Chemistry 433 Section 500: Advanced Inorganic Chemistry Laboratory
Fall 2010
2 Credits

Tuesday / Thursday 2:20 – 5:10 - Room 2405 (Laboratory) and 2307 (Prelab)

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Office Hours:

Professor Dunbar: Fridays 1:00-3:00 PM, Room CHAN 2311
Heather and Ian: Tuesdays and Thursdays 1:00-2:20 PM, Room CHAN 2307

Objectives:
The purpose of this laboratory is to provide you with practical knowledge and hands-on experience in experimental techniques commonly used in a modern inorganic research laboratory. Inorganic compounds chosen for synthesis and characterization will introduce you to various major areas of current inorganic research and will cover some or all of the following topics:

- Bioinorganic chemistry
- Organometallic chemistry
- Metal-metal bonding
- Classical coordination chemistry

Since many of the experiments in this course require specialized, expensive equipment, the experiments will sometimes be performed on a rotating basis. At all times students are expected to work independently in his/her group. There are two three-hour laboratory periods a week. Always review references provided on the chemistry involved with the experiments.

Prerequisite:
Chemistry 362 or 462 or currently registered.

Laboratory Rules:

- Never work alone in the laboratory.
- Wear appropriate eye protection, such as goggles, at all times. Contact lenses are not recommended in the laboratory. Gloves are required when handling chemicals. Lab coats are recommended during any chemical work, but are required when using caustic chemicals, such as using the base/acid baths or cleaning fritted filters.
- Keep all working areas you are using clean. Daily cleaning and an end-of-the-semester cleaning are required.
- Prevent accidents by anticipating any undesirable consequences that may occur in addition to the expected outcome of an action. When in doubt always ask! Always stay alert for actions that may lead to imploding vacuum systems, exploding reaction mixtures, rupturing water hoses, evolution of noxious gases, flying syringe plungers and needles, etc. Repeated mishaps will result in a zero for lab performance.
- Glassware used in this laboratory is cleaned in base and acid baths. It is the student's responsibility to rotate glassware through the cleaning media. Follow the washing roster posted in the laboratory. *Caution:* Always wear a lab coat, protective gloves and eye protection while using washing solutions.
- Clean syringes, needles, cannulas, and sintered-glass filters as soon as possible after using them to avoid clogging — as residual chemicals in them decompose and solidify. Clean NMR/magnetic susceptibility tubes and IR plates as soon as you have finished collecting your data. Students who use them should clean these individually. Remember base destroys ground glass joints so any glassware with joints must not be left to soak for long periods. **Fritted glass filtration funnels must NEVER be subjected to base cleaning – acid only. Do not ever put syringes, needles, spatulas and metal or rubber objects into the cleaning baths.**

Glassware cleaning:

NMR tubes: fill the tubes to the rim with the base bath solution using a disposable pipette and let it sit for ca. 2 hours in an Erlenmeyer flask outside the tank. Then pour the cleaning solution back into the base bath, rinse the tube with water and fill it with solution from the acid bath. Soak briefly and rinse with distilled water followed by ethanol/acetone. Dry in the oven.

Cannula needles and syringe needles: poke one end through a septum on a suction flask connected to an aspirator and pull a few milliliters of acetone from a clean beaker or Erlenmeyer flask. Dry in oven.

Fritted (sintered glass) filtration funnels: rinse with acetone or a solvent in which the residue is soluble. If this is not enough, rinse with H_2SO_4 and H_2O_2 while connected to a water aspirator. Dry in oven.

Caution: Do not soak fritted funnels in base bath. **Use of H_2SO_4/H_2O_2 cleaning solutions is to be done in a working fume hood with full protective attire (lab coat, protective eyewear and gloves) under TA supervision at all times—no exceptions! NEVER mix this solution or either of its components with organic solvents—rinse filter thoroughly with water prior to and after use and use a separate filter flask for the cleaning solution waste.**

Glove Box Rules:

1. Pump down the small antechamber for at least three 5-minute periods. Pump down the large antechamber for at least three 10-minute periods.
2. To load material into the glove box *via* the small antechamber:
    a. Antechamber should be under vacuum at the start (if not, ensure that the inner door is sealed before opening the outer door). Turn the black handle underneath the antechamber so that it points to the right (N_2).
    b. Open the outer antechamber door.
    c. Insert material, ensuring the following criteria are met:
        i. Glassware is oven/flame-dried and inserted while still hot.
        ii. Solid chemicals are in open containers covered with a Kimwipe (to prevent dispersal of the solid) along with the container lid.
        iii. Liquids are sealed in screwtop/Teflon plug-fitted containers (avoid using glassware with ground glass joints to contain liquid) under slight vacuum (if possible).
        iv. If a Schlenk flask must be used to pump in a solution, put it under vacuum and secure the stopper to the flask using a rubber band. Inform a TA or the instructor.
    d. Close outer door and ensure it is properly sealed.
    e. Turn the black handle to the left (vacuum). Leave under vacuum for 5 minutes.
    f. After 5 minutes, turn the handle to the right (N_2) until filled.
    g. Repeat evacuation/backfill 2 more times.
    h. Open inner door after backfilling for the last time and bring in your materials. Make sure to take them back out once done.
3. To bring material out of the glove box *via* the small antechamber:
    a. If the antechamber is still under box atmosphere, you can open the inner door, load the material, seal the inner door, then open the outer door and remove your material.
    b. If you are unsure whether the antechamber is under N_2, do NOT open the inner door until the antechamber has been pumped down three times as outlined above in steps 2e-g. Follow step 3a above once the purge cycles are complete.
4. Using the large antechamber:
    a. A similar procedure to that above in 2a-2h, 3a-b is used, though manipulation of the N_2/vacuum valves is different.
    b. To put the large antechamber under nitrogen, close the needle valve below the antechamber (turn to the right until it stops turning). Then deselect Evac Ante on the control panel, and select Fill Ante. The chamber will fill with the box atmosphere.
    c. To evacuate the antechamber, deselect Fill Ante, select Evac Ante and then open the needle valve by turning to the left. The vacuum pump will get louder as it pulls vacuum.
5. Always use disposable gloves when working in the glove box.
6. Remove watches, bracelets, diamond rings, etc. that may pierce the gloves.
7. If solvent must be used inside the glove box, turn off the circulation on the control panel. Do your work into the glove box (clean any spills immediately), put all solvent-laden materials in the antechamber of your choice, seal and then have a TA purge the glove box.
8. Register the time, your initials, whether the antechamber is loaded or not and any appropriate comments (solvent use etc.) on the log near the antechambers.

Oral Pre-Laboratory Presentations:

Before each new laboratory experiment, the students will meet with Professor Dunbar and the teaching assistants during an oral pre-laboratory meeting. The purpose of this exercise is for the student to demonstrate appropriate understanding of the materials and techniques as well as safe handling of chemicals. You must show your instructor a plan outlining a procedure for each experiment and be prepared to discuss the chemistry associated with the corresponding experiment. Questions will be asked and the student should be prepared to go to the board. Professor Dunbar will also lecture on aspects of techniques and theory that is not familiar to the student from previous chemistry courses.

Note: When preparing for the oral pre-laboratory presentation and writing your reports, keep in mind that:
IR spectroscopy is a technique that allows: 1) Identification of functional groups in organic compounds. 2) Determination of the type of certain ligands bound to a metal atom and the symmetry of their arrangements (good examples are CO and CN), as well as the relative electron density on the metal center in carbonyl and cyanide complexes (know why this is so.)

'H NMR spectroscopy allows you to determine the number of hydrogen atoms and their chemical environment in (preferably) diamagnetic compounds. Know chemical shifts for H atoms in most common types of organic compounds and solvents you will be using. Also, have an idea about 'H NMR of metal hydrides and diamagnetic anisotropy of multiple bonds, e.g. C=C and multiple metal-metal bonds.

^{31}P NMR (^{31}P, I =1/2) spectroscopy allows for similar identification as ^{1}H NMR spectroscopy but for compounds that contain P atoms. The effect of P—P coupling is similar to that of H—H coupling.

CV (cyclic voltammetry) of inorganic/organometallic compounds allows you to find out whether there are reversible (and irreversible) oxidation processes that may be chemically accessible. CV also provides an indication of how stable the reduced or oxidized species are. You should know the oxidation numbers for transition metal atoms in your compounds.

Magnetic susceptibility measurements allow for the determination of whether a compound is dia- or paramagnetic and how many unpaired electrons are present in a molecule.

TGA (thermogravimetric analysis) allows accurate determination of weight loss of a heated sample as a consequence of evaporation of volatile species within.

