determines a good choice of wavelength? What determines a poor choice of wavelength? What other wavelengths would be good choices for this experiment? What wavelengths would be poor choices?

7. Where did you observe isosbestic points in your spectra? What is true in terms of
absorption by the reactant and the product at these wavelengths?

VII. Other Questions

8. Explain why Co(II) complexes are readily substituted, in contrast to Co(III) complexes.

9. How is carbonate bound to cobalt in $[Co(NH_3)_4(CO_3)]NO_3$?

10. Rationalize why nitrate is a poorer ligand than carbonate, i.e., why $[Co(NH_3)_4(CO_3)]NO_3$ is not actually $[Co(NH_3)_4(NO_3)]CO_3$.

11. What is the role of hydrogen peroxide in the first experiment?

12. The colors of the cobalt complexes can be assigned to relatively weak ("not allowed") "dd" transitions. If $(t_{2g})^6(e_g)^0$ is the ground state of a given complex, what is the excited state configuration after absorption of a photon.

Appendix 1: Guidelines for Using the Cary 100 UV-Visible Spectrophotometer to Obtain Beer's Law and Kinetics Data

To launch the software click on the icon **Cary WinUV**. Follow the column on the left of the table below for common commands and the details for the particular experiment in the appropriate column to the right. Note: items not checked off on the screen or not highlighted for change are not listed below.

	Day 1	**Day 2**	**Day 3**
Experiment	**Beer's Law**	**Scanning Kinetics**	**Kinetics @ 550 nm**
Click on the icon:	**Scan**	**Scanning Kinetics**	**Kinetics**
On the menu bar click on **File** then on **Open Method** Go to the **Look In** Window and select **Cary WinUV**[2], then select:	**5_311_Lambert-Beer_Cobalt** Click on **Open**	**5_311Scanning KineticsCobalt** Click on **Open** Note: if it puts up a dialog box about baseline info. close it and go on	**5_311KineticsCobalt** Click on **Open**
Click on the **Setup** button. Check that the parameters are correct. See below:			
Setup: Cary	**X mode**:nanometers **Start:** 700.00 **nm** **Stop**: 300.00 **nm** **Y mode:** Abs **Y min:** 0.00 **Ymax:** 1.20 **Scan Controls** **Ave time(s)** 0.100 **Data interval:** 1.000 **Scan rate:** 600.000 **Temperature** **Monitor:** Block x **Show Status Display**	**X mode**:nanometers **Start:** 700.00 **nm** **Stop**: 300.00 **nm** **Y mode:** Abs **Y min:** 0.00 **Ymax:** 1.00 **Scan Controls** **Ave time(s)** 0.100 **Data interval:** 1.000 **Scan rate:** 600.000 **Collect Timing:** > **Simple collect** **Stage:** 1 **Cycle(min) :** 20.00 **Stop(min):** 180.00 **Temperature** **Monitor:** Block x **Show Status Display**	**Wavelength(nm):** 550.00 **SBW(nm):** 1.0 **Monitor:** Block **Ave Time (s):** 0.100 **Y mode:** Abs **X mode:** Min **Y Min:** 0.000 **Y Max:** 1.0 **Collect Timing:** > **Simple collect** **Stage:** 1 **Dwell (s)**: 1.00 **Cycle(min) :** 20.00 **Stop(min):** 180.00 x **Show Status Display**

[2]Desktop/My Computer/Local Disk C:/Varian/CaryWinUV

Set-up: Options	**SBW(nm):** 2.0 **Source:** UV-VIS **Source changeover:** 350 nm > **Overlay data** x **Show Status Display**	x **Auto Lamp Off** **SBW(nm):** 2.0 **Energy:** 1.00 **Source:** UV-VIS **Source changeover:** 350 nm x **Show Status Display**	x **Auto Lamp Off** **Source:** VIS **Source changeover:** 350 nm > **Individual data** x **Show Status Display**
Setup: Baseline	> **Baseline correction** x **Show Status Display**	> **Baseline correction** x **Show Status Display**	Not available
Setup: Accesories 1	**Cells:** x **Use Cell Changer** > **Select cells** x check off cells to be used Cell 1-Cell 6 > **6x6** **Temperature:** x **Automatic Temperature Setting** > **Temperature Controller** **Block** 25.0°C **Temperature Display:** x **Block** x **Show Status Display**	**Cells:** x **Use Cell Changer** > **Select cells** x check off cells to be used Cell 1-Cell 6 > **6x6** **Temperature:** x **Automatic Temperature Setting** > **Temperature Controller** **Block** 60.0°C **Temperature Display:** x **Block** x **Show Status Display**	**Cells:** x **Use Cell Changer** > **Select cells** x check off cells to be used Cell 1-Cell 6 > **6x6** **Temperature:** x **Automatic Temperature Setting** > **Temperature Controller** **Block** 45.0 OR 75.0°C **Temperature Display:** x **Block** x **Show Status Display**
Setup: Accesories 2	Not Used	Not Used	Not Used
Setup: Accesories 3	Not Used	Not Used	Not Used
Setup: Analyze	Not Available	Not Used	Not Used
Setup: Accesories 3	Not Available	Not Available	Fill in: **Number of Samples** **Sample Names**

