CHEMISTRY 202

ADVANCED CHEMISTRY LABORATORY FALL 2014

LABORATORY:	Wednesday 12:50 - 5:00	Rm A207
LECTURE:	Monday 1:55	Rm B104
	Friday 1:55	Rm B104
INSTRUCTORS:	Prof. William Geiger	Rm 221
	Will Barker	Rm 208
	Joe Wright	Rm 123

MEETING WITH INSTRUCTORS: Although formal office hours are not scheduled, your instructors are eager to meet with you. Please make individual appointments to do so.

LAB SCHEDULE: The lab will begin with an introduction on Wednesday, Aug 29. Although labs times are scheduled through Dec 3, you will have only **six** Wednesdays assigned for experimental time in which to carry out the **three** major experiment sequences. Check the lab schedule on page 10A for details. You have no obligations on the lab day for which you are not scheduled. You will also be responsible to submit a report based on magnetic resonance data that you will be given.

EXPERIMENTS: In Chem 201, the emphasis was on exposing you to a number of physical and analytical techniques. You completed the following:

*** gas-liquid- and liquid-solid-(high performance) chromatography

******* NMR spectroscopy

******* IR spectroscopy

******* UV-VIS spectroscopy

******* Atomic Absorption spectroscopy

******* Molecular spectroscopy

******* Vacuum line reactions

Experiments to be performed this semester. This semester's work will consist of three experimental sections, a lab report based on magnetic resonance data that you will be given, and an electronic literature search.

Expt **1**: **Preparation of Nickel Group Dithiolate Complexes** (2 periods)

Expt **2**: **Preparation of Decamethylferrocene, $(C_5Me_5)_2Fe$** (2 periods)

Expt **3**: **Organometallic Radicals: The Decamethylferrocenium Ion** (2 periods)

In addition to completing the three assigned experiments, you will also:

- Write a complete "lab" report based on NMR and ESR (electron spin resonance) measurements made on paramagnetic compounds. You will be given spectra to evaluate and use as the basis of your report.
- Submit a two-page (SciFinder) report answering questions about the physical and chemical properties of the types of compounds experienced in this course.
- Give an **oral presentation**
- Attend a **Schlenk-technique** tutorial (August 27)
- Complete a **glassblowing** tutorial (before Thanksgiving break)

HOW WILL YOUR LAB EXPERIENCE BE BROADENED? By the semester's end you will have new or additional exposure to the following **TECHNIQUES and CONCEPTS :** NMR (expts 2,4); IR (expts 1,3); Optical (expts 1,2,3); Voltammetry (expt 3); Conductivity (expts 1,3); Schlenk-based synthetic methods (expts 2,3); ESR (expt 4) and to **SCIENTIFIC WRITING**, which is a major component of the course.

YOUR LEARNING GOALS may be viewed as part of the overall goals set for Chemistry majors by our Department: 1) to be able to apply chemical and physical principles to the solution of chemical problems, 2) to understand the interplay of data and hypothesis-driven experiments, 3) to become proficient in important chemical lab techniques and to be able to apply them to research problems, 4) to be able to read and to critically evaluate the chemical literature, and 5) to learn to present scientific data clearly and effectively through both written and verbal communication.

LAB REPORTS: The semester's SIX reports will consist of:

- ******* FIVE WRITTEN REPORTS (1-**Manuscript-level**; 3-Short; 1-SciFinder report).
- ******* ONE ORAL PRESENTATION.

<u>WRITTEN REPORTS</u>

The FIVE WRITTEN REPORTS are based on the four experiments (three carried out and one 'dry') and the SciFinder electronic search. The last of these requires a concise (usually two-page) report, whereas the former will take one of two possible forms, being of either <u>SHORT</u> or <u>MANUSCRIPT</u> length. The SHORT report has a maximum of **six** pages of text and tables, but it will generally <u>include as attachments</u> photocopied figures of important spectra or voltammograms. Also **<u>attach photocopies of your lab notebook pages</u>** that describe the experiment. MANUSCRIPT reports should be more like those relatively complete papers that one might submit for a journal article. The manuscript-level report should be **<u>at least</u> 12**, and **no more than 15** pages of text and tables. Figures, including spectra and other "raw" experimental data, <u>do not count as part of the number of written pages</u> in *either* the MANUSCRIPT (**MS**) or SHORT (**SH**) reports. The MANUSCRIPT report will be read by WEG, given a <u>preliminary</u> grade, and <u>returned to you for redrafting</u> as part of the scientific writing part of the course curriculum. You may resubmit your corrected and rewritten MANUSCRIPT report for regrading .

