Undergraduate Research in Project-Based Courses: Advice from a Practitioner

Tim Hubin
Southwestern Oklahoma State University
Outline

• Background
  – The Classical Inorganic Chemistry Lab
  – Hubin’s Research Experience/Interests
  – Motivations for a Project-Based Lab Course

• Project-Based Lab Design at SWOSU
  – Synthetic Scheme
  – Course Mechanics
    • Weekly Schedule
    • Specific Assignments
    • Rubrics

• Outcomes
  – Grades
  – Course Evaluations
  – Research Publications
I. Background

• The Classical Inorganic Chemistry Lab
  – From the 2015 Revision of the ACS Committee on Professional Training “Inorganic Chemistry Supplement”

Practical Topics

“The goal of the inorganic laboratory is to give students experience with a range of techniques used in the synthesis and characterization of inorganic compounds and to give them experience in preparing and analyzing various classes of inorganic compounds... Among the techniques that are recommended for inclusion in the inorganic laboratory are the following:”

• Synthetic Methods that make use of inert atmospheres (dry box/bag, Schlenk methods), a high temperature furnace/heated tube, a vacuum line, a high pressure autoclave, and electrochemical apparatus.

• Purification Methods such as column/ion exchange chromatography, sublimation, recrystallization and resolution of optically active compounds.

• Characterization Methods that involve measurements of magnetic susceptibility, conductivity, oxidation-reduction potentials, X-ray diffraction, IR, UV-vis, NMR (variable temperature, multinuclear, multidimensional), optical rotation, ESR, Mössbauer, and mass spectrometry, electronic properties (band-gaps, conductivity, etc.)..
“In the ideal case, experiments should be more than a list of instructions to be followed. Instead, they should illustrate how characterization methods provide insight into fundamental electronic structure and structure-property relationships (by studying families of related compounds for instance)... The list below provides examples of complexes that have been described in the chemical education literature, as a starting point for development of laboratory projects.”

• **Coordination Compounds** – [Co(NH$_3$)$_5$Cl]Cl$_2$, Mn(acac)$_3$, [Co(en)$_3$]Cl$_3$, CrCl$_2$(H$_2$O)$_4^+$, Cr(acac)$_3$, [Cr(NH$_3$)$_6$](NO$_3$)$_3$, Cu(O$_2$CMe)$_3$)$_2$•H$_2$O, [Co(en)$_2$Cl$_2$]Cl, [Co(o-phen)$_3$]Br$_2$, Co(salen), Mo$_2$(O$_2$CMe)$_4$, K$_4$Mo$_2$Cl$_8$.

• **Organotransition Metal Compounds** – (η$^6$-1,3,5-Me$_3$C$_6$H$_3$)Mo(CO)$_3$, Cp$_2$Fe$_2$(CO)$_4$, Ir(Cl)(CO)(PPh$_3$)$_2$, Cp$_2$Ni, PtCl$_2$(1,5-cyclooctadiene), [Pd(Cl)(η$^3$-allyl)]$_2$, Cp$_2$Fe, Rh(Cl)(CO)(PPh$_3$)$_2$, Fe$_3$(CO)$_12$.

• **Main Group Element Compounds** – BH$_3$:NH$_2$(tBu), B(OR)$_3$, C$_{60}$, GeH$_4$, Sn(Cl)$_2$(R)$_2$, Ph$_2$PCH$_2$CH$_2$PPh$_2$, K$_2$S$_2$O$_8$, PhBCl$_2$, K(C$_2$B$_9$H$_{11}$), ICl$_3$, [l(pyridine)$_2$](NO$_3$), [PCl$_4$][SbCl$_6$], Me$_3$N:BF$_3$, siloxane polymers.

• **Solid State Compounds** – YBa$_2$Cu$_3$O$_7$, VO(PO$_4$)(H$_2$O)$_2$, a zeolite, CrCl$_3$.