Laboratory Notebook:

You will keep a notebook, *written in ink.* This notebook will be extremely helpful for your laboratory reports. No calculations or notes should be made on scrap paper or paper towels — if it is important enough to write down at all, write it in the notebook to avoid wasting time recopying and possibly introducing mistakes to the data. **All** procedure details, observations, calculations, characterization data, product yield and any other relevant data should be recorded in a manner that should be intelligible to someone not entirely familiar with the detailed experimental procedure. How much information to record is a matter of judgment that develops with experience. It is better, however, to be too detailed than to skip observations that you might find useful later. Data should be recorded on the white pages of a carbon-copy style laboratory notebook. The notebook page(s) will be signed by the laboratory instructor. The additional yellow copy should be attached to the laboratory report.

Laboratory Reports:

The laboratory reports are due no later than two weeks after each of laboratory experiments is completed, but only one week after the last experiment. Reports turned in late will have ten points (out of a possible 100) deducted from the final score per day of delay. The reports should be type written. The reports have to be comprehensive – All data collected during the experiments should be presented and discussed. The reports do not have to be long and are not intended to be tedious, either to write or to grade.

Laboratory reports should have the format of a scientific paper submitted for publication to *Inorganic Chemistry, Organometallics,* or *Journal of the American Chemical Society* for example. They should include:

- *Title and author(s)*
- *Abstract* (in a few sentences indicate what your report is about)
- *Introduction* (what is the background of what you have done?)
  A description of the chemistry pertinent to the experiment with a brief summary of the goals of the experiment. This should not take more than 2 or 3 pages. Some relevant questions listed in the description of each experiment ought to be addressed here.
- *Experimental Section* (what did you do?)

Very detailed (yet short) description of the laboratory procedure, including chemical brands used, whether the solvents and reactants were purified, and how. Also include observations- color and temperature changes, crystal color, morphology, etc. What means of identification and characterization were used (include makes and models of instruments)? Yields, melting points, IR and NMR peak positions, magnetic data and other relevant data should be reported here. Look in recently published papers in the above journals to write this section. Simply copying the experimental procedure from literature sources will result in point deductions.

- *Results* (what happened?)
  Did you get what you wanted? IR, NMR data, yield description (e.g. high or poor), and spectroscopic evidence of the purity of your product should be given here (this section may be combined with *Discussion,* although this is generally discouraged.)
- *Discussion* (so what?)
  This section should contain comparisons with the literature data, such as magnetic, IR, and NMR data interpretation. If something went wrong explain what happened and why, then offer suggestions as to how to avoid those problems. Attach spectra such as IR and NMR, and also copies of relevant pages of your laboratory notebook, as these are worth up to 10 points.
  In your *Discussion Section* elaborate on techniques used to identify and characterize your products. Compare your results with those expected or reported in the literature for a given compound. The questions listed in the description of each experiment might be helpful here. Present conclusions.

Grading:
Grading will be based on:
1. Maintenance of an accurate and up-to-date notebook and written reports. (50%)
2. Laboratory performance, including competency, knowledge of techniques, application of techniques, understanding of experiment, compliance with safety rules and lab duties. (30%)
3. Pre-laboratory oral presentation. (20%)

Reference Books:
There is no textbook for this course. Some references for the experiments are given along with the description of each experiment. There are also some general references that might be useful to understand the background of the chemistry, spectroscopy and techniques for the manipulation of air-sensitive compounds. These are listed below:

G. S. Girolami. T. B. Rauchfuss, R. J. Angelici, *Synthesis and Technique in Inorganic Chemistry.*
W. L. Jolly, *The Synthesis and Characterization of Inorganic Compounds.*
A.L. Wayda. M. Y. Darensbourg, *Experimental Organometallic Chemistry.*
D. F. Shriver, *The Manipulation of Air Sensitive Compounds.*
A. J. Gordon, R. A. Ford. *The Chemist's Companion.*
K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds.*
R. M. Silvestein, G. C. Bassler,T. C. Morril, *Spectrometric Identification of Organic Compounds.*
F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry.*
F. A. Cotton, G. Wilkinson, P. Gauss, *Basic Inorganic Chemistry.*
D. F. Shriver, P. W. Atkins, C. H. Langsford, *Inorganic Chemistry.*

ADA STATEMENT: The Americans with Disabilities Act (ADA) is a federal anti-discrimination statute that provides comprehensive civil rights protection for persons with disabilities. Among other things, this legislation requires that all students with disabilities be guaranteed a learning environment that provides for reasonable accommodation of their disabilities. If you believe you have a disability requiring an accommodation, please contact the Department of Student Life, Services for Students with Disabilities, in Room 126 of the Koldus Building or call 845-1637.