Written reports are due on the dates shown on page 10. Unless granted an extension by Dr. Geiger, late submissions may result in a penalty of a full letter grade for the report.

Note that you may choose any one of the three lab experiments or the magnetic resonance data as the subject of your oral presentation. It is also possible to give your talk on a topic that is not strictly on one of the labs, but related to one of the general ideas or techniques covered in the course. Such a broader topic must be approved by Dr. Geiger and should not originate in your undergraduate research problem. See page 6 for details on oral presentations.

N.B.: The glassblowing requirement (see below) must be completed before Thanksgiving break. No reports or re-drafts of any type will be accepted after noon on Tuesday, December 9.

GUIDELINES FOR WRITTEN REPORTS

Manuscript-level Report

12-15 pages, intended to be suitable for submission to a journal published by the American Chemical Society. Follow the format of the **sample report** included in your handout "Mixed-Valent Complexes of Manganese".

Short Report

6 pages.

- Provide an Abstract in an uncounted cover page
- Shorten the Introduction to no more than ½ page
- For Experimental section: (a) if the lab handout procedure was followed successfully and without change, simply say so. Include any details likely to be unique to each procedure, such as % yields; (b) detail any specific changes in procedure or other problems encountered in the work.
- Use the same <u>rigorous</u> approach to providing data and results that you use in the manuscript-level report. Include Tables and Figures as needed (see below).
- Discussion of the results should be based on thoughtful evaluation of the data. Make sure to *include your responses to any questions posed in the lab handout.*
- **Use the usual ACS-type referencing system**. Check any ACS journal or the sample report "Mixed-Valent Complexes of Manganese" for the approved format.
- Include any Figures, Drawings, and Sample calculations in an Appendix. You may include Tables in the text or in the Appendix. The 6-page limit excludes the Appendix.

<u>Plagiarism-free referencing of the Literature</u>

The following sentence begins a paper by Balch, *et al*, *J. Am. Chem. Soc.* **2002**, *124*, 2327:

Gold (I) complexes typically are colorless, two-coordinate species that readily self-associate to form dimers, trimers, and extended chains connected by Au ••• Au contacts that are less than the van der Waals separation of *ca* 3.6 Å. [1-3] {*references 1-3 give the authors' literature-based support for their statement*}

Suppose that you are writing a report or paper on a subject that is somehow related to the above statement in the Balch paper, and you want to include this information in your document. How do you do so with integrity, so that the reader knows the basis of your statement or claims? Here are some possible approaches with a comment on the ethical aspects of each:

If, in your paper, you:

- (i) repeat the sentence without giving reference to either the Balch paper or to the literature references: this is **plagiarism**
- (ii) repeat the sentence but give reference to Balch paper: this is **plagiarism**
- (iii) repeat the sentence and put it *entirely* within quotation marks, also giving reference to Balch paper: this is **ethical but awkward writing**
- (iv) paraphrase *without* reference to the literature: this is **plagiarism**[a]
- (v) paraphrase *with* reference to literature: **ethical and recommended**

An example of the recommended approach (v): The ready self-association of Au (I) complexes into dimers and higher oligomers is accompanied by Au---Au contacts that are less than 3.6 Å, the van der Waals separation for this nucleus.[4]

[4] White-Morris, R.L.; Olmstead, M.M.; Jiang, F.; Tinti, D.S.; Balch, A.L. *J. Am. Chem. Soc.* **2002**, *124*, 2327, and references therein.

[a] An exception to the charge of plagiarism under choice (iv) relates to information that constitutes "common knowledge" for workers in the scientific field under discussion. Most information found in undergraduate-level textbooks can be assumed to be in this category, so that paraphrasing (not copying!) textual information without referencing is generally acceptable. Good judgment must be used, however, in using this rationale, especially if a large section of material or ideas is taken from a textbook, even if the book is being used as an introduction to chemistry. One example: "Aliphatic C-H bonds are strong" (common info); "The strength of an aliphatic C-H bond is about 110 kcal/mol" (common info, in my mind, but not all would agree); "The strength of a C-H bond which is alpha to a C-Cl bond is weaker than that alpha to a C-H bond" (reference needed).