• **Bioinorganic Compounds** – Ni(glycinate)$_n$(2-n)$^+$, copper(II) tetraphenylporphyrin, Pd(nucleoside)$_2$(Cl)$_2$, Cu(saccharin)$_2$(H$_2$O)$_4$, Cu(glycinate)$_2$, cis-platin, cobaloxime model complexes.

• **Special Topics** – quantum dots, nanocrystals, templated synthesis of nanowires, self-assembled monolayers.
# My First Inorganic Lab Syllabus

<table>
<thead>
<tr>
<th>Subjects (Assigned Reading)</th>
<th>Lecture Dates</th>
<th>Lab</th>
<th>Compound Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Bonding Theory (Ch 3)</td>
<td>Aug. 29, 31</td>
<td>No Lab (Aug. 28)</td>
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<tr>
<td>Group Theory (Ch 4)</td>
<td>Sept. 3, 5, 7, 10</td>
<td>Mn(acac)_3 (Sept. 4)</td>
<td>Coordination Chemistry</td>
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<td>Molecular Orbitals (Ch 5)</td>
<td>Sept. 12, 14, 17, 19</td>
<td>Cyclam 1 (Sept. 11)</td>
<td>Coordination Chemistry</td>
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<td>Cyclam 2 (Sept. 18)</td>
<td>Template Synthesis</td>
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<tr>
<td><strong>Exam 1</strong></td>
<td>Sept. 21</td>
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<tr>
<td>Acid Base Theory (Ch 6)</td>
<td>Sept. 24, 26, 28, Oct. 1</td>
<td>Ni(glycinate) (Sept. 25)</td>
<td>Bioinorganic</td>
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<tr>
<td>Main Group Elements (Ch 8)</td>
<td>Oct. 3, 5, 8</td>
<td>Cobaloximes (Oct. 2)</td>
<td>Bioinorganic</td>
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<tr>
<td>Structures and Isomers (Ch 9)</td>
<td>Oct. 10, 12, 15</td>
<td>Cu(porphyrine) 1 (Oct. 9)</td>
<td>Bioinorganic</td>
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<tr>
<td></td>
<td></td>
<td>Cu(porphyrine) 2 (Oct. 16)</td>
<td>Bioinorganic</td>
</tr>
<tr>
<td><strong>Exam 2</strong></td>
<td>Oct. 17</td>
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<tr>
<td>Coordinate Bonding (Ch 10)</td>
<td>Oct. 19, 24, 26, 29</td>
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<td>Main Group</td>
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<tr>
<td>Electronic Spectra (Ch 11)</td>
<td>Oct. 31, Nov. 2, 5</td>
<td>C_{80} 1 (Oct. 30)</td>
<td>Coordination Chemistry</td>
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<td>C_{80} 2 (Nov. 6)</td>
<td>Organometallic</td>
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<tr>
<td>Reactions and Mechanisms (Ch 12)</td>
<td>Nov. 9, 12, 14, 16,</td>
<td>Ion Exchange (Nov. 13)</td>
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<td>Co(NH$_3$)$_3$Cl (Nov. 20)</td>
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<tr>
<td><strong>Exam 3</strong></td>
<td>Nov. 19</td>
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<tr>
<td>Organometallics (Ch 13)</td>
<td>Nov. 26, 28, 30</td>
<td>M(CO)$_x$ (Nov. 27)</td>
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<tr>
<td>Catalysis (Ch 14)</td>
<td>Dec. 3, 5, 7</td>
<td>No Lab (Dec. 4)</td>
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<tr>
<td><strong>Final Exam</strong></td>
<td>Dec. 12, 2:00 pm</td>
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Motivations for a Project-Based Inorganic Lab

• Advantages of the “Classical” Lab
  – Coverage of all different types of inorganic compounds and techniques possible
  – Straightforward course design—like any other chemistry lab
    • Prep one lab at a time
    • All students working on the same lab at the same time
    • Grade one kind of lab report at a time
  – Can choose inexpensive materials, methods, and instrumentation

• Disadvantages of the “Classical” Lab
  – Doesn’t focus on instructor’s expertise throughout
  – Students make something, run a characterization or two, and throw it away
  – Lacking “Discovery” element
  – Lacking in-depth study of any one system
  – Unlike what “real chemists” do
Motivations for a Project-Based Inorganic Lab