AGGIE HONOR CODE: "An Aggie does not lie, cheat, or steal or tolerate those who do."Upon accepting admission to Texas A&M University, a student immediately assumes a commitment to uphold the Honor Code, to accept responsibility for learning, and to follow the philosophy and rules of the Honor System. Students will be required to state their commitment on examinations, research papers, and other academic work. Ignorance of the rules does not exclude any member of the TAMU community from the requirements or the processes. For additional information please visit: www.tamu.edu/aggiehonor/.

Experiment 1:

Synthesis of Metal Chelates: $[Cr(en)_3][Cl]_3 \cdot 3H_2O$, $Cr(acac)_3$ and $Mn(acac)_3$ (acac = Tris(2,4-pentanedionate; en=ethylenediamine)

Main Objectives:

1) Synthesize and characterize $Cr(acac)_3$.
2) Synthesize and characterize $Mn(acac)_3$.
3) Synthesize and characterize $[Cr(en)_3][Cl]_3 \cdot 3H_2O$.
4) Learn to write a succinct yet detailed Experimental section.

Characterization should involve: yields,melting and/or decomposition points and IR spectra measured as Nujol mulls

Sample references: *Inorg. Chem.* **1979**,18, 720. *Inorg. Chem.* **1977**,16, 709. *J. Phys. Chem.* **1984,** 88, 3356. *Inorg. Chem.* **1975,** 14, 703. *Inorg. Chem.* **1988**, 27, 986. **Look for others**. **There are many papers on this topic.**

Problems to be addressed in the report (and in the oral prelab to some extent):

1. What is a chelate and what is meant by the 'chelate effect'?
2. Write and balance the half-reactions for any redox reactions in this experiment.
3. Chromium has several common oxidation states other than III. What are they? What color are solutions of these species? Suggest an easy way of determining whether an oxidation or reduction of a chromium containing solution has taken place.
4. The tris-chelate compounds are chiral and exhibit two isomers. What are they? Explain.
5. In acetone, the alkyl hydrogen atoms are quite difficult to remove in the presence of base. In acetylacetone, however, a proton is readily lost, forming the acac anion. Why is there a difference between the two similar compounds?
6. Manganese(II) (d^5) is nearly colorless, whereas Mn(VII) (d^0) is dark violet. Explain.
7. Explain why Mn(II) and Mn(VII) are used in a roughly 4:1 ratio in this experiment.
8. What is the Jahn-Teller effect? Would either the $Cr(acac)_3$ or $Mn(acac)_3$ exhibit it? Explain.
9. Would you expect the compounds to be paramagnetic or diamagnetic?

Experiment 2:
Investigation of the electronic configuration in various trivalent transition metal complexes

Main Objectives:

1) Investigate the electronic spectra of several trivalent transition metal complexes: $[Cr(H_2O)_6](NO_3)_3 \cdot 3H_2O$, $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$, $[Cr(en)_3]Cl_3 \cdot 3H_2O$, $[Cr(acac)_3]$, $[Mn(acac)_3]$ and $[Fe(acac)_3]$.
2) Determine Δ_o for each compound and arranging the ligands and metal ions in order of crystal field strength.
3) Determine the number of unpaired electrons in the ground state *via* magnetic susceptibility measurements.
4) Interpret the changes in a series of spectra of $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ obtained over an extended period of time.
5) Learn to write a detailed and informative discussion section (including a description of the electronic structure of each compound studied as determined using electronic spectroscopy and magnetic susceptibility data).

Sample references: *Inorg. Chem.* **1973**,12, 135. *Inorg. Chem.* **2009**,48, 11843. *J. Chem. Soc. A.* **1968**, 2129. *J. Phys. Chem.* **1981,** 85, 4153.

Problems to be addressed in the oral prelab:

1. What is the spectrochemical series?
2. Define Δ_o.
3. What determines the UV/vis absorbance of a molecule?
4. How would you determine the concentration needed of each solution to use for measurement (hint: think of Beer's Law)? Calculate concentrations necessary for each compound to observe the visible transition at 0.5 absorbance.
5. Mn(II) and Fe(III) are examples of transition metal ions that are usually much more weakly colored than "normal" transition metal ions. Why are they so weakly colored?
6. Unlike most manganese(II) complexes, $[Mn(CN)_6]^{4-}$ is highly colored. Why? (Hint: The ligand is not colored and has a large Δ_o splitting.)