W.Geiger 8/08: 202 plagiarism.doc

ORAL PRESENTATION

Dates for the oral presentation will be assigned at the beginning of the semester. Here are some pertinent points concerning the oral presentation.

1. **Topic**: Choose any one of the four lab experiments as the basis of your oral presentation. Since you are submitting a written (either MS-level or short) report on each lab, there will be overlap of oral presentation with the written one. Approach the two means of communication independently. In a written report, you are covering all the points necessary for another chemist to replicate your work. In an oral presentation, you are telling a story. You may want to choose a sub-topic to emphasize, such as either ESR or NMR from the magnetic resonance lab. Your topic must be approved by Prof. Geiger, and will be approved on a first-come, first-served, basis.

2. The presentations should be **20 min** in length, with an additional 5 min available for questions and discussion. <u>Practice your talk to make sure that the time length is appropriate!</u> Try not to finish more than two minutes before the allotted time. You will lose a letter grade for a talk that is abnormally short.

3. You should make a Power Point presentation. It is always the speaker's responsibility to see that his/her presentation can be performed with the available visual aids. You may want to work some blackboard usage into your presentation.

4. How should the talk be structured? (Prof. Geiger will give a presentation on "Hints for Oral Presentations" as the time approaches)
   - Intro including goals of experiment and sufficient theory to understand results
   - Results
   - Significance of results (how do these results relate to other concepts and chemistry in a broader sense?)
   - Analysis of errors and/or experimental pitfalls
   - What new skills and/or knowledge was gained in the experiment?

   These are very rough guidelines and not all may be important for every subject.

5. Your presentation will be evaluated by the instructors and we will inform you of your grade within one week of the presentation. We will consider <u>presentation style</u> (length, delivery, quality of slides, etc.), <u>clarity</u>, <u>content</u> <u>and</u> <u>depth</u> in evaluating your talk. Prof. Geiger will meet with you to go over the strengths and weaknesses of your presentation.

Oral presentations are scheduled for Nov 7, Nov 10, Nov 14, Nov 17, Nov 21 and Dec 2.

Glassblowing: Every student is required to work in a tutorial session with the Department glassblower, **Ms. Angie Gatsey**. Grading will be on an S/U basis and will be included in your "lab performance evaluation" grade (see below). **Please complete this requirement during September or October.** In any case, the glassblowing requirement *must be completed before the Thanksgiving break.* A summary of the glassblowing tutorial plan may be found at the end of this handout.

Grading:	Written Reports	60%	MS 30%; Short 24%; SciFinder 6%
	Oral presentation	20%	
	Lab performance evaluation	20%	
	Total	100%	

What is the "lab performance evaluation" grade? This is an evaluation by all the course instructors of the intangible aspects of your lab performance. Among the factors to be considered are: **your *preparedness* in coming to lab**; your motivation; your lab skills; your *attention to safety*; your creativity and independence; your ability to work effectively and efficiently in the lab; your cooperation with instructors and fellow students.

LAB SAFETY:

Safety comes first. You will be constantly reminded of this statement, but you must work on making this attitude an integral part of your approach to chemistry lab work. The first-line of defense, after informed common sense, is safety glasses. **Any student not wearing safety glasses in lab will be warned once, and subsequent violations may lead to expulsion for that lab period.** Furthermore, never eat or drink in any laboratory! The lab is long, so you may want to keep or have some food and beverage outside the lab and step out for it at your convenience, or take a break at a coffee shop (let us know if you are going out and talk about what needs to be watched in your absence). Make sure to wash your hands before eating.

LAB NOTEBOOKS:

You are required to maintain a lab notebook for the course. You are expected to come to lab prepared with appropriate background material and procedures already in your notebook. You will make all data entries and notes into your notebook. Do not copy notes and data from scratch paper into your notebook. The notebook, which must be bound (not spiral) will not be collected and graded, but it will be checked regularly during the lab. How well you maintain your notebook will affect your lab performance grade.