• Advantages of the Project-Based Lab
  – Focuses on instructor’s expertise throughout
  – Students become invested with semester-long series of related experiments
  – Focuses on the “Discovery” element of doing science
  – Centered on an in-depth study of one system
  – More like what “real chemists” do
  – Opportunity to write-up, present, (and publish) original research

• Disadvantages of the Project-Based Lab
  – Can’t cover all types of inorganic compounds
  – Complex course design—unlike any other chemistry lab
    • Prep for multiple experiments
    • All students not working on the same lab at the same time
    • Each Lab report is unique, at least for parts of the semester
  – More expensive/rare materials, methods, instrumentation may be required
My Research Experience and Interests

Metal | Ligand | $t_{1/2}$ 1M H$^+$
---|---|---
Cu$^{II}$ | Me$_2$B14N4Me$_6$ | > 8 yr
Cu$^{II}$ | Me$_2$B14N4 | > 6 yr
Cu$^{II}$ | Me$_2$B13N4 | >8 yr
Cu$^{II}$ | Me$_2$B12N4 | 30 h

Complex | Conversion % | Yield % Sulfoxide | Yield % Sulfone
---|---|---|---
Mn(Me$_2$EBC)Cl$_2$ | 99.8 | 44.3 | 46.5
II. The Project-Based Inorganic Lab at SWOSU

- Synthetic Scheme: 9/10-step synthesis completed in 8 weeks
### Inorganic Chemistry Lab Schedule Fall 2009

#### Ligand Synthesis

<table>
<thead>
<tr>
<th>Week Reading Due</th>
<th>Cyclam Synthesis</th>
<th>Bridged Ligand Synthesis</th>
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</thead>
<tbody>
<tr>
<td>1. Aug. 19</td>
<td>Amine + glyoxal setup—30min</td>
<td>Macrocycle + glyoxal setup—30min</td>
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<tr>
<td></td>
<td></td>
<td>Reaction time—2hr</td>
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<tr>
<td></td>
<td></td>
<td>Rotovap/Extract—1hr</td>
</tr>
<tr>
<td>2. Aug. 26</td>
<td>NaBH₄ reduction—1hr</td>
<td>Column Chromatography, Rotovap—2.5hr</td>
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<tr>
<td><strong>Ch 1, 4</strong></td>
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<tr>
<td>3. Sept. 2</td>
<td>Setup KCN reflux—30 min</td>
<td>Set up iodomethane rxn—30min</td>
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<tr>
<td></td>
<td>Reaction time—2hr</td>
<td></td>
</tr>
<tr>
<td>4. Sept. 9</td>
<td>Rotovap, filter, extract—2.5hr</td>
<td>Filter, wash, dry—30 min</td>
</tr>
<tr>
<td><strong>Ch 2</strong></td>
<td></td>
<td>Setup NaBH₄ reduction—30min</td>
</tr>
<tr>
<td>5. Sept. 16</td>
<td>Filter, rotovap—1hr; Dry—1hr</td>
<td>Work up final product—3hr</td>
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<tr>
<td></td>
<td>Collect product—30 min</td>
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<tr>
<td>6. Sept. 23</td>
<td>Catch up, characterization</td>
<td>Vacuum distill product—1 hr</td>
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<tr>
<td><strong>Ch 3</strong></td>
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Notes on the Organic Synthetic Part

- Students work in pairs to make:
  - Cyclam Starting Material
  - One of two possible Cross-Bridged Ligands: Bcyclam or Bcyclen

- Pre-Lab lecture prior to each lab:
  - Fairly short—need the time in the lab
  - Covers: reactions of the day, safety, techniques
  - Detailed “Procedure” sheets are handed out
  - Primary Literature and Notebook pages distributed in “Inorganic Lab Manual”