Setup: Reports	**Operator:** **Name:** your names **Comment:** a brief description **Options:** x **User Data Form** x **Graph** 50 **%Page Height** > **All traces** **Peaks** x **Maximum Peak** x **All Peaks** **XY Pairs Table:** x **Include XY Pairs Table** > **Use Actual Interval** **Autoconvert:** > **Select for ASCII(csv)** x **Show Status Display**	**Operator:** **Name:** your names **Comment:** a brief description **Options:** x **User Data Form** x **Graph** 50 **%Page Height** x **Results** x **Parameters** **XY Pairs Table:** x **Include XY Pairs Table** **Autoconvert:** > **Select for ASCII(csv)** x **Show Status Display**	**Operator:** **Name:** your names **Comment:** a brief description **Options:** x **User Data Form** x **Graph** 50 **%Page Height** x **Results** x **Parameters** **XY Pairs Table:** x **Include XY Pairs Table** **Autoconvert:** > **Select for ASCII(csv)** x **Show Status Display**
Setup: Autostore	> **Storage on (prompt at start)** x **Show Status Display**	> **Storage on (prompt at start)** x **Show Status Display**	> **Storage on (prompt at start)** x **Show Status Display**
Setup: Click on the **OK** button. Wait for the green traffic light.			

	To obtain the baseline click on **Baseline** button then: Name **cell 1** "0.5M HNO_3" Insert cuvet filled with 0.5M HNO_3 into cell holder slot 1, close the lid and click **OK** Wait while the graph of Absorbance vs wavelength appears on the screen. Wait for the green traffic light.	To obtain the baseline click on **Baseline** button then: Name **cell 1** "0.5M HNO_3" Insert cuvet filled with 0.5M HNO_3 into cell holder slot 1, close the lid and click **OK** Wait while the graph of Absorbance vs wavelength appears on the screen. Wait for the green traffic light.	Baseline correction is not used. To zero the instrument at 550 nm click on **Zero** then: Name **cell 1** "0.5M HNO_3" Insert cuvet filled with 0.5M HNO_3 into cell holder slot 1, close the lid and click **OK** Wait for the green traffic light.
To collect absorbance data click on **Start.** In the **Save As** window open the folder corresponding to *your section/group*. Provide a *unique file name*. File name should include the date. Then click on **Save**		Note: There will be three groups/ instrument. Work together to name the file and load cells	Note: There will be six groups/ instrument. One instrument will be set to 45°C, the other to 75°C. Work together to name the file and load cells
The **Cell Loading Guide** will pop-up. Provide *names* for each cell then load each cell in the proper chamber. When everyone has loaded their cells, close the lid and click on **OK**.		Note: The temperature MUST be monitored throughout the run. This should be a shared responsibility.	Note: The temperature MUST be monitored throughout the run. This should be a shared responsibility.
Automatically the **SyncStart** window opens. Click **OK** or wait the 2 minutes for the run to start. The run will not start unless the correct temperature has been reached.			

To view the numerical data click on **View** and then **Report.** Save your files to a 31/1 inch floppy disk OR CD OR USB memory stick for further analysis. Be sure to save the files in **Spreadsheet Ascii (*.cvs)** format		NOTE: Only analyze your own group's set of data.	NOTE: Only analyze your own group's set of data.

To open the files in Excel use the least restrictive criteria to choose the file.

Explore the various icons immediately above the graph for scaling graphs, using a cursor, examining multiple plots, selecting which traces to view and the like.

Please be sure the Cary100, temperature controller and computer are shutdown at the end of the day.

Note: lifting up on the knob in the sample compartment will facilitate removal of the cells.

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