WRITTEN REPORTS:

General considerations. The best report is one in which the experiment is described fully but concisely. It takes good judgement to know what should be included and what may be omitted. The length of the report is guided by whether it is in the class of MS (12-15 pages), Short (6 pages), or Abstract (2 pages) form. The text length is separate from pages used for figures and graphs. Include actual experimental curves (e.g., spectra) whenever appropriate. You may submit photocopies of original data. Label any experimental data and spectra with appropriate information about compound, conditions, etc. For guidance on this, **see the Figure Captions in the sample MS-level report**.

IMPORTANT: Lab partners may discuss with each other the results of the experiment, but the reports MUST be written up separately.

A preferred general format is given here which is modified according to the report class.

a) **TITLE**. Name, dates of expt, date submitted, lab partner

b) **INTRODUCTION.** Outline of background material relevant to the experiment. Summary of pertinent ideas and theories**. Objectives and rationale for doing experiment.** Usually three pages or less for a MANUSCRIPT report

c) **EXPERIMENTAL** Give a description of any preparations and physical measurements. These descriptions may be brief, but give details whenever your procedures deviate significantly from those in the lab handout and give quantities and yields where appropriate.

d) **RESULTS AND DISCUSSION.** Observations, data, and their meanings. Present the data in a logical, concise format. Always ask yourself if you are in any way prejudicing your results by your prior expectations. Discuss things that may have gone wrong (or, at least, differently). This is a good place to discuss modifications or extensions of the experiment that would improve it.

e) **CALCULATIONS AND ERRORS**: Sample calculations should be included to help us see if you have done these properly. A statistical error analysis should be included where replicate measurements are involved.

f) **SAFETY APPENDIX:** Every chemical experiment involves potentially dangerous materials. Before starting your experiment, make a list of all the chemicals to be used in the expt and try to find out as much as possible about their toxicities. Include this information as an Appendix in your report. Two of the more important and useful sourcebooks to be found in the Reference section of the Cook Library are (1) "Handbook of Industrial Chemicals" and (2) "Merck Index" and one may use the WEB at ccinfoweb.ccohs.ca/msds/search.html. If there are any lingering doubts about handling a chemical, check them out with a TA or with WEG before starting the experiment. Look up the safety data **before** doing the expt.

g) **REFERENCES AND FOOTNOTES:** Collect at the end of the report. Use the format preferred by the American Chemical Society. **Pick up a recent ACS Journal to see how journal articles, books, etc. are referenced**. Avoid the use of Ibid. Do not use a different reference number for the same article.

GLASSBLOWING TUTORIAL

Instruction in glassblowing is provided in the Glass Shop (Cook A213) by the Department's resident specialist, Angie Gatesy. Her tutorials serve as a basic introduction to scientific glassblowing and include two intensive sessions which will be scheduled in either 8:00-10:00 AM or 1:30-3:30 time slots. It is up to you to schedule your times with Angie, but make sure to do so *early* in the semester before you get too busy. The glassblowing tutorial must be completed **prior to Thanksgiving recess**.

The following course description has been provided by Angie.

Session 1

- Glass shop orientation, including torches and how to safely cut glass
- Straight seals and bulbs
- T-seals
- Fire polishing
- Introduction to polariscope and to annealing

Session 2

- Ring seals
- Fire cutting
- Test tube ends
- Bending glass
- Construction of a bubbler or trap

Safety in the glass shop is a major concern and must be one of your learned 'skills'. The opportunity exits to burn or cut oneself. **Hot glass looks like cold glass** and stays hot longer than one would expect.

Glassblowing is a skill which is developed over time. While this general introduction attempts to teach basic skills, it in no way can be assumed that glassblowing can be perfected in this short course. At the end of this tutorial, you should be able to determine what a safe seal looks like, to make basic repairs should the need arise, and be more aware of the problems and restrictions faced by expert glassblowers when you design a new experimental system.