- Organic Compound Characterization
  - Cyclam synthesis is one-pot, so only final product characterized
  - Each step of the Bridged Ligand synthesis is worked up and characterized
  - GC-Mass Spec or Electrospray, $^1$H NMR, and $^{13}$C NMR is required for each compound

- Purification techniques: column chromatography, vacuum distillation

- Each student writes two lab reports: Cyclam and Bridged Ligand
  - 25pts each for a total of 50pts out of 210pts total for the class
Cyclam Synthesis

1. Dissolve 35.66 g (0.15 mol) NiCl₂ · 6H₂O in 400 mL DI water in a 2 L erlenmeyer flask.
2. Add 26.0 g (0.15 mol) H₂N(CH₂)₃NH(CH₂)₃NH(CH₂)₃NH₂ to the stirring metal salt solution.
3. Cool the solution to -5 °C using a plastic tube as an ice-water bath.
4. Add glyoxal to the cooled, stirring solution. Glyoxal comes as a 40% by mass solution in water. Add 22.5 mL (28.5 g; 0.196 mol) of the 40% solution. Do your own calculations to confirm the amount. This is a near 25% molar excess of glyoxal.
5. Remove the ice bath and allow the reaction to continue stirring for up to 3 hours.
Store the solution in the refrigerator until next lab period.

Tetracycle Synthesis

1. Use 10 g of your assigned macrocycle in this reaction. Some groups will be using cyclam (14-membered ring) and others cyclen (12-membered ring).
2. Add 10 g of the macrocycle to a 100 mL round-bottom flask from your organic kit, along with 40 mL of acetonitrile. Calculate the number of moles of macrocycle.
3. Flush the round-bottom flask with N₂ for 3 minutes by opening the gas inlet. Test to make sure the N₂ is reaching your flask by breaking the seal while observing the bubbler. The bubbler should stop bubbling when you break the seal if N₂ is flowing to your flask.
4. Quickly add a 10% molar excess of glyoxal solution to the reaction. Your calculations should indicate you need 7-10 g of the glyoxal solution. Weigh the glyoxal solution this time, rather than using volume to measure it out.
5. Stir the reaction under N₂ at a temperature of 50-65 °C for 1-2 hr.
6. Use a rotary evaporator to remove most of the liquid from your reaction flask. A brown-black oily residue, potentially with some dark solids, will remain.
7. Extract the residue with 4-5 30 mL portions of CHCl₃ using a separatory funnel. If solid remains in the round-bottom, wash it with the CHCl₃ as you add portions to the sep funnel. Keep the chloroform (bottom) layers.
8. Filter the combined chloroform layer through fast filter paper and store in the fridge.
Inorganic Lab Report Format
Tim Hubin

**Preliminary Write-up**
This section includes items and descriptions that should be known prior to carrying out the experiment. Much of this information can be gathered from the Lab Manual. Things to include in this section include:

**Title**—The three written labs for this course will be titled: “Cyclam Synthesis and Characterization”; “Bridge Cyclam/Cyclen Synthesis and Characterization”; and “Synthesis and Characterization of [M(Bcyclam/Bcyclen)(OAc)]PF₆.”

**Name**

Chemicals, Reactions, Precautions— I want you to include the reaction(s) performed at the top of each report. You should include the exact reaction you will be carrying out with the expected product(s). Use a chemical drawing program (ChemDraw is available on the CPP Computer Lab computers under Start—All Programs—ChemOffice—ChemDraw. Under each reagent, list its molecular weight. Be sure to note any precautions that should be taken with any chemical.

**Introduction and Theory:** (including purpose and background)
Purpose—concisely answers the question “Why am I doing this experiment”. No more than a few sentences are needed.

Background—gives the theoretical basis for the experiment. This should include general reaction conditions and considerations for the type of reaction you are doing. This section should contain only words, not figures. It should be brief, but should inform the reader of how this particular experiment fits within the project.

**Setup and Techniques**—You should draw the glassware setup for each experiment. “Chipware” of glassware pieces is available in the ChemDraw Templates (example below). List any new techniques (ex: vacuum distillation) with a brief description of how it is performed.