Items to be addressed in the discussion section of the written report in addition to the prelab concepts:

1. Determine the Δ_o for each metal complex. Rank the ligands and metal ions in order from weakest field to strongest field.
2. Does the order of ligands and metal ions obtained in this experiment correspond to the established order in the spectrochemical series? Explain any deviations.
3. The visible spectrum of $Cr(acac)_3$ is significantly different from the other Cr(III) complexes. Why?
4. Account for the changes in the highest wavelength maximum for $CrCl_3 \cdot 6H_2O$ with time. What reaction is occurring in solution?
5. How many unpaired electrons are in $[Cr(en)_3]Cl_3 \cdot 3H_2O$, $[Cr(acac)_3]$, $[Mn(acac)_3]$ and $[Fe(acac)_3]$? Determine this from the magnetic susceptibility data of each of these complexes.

Experiment 3:
Preparation of Tetrabutylammonium Octachlorodirhenate(III,III)

Main Objectives:

1) Synthesize and characterize tetrabutylammonium octachlorodirhenate(III,III).
2) Learn to write an informative Introduction detailing the importance of the work and the history behind it.

Characterization should involve: yields, melting/decomposition point and IR spectroscopy in Nujol mull.

Problems to be addressed in the report (and in oral prelabs to some extent):

1. What is a quadruple bond? How can it be explained using *d* orbital overlaps? Be able to draw the overlaps.
2. Quadruple bonds are fairly common in transition metal complexes, but are never seen in organic chemistry. Why?
3. Why is the dirhenate complex diamagnetic? Be able to explain using molecular orbital diagrams.
4. What do you expect will happen to the bond order if there is a one-electron oxidation?
5. The $[Re_2X_8]^{2-}$ ion can be reduced to form both $[Re_2X_8]^{3-}$ and $[Re_2X_8]^{4-}$ species. What structure would you expect those ions to have? What would you expect the Re-Re bond order to be?
6. Several transition metals other than rhenium for complexes containing quadruple bonds. Cite two examples from literature, and discuss the structure and bonding in each. Can you find any examples of first row transition metal complexes containing quadruple bonds? Explain.

STUDENTS FOR CHEM 433 FALL 2010	**GROUP #**
BURROWS, SAMANTHA	Group ____
CHITOLIE, TRAVYSS	Group ____
COSTANZO, CHRISTOPHER	Group ____
DELKA, BRYANT	Group ____
FISH, MEGAN	Group ____
GOINES, SIMONE	Group ____
JOHNSON, KURT	Group ____
ORTEGA, ERIC	Group ____
SCHEPP, ERICA	Group ____
WOOLFORD, CHRISTOPHER	Group ____

Cleaning Roster for Fall 2010

If it is your group's day to cycle glassware through the acid/base baths, you are to cycle the baths at least once, regardless of the amount of glassware in each bath. Remember to wear full protective attire (lab coat, protective eyewear and the thick rubber gloves). Instructions are as follows:

1. Put dried glassware away in the proper location.
2. Carefully remove glassware from the acid bath, pouring out the solution back into the bath. Rinse each piece thoroughly with distilled water, then place on the drying rack provided so that the glassware can drain. Alternatively, you can rinse with acetone to speed the drying process (ideal if glassware needs to be dried in the oven).
3. Remove glassware form the base bath, returning the solution to the base bath, and rinse thoroughly with distilled water. Carefully place in acid bath, ensuring that the vessel is completely filled with the acid solution (NO bubbles).
4. Add new glassware (already rinsed by other group members) into the base bath, ensuring that the vessels are completely filled and submerged (again, no bubbles). If there is no room, leave the excess glassware out—it won't get cleaned anyway, so don't risk breaking glassware to cram it in.
5. Make sure both baths are covered before you leave, and rinse off the gloves and set aside to dry on the sink edge.

Day	Group Responsible
6 September	1
9 September	2
14 September	3
16 September	4
20 September	1
22 September	2
28 September	3
30 September	4
5 October	1
7 October	2
12 October	3
14 October	4
19 October	1
21 October	2
26 October	3
28 October	4
2 November	1
4 November	2
9 November	3
11 November	4
16 November	1
18 November	2
23 November	3