Laboratory Schedule for Chem 202: Fall, 2014

Date	Alpha 1	Alpha 2	Alpha 3	Beta 1	Beta 2	Beta 3
Sept 3	Off	Off	Off	Expt 2 (synthesis)	Expt 1 (Ni, oxdn A)	Expt 1 (Pt)
Sept 10	Expt 2 (synthesis)	Expt 1 (Ni, oxdn B)	Expt 1 (Pt)	Off	Off	Off
Sept 17	Off	Off	Off	Expt 2 (character-ization)	Expt 1 (Ni, oxdn A)	Expt 1 (Pt)
Sept 24	Expt 2 (character-ization)	Expt 1 (Ni, oxdn B)	Expt 1 (Pt)	Off	Off	Off
Oct 1	Off	Off	Off	Off	Expt 2 (synthesis)	Expt 3 (echem)
Oct 8	Expt 1 (Ni, oxdn A)	Expt 2 (synthesis)	Expt 3 (echem)	Expt 1 (Ni, oxdn A)	Off	Off
Oct 15	Expt 1 (Ni, oxdn A)	Off	Off	Expt 1 (Ni, oxdn A)	Expt 2 (character-ization)	Expt 3 (synthesis)
Oct 22	Off	Expt 2 (character-ization)	Expt 3 (synthesis)	Off	Off	Off
Oct 29	Expt 3 (echem)	Off	Off	Off	Expt 3 (echem)	Off
Nov 5	Expt 3 (synthesis)	Expt 3 (echem)	Off	Off	Off	Expt 2 (synthesis)
Nov 12	Off	Off	Expt 2 (synthesis)	Expt 3 (echem)	Expt 3 (synthesis)	Expt 2 (character-ization)
Nov 19	Off	Expt 3 (synthesis)	Expt 2 (character-ization)	Expt 3 (synthesis)	Off	Off
Dec 3 Makeup?	Off	Off	Off	Off	Off	Off

Due Dates for Reports

- SciFinder report: September 27 (all teams)
- Mag Res (ESR) report: Oct 8 (α1,β1); Nov 12 (α2,β2); Nov 19 (α3); Dec 3 (β3)
- α1: Oct 1 (**2**); Oct 29 (**1**,MS); Nov 19 (**3**)
- α2: Oct 15 (**1**,MS); Oct 29 (**2**); Dec 3 (**3**)
- α3: Oct 15 (**1**); Nov 5 (**3**, MS); Dec 3 (**2**)
- β1: Oct 1 (**2**); Oct 29 (**1**, MS); Dec 3 (**3**)
- β2: Oct 8 (**1**,MS); Oct 22 (**2**); Nov 19 (**3**)
- β3: Oct 8 (**1**); Oct 29 (**3**,MS); Nov 19 (**2**)

<u>Lecture Schedule</u> (Rm B104 at 1:55)

Wed	Aug 27	Introduction, overview of experiments (**Rm 229**)
Fri	Aug 29	Metal dithiolate chemistry
Fri	Sept 5	Electrochemistry I
Mon	Sept 8	Electrochemistry II
Fri	Sept 12	Electron spin resonance I
Mon	Sept 15	Electron spin resonance II
Fri	Sept 19	Organometallics I
Mon	Sept 22	Organometallics II
Fri	Sept 26	Oral presentation hints
Mon	Sept 29	Extra lecture time

Selected References: Fall 2014

Expt **1**: **Preparation of Nickel Group Dithiolates**

Ref(s) 1 (a) McCleverty "Metal Dithiolene and Related Complexes" (general review of early work; copy available to check out) and (b) Stiefel "Progress in Inorganic Chemistry" (series of 2004 review articles; book on Reserve; do not mark on the book!)

Ref 2 Holm *et al.* "Nickel Dithiolenes Revisited…"

Ref 3 Drago "Physical Methods" 2nd ed, pp 433-447

Ref 4 Rieger "Electrolytic Conductance"

Ref 5 Geiger, notes on conductivity

Expts **2** and **3**: **Preparation of $(C_5Me_5)_2Fe$ and $[(C_5Me_5)_2Fe][BF_4]$**

Ref 6 Connelly and Geiger "Chemical Redox Agents…"

Ref 7 Mabbott "Introduction to Cyclic Voltammetry"

Ref 8 Kissinger and Heineman "Cyclic Voltammetry"

Ref 9 Crabtree "Organometallilc Chemistry of the Transition Metals", 2nd ed. (also see first ed of this on reserve for Chem 202, pp 20-34 and 104-112)

Ref 4 Rieger "Electrolytic Conductance"

Ref 5 Geiger, notes on conductivity

Evaluation of **Solution Magnetic Properties (ESR, NMR)**

Ref 10 Bersohn and Baird "Introduction to Electron Paramagnetic Resonance"

Ref 11 Evans "Determination of Paramagnetic Susceptibility of Substances…"