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**Assessment of Inorganic Lab Reports**

<table>
<thead>
<tr>
<th></th>
<th>0 points</th>
<th>1 point</th>
<th>2 points</th>
<th>Score</th>
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<tr>
<td><strong>Preliminary Writeup</strong></td>
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<tr>
<td>5 points possible</td>
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<td><strong>Reaction, Names, Masses</strong></td>
<td>Not present</td>
<td>Present, but with errors</td>
<td>Correct reaction for this lab in ChemDraw</td>
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<tr>
<td><strong>Introduction and Theory</strong></td>
<td>Serious theoretical error(s), unorganized, incomplete</td>
<td>Competent theoretical discussion, but missing crucial points</td>
<td>Complete discussion demonstrating understanding of goal</td>
<td></td>
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<tr>
<td><strong>Precautions</strong></td>
<td>Incomplete and Unorganized</td>
<td>Complete and Organized</td>
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<tr>
<td><strong>Setup and Techniques</strong></td>
<td>No sketch, incomplete or erroneous steps</td>
<td>Sketch, nearly complete technique description</td>
<td>Clear sketch, complete correct technique description</td>
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<td><strong>Experimental Section</strong></td>
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<tr>
<td>10 points possible</td>
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<td><strong>Procedure</strong></td>
<td>Not present or incorrect</td>
<td>Present, but errors or not enough detail</td>
<td>Detailed, Correct Procedure</td>
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<tr>
<td><strong>Data</strong></td>
<td>Incomplete, Unorganized</td>
<td>Unorganized or missing units or errors</td>
<td>Complete, tabulated, with units and est. errors</td>
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<tr>
<td><strong>Comments, Description</strong></td>
<td>Absent or Erroneous</td>
<td>Missing crucial observation(s)</td>
<td>Complete report of all critical observations</td>
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<td><strong>Calculations</strong></td>
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<td>A few errors</td>
<td>Completely correct</td>
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<td><strong>Results and Discussion</strong></td>
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<tr>
<td>10 points possible</td>
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<tr>
<td><strong>Spectra and Graphs</strong></td>
<td>Absent, Incorrect, illegible</td>
<td>Lacking units, context, or clarity</td>
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<td><strong>Summary of Results</strong></td>
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<td>Largely correct, but some errors</td>
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<td>Sloppy, numerous errors</td>
<td>Few, but substantial errors</td>
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<td><strong>Error Analysis</strong></td>
<td>Absent or not thought out</td>
<td>Most errors identified, but relevant omissions</td>
<td>Complete error discussion; Thorough analysis</td>
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<td><strong>Sugg. Improv.</strong></td>
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Final Score out of 25 possible points

/25
Notes on Part 2—Inorganic Synthesis

<table>
<thead>
<tr>
<th>Date</th>
<th>Description</th>
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<tbody>
<tr>
<td>7. Sept. 30 Ch 5</td>
<td>Complexation Reaction in the glovebox, Catch up</td>
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<tr>
<td>8. Oct. 7</td>
<td>Oxidize complexes, Work up complexes, set up crystallizations</td>
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</tbody>
</table>

- Student partners shuffled—keep bridged ligand, paired by metal
  - Each student will make a unique complex: \([\text{Fe(Bcyclam)Cl}_2]\text{PF}_6\)
  - Synthetic steps and characterization organized by metal ion
- Labile M^{2+} salts complexed to Ligands in Inert Atmosphere Glovebox
  - Cr, Mn, Fe, Co are air sensitive; Ni, Cu are not
  - Bridged ligands are air/water sensitive due to extreme basicity
- Chemical Oxidation to air stable M^{3+} complex eases characterization
  - Cr, Mn, Fe oxidized by \(\text{Br}_2\); Co oxidized with air under acidic conditions
  - Ni, Cu are air stable at 2+ and will not be oxidized to 3+

Metal complexes produced in Fall 2007.
From left: Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}.
### Part 3—Inorganic Characterization

<table>
<thead>
<tr>
<th>Handouts</th>
<th>Characterization of Metal Complexes</th>
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<tbody>
<tr>
<td><strong>Ch 6</strong></td>
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<tr>
<td>12. Nov. 4</td>
<td>Conduct.</td>
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<tr>
<td><strong>Ch 7</strong></td>
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<tr>
<td><strong>Ch 8, 9</strong></td>
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<td>15. Dec. 2</td>
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<tr>
<td>16. Dec. 9</td>
<td>Poster Presentation, Written Papers Due</td>
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</table>
Notes on Inorganic Characterization Part

- **Pre-Lab:** Theory, Data Workup, and Conclusions for our Complexes for a different technique each week—Powerpoint Lecture
  - More time for pre-lab as characterization is quicker than synthesis
  - I work up actual data for a different technique each week

- **Students rotate to different instrument(s) each week w/partner**
  - SWOSU only has one instrument of each type
  - Elemental Analysis done on-site
  - Data Analysis for these covered during NMR slot (already know NMR)
  - Electrospray mass spectra obtained on each sample

- **Handout on Procedure for each instrument/technique**
  - Specific to SWOSU’s instrument holdings
  - Instructor (and TA) rotate among groups troubleshooting problems

- A written lab report for the Inorganic Synthesis and Characterization is written in the same format as above. 50pts out of 210pts total.
Inorganic Lab—IR Procedure

Sample Preparation
1. We will be taking IR spectra using a KBr pellet.
2. Add ~100mg of dry KBr (spectral grade) to a mortar. Add ~5 mg of your solid sample to the KBr in the mortar.
3. Using a pestle, grind the KBr and sample into a very fine powder.
4. Insert the first bolt into the pellet press and add enough of the KBr mixture to the pellet press to cover the bottom with a layer 1-2 mm thick.
5. Insert the second bolt and use two wrenches of the appropriate size to tighten the bolts about as much as you can with one hand.
6. Let the pellet press set for 2-5 minutes. Then carefully unscrew the bolts. The transparent pellet should stay in the press.
7. If your pellet falls apart or is not very transparent, you may want to redo procedure 1-6 again.

Instrument Procedure
1. Open the EZ-Omic software on the IR computer.
2. Insert the transmission sample holder into the IR, if it is not already present. The software should recognize the hardware change (if made) and a message should appear on the screen.
3. Collect a background of 8 scans. There is no need to save it to a window; it automatically replaces the previous background.
4. Set the pellet press with your pellet on the sample holder. Collect your spectrum of 8 scans.
5. You may auto adjust the baseline; this has to be done while viewing the spectrum in Absorbance format.
6. Peak picking may be done automatically or manually. You may want to type the numerical values of the peaks in as text boxes.
7. Output the data as a file that can be transferred to Excel and print a copy of the spectrum in the percent transmittance format.

Interpretation
1. Use the lab handout regarding IR to identify any functional groups that can be confirmed from the IR Spectrum.

Magnetic Susceptibility

A. Why are we doing this experiment?
1) Magnetic Properties reveal numbers of unpaired electrons
2) The number of unpaired electrons tell us about oxidation state, geometry, ligand field strength, etc…

B. How are we doing this experiment?
1) We are using a Johnson-Matthey MSB-Auto Magnetic Susceptibility Balance
2) It uses the Evans’s detector which is a modified Gouy Method

C. How do we work up the data?
1. The MSB-Auto output data is Volume Susceptibility = χ_v
   Example: [Mn(B113Na4Cl)]PF6 χ_v = 3.80 x 10^-6 (milliters) average value
2. We will need the volume of our sample:
   V = πr²h = (3.1416)(0.162cm)²(0.01cm) = 0.248 cm³
3. We will need the density of our sample:
   d = m/V = (0.1549g)/(0.248cm³) = 0.624 g/cm³
4. We can calculate Mass Susceptibility = χ_m
   χ_m = χ_v/d = (3.80 x 10^-6)(0.624 g/cm³) = 6.09 x 10^-4 cm³/g
5. Next we need to calculate Molar Susceptibility = χ_m
   χ_m = χ_m/(Mol. Wt) = (5.61 x 10^-4 g/cm³)(511.200 g/mol) = 3.11 x 10^-3 cm³/mol
6. We now need to correct for diamagnetic influences of the ligands
   a. We are wanting the metal only, but the ligand is interfering
   b. Ligand atoms (and even the metal core electrons) are diamagnetic
   c. We need to add back in the sum of the ligand diamagnetism