Ref 12 Sur "Measurement of Magnetic Susceptibility…. FT NMR Spectrometer"

See also Jolly, "Modern Inorganic Chemistry", 1991, pp 454-462 (on reserve for Chem 202) and Huheey, 4th Ed, pp 459-468 (on reserve for Chem 131)

Preparing for Individual Experiments

Preparation of Nickel Group Dithiolates

Before doing this experiment, review the *Inorganic Chemistry* paper by Holm *et al*, which is provided to you. This paper gives a good introduction for the concept of 'ligand non-innocence' and metal-ligand delocalization which is crucial to understanding the preparations and physical studies that you will conduct. Pay attention to the spectral probes discussed in the Holm paper. Be cognizant of the ways in which people have prepared the formal Ni(II) and Ni(III) complexes in this family. You will find this kind of information in references contained in the Holm paper, and leading references to metal dithiolates in general are in the McCleverty review (reference 1 in your Selected References (SR) handbook). You will be running IR and UV-VIS spectra and making a solution conductivity measurement. Basic conductivity procedures may be reviewed in any P-chem text or in references 4 and 5 of your SR handbook.

Make sure to review the relationship between oxidation state and d-orbital count for the Ni and Cu-group metals.

Preparation and Oxidation of Decamethylferrocene

Make sure to review the basic ideas involved in the manipulation of air-sensitive compounds (Salzer article in blue handbook). Look up the melting point and ^{1}H NMR data reported for decamethylferrocene. Anticipate the main features in the IR spectrum of decamethyl-ferrocenium tetrafluoroborate.

Review cyclic voltammetry (CV), which was covered in Chem 221 and is treated adequately in references 7 and 8 of the SR handbook. Pay attention to the topics of chemical and electrochemical reversibility and how those ideas are addressed by CV.
You will also need to understand the difference between linear scan voltammetry (LSV) and CV to know why the former is used to monitor the chemical oxidation reaction.

The conceptual aspects of the experiment are based on the interplay between electrochemical measurements and chemical redox reactions. The Connelly/Geiger article (SR reference 6) reviews this area and pages 877-881 are particularly informative. The calculational and mechanistic aspects of this experiment have their basis in this review article.

One important analytical aspect of the experiment is the use of a 'standard addition' method for the analysis of nitrobenzene produced in the reaction. Make sure to review the concept of standard addition methods in analytical chemistry.

You will obtain optical spectra of the reaction products. Before the second day of the experiment, make sure to look up or anticipate what you should see for the visible spectrum (400-900 nm) of decamethylferrocene, decamethylferrocenium ion, and nitrobenzene.
It will also be helpful for you to know the $E_{1/2}$ values for three different redox couples: $[FeCp^*_2]^{0/1+}$; $[4\text{-}NO_2C_6H_4\text{-}N_2]^{0/1+}$ and $[NO_2C_6H_5]^{0/1-}$. You will find the potential of the first of these in the Connolly article; the second can be approximated by the analogous diazonium ion in which F replaces NO_2 (also given in the Connolly article). The potential for the one-electron reduction of nitrobenzene may be found in books detailing organic electrochemistry or in the original literature through SciFinder.

Solution Magnetic Properties (included even though we are not physically doing this experiment in 2014)

For the ESR section, you need to review the basic ideas behind the experiment (SR reference 10), including the approximate values for the frequency of the microwave radiation and the strength of the magnetic field that are used to accomplish the resonance. Review the relation between metal formal oxidation state and d-orbital count to know which metal dithiolene complex can be expected to be paramagnetic. You will be measuring the spectra of complexes containing Ni, Cu, and Pt nuclei. **For each of the metals, know which of the naturally-occurring isotopes of each metal have non-zero values of I, and be aware of the % natural abundance of each of those isotopes.** Compute the expected relative signal intensities for the $I = \frac{1}{2}$ spin vs the $I = 0$ spin for the Pt complex. You can find nuclear information in books on magnetic resonance or in the CRC Handbook of Chemistry and Physics. Be prepared to answer questions about how many lines, including hyperfine lines, are expected in each of the spectra.

For the Evans NMR method, review the references given in your Selected References handbook (refs 11 and 12). Know what the approximate value of μ_{eff} is for a spin-1/2 system. You can find this in books on P-chem and advanced inorganic.