D. How do we interpret the results?
1. We can compare the magnetic moment with literature values for that ion
2. We can decide if the expected oxidation state of the metal matches
3. We can decide what the geometry of the complex is
4. We can decide if the complex is high spin or low spin
5. We can decide if the ligand(s) is are weak or strong field
Reporting Their Results

• Scientific Research isn’t finished until the results are communicated

• Each student prepares a manuscript containing all experimental procedures, results, discussion, and conclusions

• “Cantaurus” (Bulldog) format is required
  • Format adapted from Prof. Jonathan Frye (McPherson College)
  • Each student is given a formatted template file in Word
  • “Guide to Authors” adapted from Prof. Frye as well

• A general introduction and general experimental are provided
  – This is not a literature course; I don’t ask them to justify the project
  – The general experimental provides sources of chemicals, instrument details

• Each student prepares a poster, following a generic template
The Synthesis and Characterization of Co(AcBcyclam)PF₆
Jonas Lichty and Timothy J. Hubin. Dept. of Chemistry, Southwestern Oklahoma State University

• Introduction
  – An Improved MRI Contrast Agent?
    - Modulate magnetic properties of water
    - Utilize Gd³⁺ because of its high magnetic moment as a result of its seven unpaired electrons
    - Complex must be stable, because Gd³⁺ is toxic to humans
    - Why Cobalt? There is an abundance of information on cobalt complexes, so comparisons can be made with similar complexes.

• Ligand Synthesis:
  - The synthesized Co³⁺ complex of 4, 11 – diacetato – 1, 4, 8, 11 – tetraazabicyclo[6,6,2]hexadecane was pure.
  - From the UV-Vis we can conclude that AcBcyclam is a strong field ligand
  - NMR, Mass Spec, and IR have all been assigned
  - Cobalt is the first metal put into this ligand that gives an NMR (diamagnetic)
  - X – ray crystal structure confirms predicted geometry

• Complex Synthesis
  - Overall Yield 56% for four steps.
    - Purity confirmed by Elemental Analysis to 0.4% CHN.
    - Identity confirmed by NMR comparison to literature.

• Conclusions
  - The synthesized Co³⁺ complex of 4, 11 – diacetato – 1, 4, 8, 11 – tetraazabicyclo[6,6,2]hexadecane was pure.
  - From the UV-Vis we can conclude that AcBcyclam is a strong field ligand
  - NMR, Mass Spec, and IR have all been assigned
  - Cobalt is the first metal put into this ligand that gives an NMR (diamagnetic)
  - X – ray crystal structure confirms predicted geometry

• Acknowledgements
  - Dr. Tim Hubin
  --Dr. David VanderVelde, of the University of Kansas
  - Dr. Steven Archibald, of the University of Hull (U.K.)
ABSTRACT

Keywords: [Click here and type keywords]

INTRODUCTION

Manganese, iron, chromium, and nickel share with copper dominance over the vast realm of redox catalysis in nature, biominimacy, and homogeneous catalysis. Cytochrome P450, catachel dioxygenase, methyl monoxygenase, and lipooxygenase display the power and selectivity found in natural iron-based oxidation catalysis while Mn catalase, mitochondrial superoxide dismutase, and Photosystem II similarly illustrate the potency of manganese derivatives. In biominimacy and homogeneous catalysis, porphin derivates have been prominent in the extensive development of catalytically effective metalloporphyrins.

We hypothesized that the principles of coordination chemistry and should allow us to design ligands that would be strongly resistant to oxidative hydrolysis while still having available sites for direct binding of the metal ion to either or both a terminal oxidant or substrate.

The importance of having two cis ligands (as in the coordination of metal complexes and photodynamic processes) has been discussed in relation to various catalytic and biomimetic processes. We propose that the optimum number of available sites may be two, since this would facilitate a decrease in coordination number at the higher oxidation level, i.e., a diqua complex of manganese(II) could transform into an oxo-complex of manganese(IV). Such a transformation would require adjacent coordination sites. Further, since the lower oxidation states, manganese(II) and iron(II), are commonly 6-coordinate, tetrodentate ligands are to be preferred. The obvious ligand to satisfy these requirements is 1,4,7,10-tetraaza cyclododecane, often labeled cyclen, or, systemically, [12]aneN12.

The thermodynamic sink represented by the mineral forms of manganese and iron often limits the utility, especially in aqueous media, of functional catalysts based on common ligands such as polynamines or polyethylenes. N,N,N,N'-tetramethyl-1,4,7-triazacyclononane, Me[8]aneN8 provides an example in which manganese and iron complexes retain some solubility and are achieved and the manganese complex is a potent oxidation catalyst. A principle feature of this and other significant catalysts having common nitrogen donors and vacant coordination sites is their tendency to form dimers in which higher valent metal ions are present.

GUIDE TO AUTHORS

GENERAL INSTRUCTIONS

Contents is the primary vehicle for written communication of senior research projects completed by SWGSU students who major in Chemistry. The editor embodies the following guidelines with this purpose in mind. Persons wishing to submit work that reports on an enterprise other than a senior research project are welcome to do so, but they should contact the editor before submission.

CONTENT

The editor welcomes any research or review article germane to the natural sciences including but not limited to biology, chemistry, environmental stewardship, and physiology. The editor may focus on original research projects, and review articles should provide a thought-provoking viewpoint. Any article submitted for publication should be an original analysis or reanalysis of previously published results and reflect new insights.

SUBMISSION

Authors assume responsibility for submitting an article with the proper content and format. The following checklist will aid the writing and formatting process. The following guidelines to publish a submission, any one of the requirements listed below is not fulfilled.

- Hardcopy Submit the article in printed form. A hardcopy of the manuscript must include those pages:
  1. A signed and dated copy of this checklist with each box checked.
  2. The editor should include a label on the manuscript.

- Electronic copy Submit the article, all figures, and captions in electronic format on a floppy disk. The disk should include the article name and MS Word File format.

STYLE

- Voice Write with precision, clarity, and economy. Use the active voice and first person whenever appropriate. Avoid statements subjective in tone ("I feel that...", "I think that..."). Informal opinions are acceptable, but the author should clearly word them in such a way that readers do not mistake them for factual statements. The editor encourages but does not require gender-inclusive language.

- Audience Assume an audience competent in the natural sciences but without expert knowledge in your field. Articles should not be simplified or be cliché in content.

- Grammar and spelling. Use the proper grammar and spelling for acceptance for publication.

GENERAL FORMAT

- Length The entire article including figures and tables should be no longer than 25 pages.

- Typeface and spacing. Use the Arial typeface for all text, figures, and tables. Captions. Use one-inch margins. Mathematical symbols and equations should be written in times New Roman. Equations with proper formatting, use the default values of the Equation Editor found with MS Word. Italics should only be used for emphasis. Put two spaces between every pair of adjacent sentences.

- Measurements Use the International System of Units, SI, for all measurements. When the denominator includes only one unit use the coidus (e.g., g/ml). If two or more units occur in the denominator use negative exponents (e.g., m^2 s^-1). Numbers should have a leading zero (e.g., 0.045 not 0.45).

- Scientific nomenclature. State the common name and IUPAC name of chemical species the first time you mention them in the text body. Use either the common or the scientific name thereafter; do not alternate between the two names.

- Acronyms and abbreviations. Define acronyms and abbreviations unfamiliar to most readers the first time you use them.

- Numerals. Spell out numbers less than or equal to ten. Use the numerical form for a unit of measure (e.g., six portions, 32 times, 6).
### Rubric for Poster Presentation of Laboratory Project

| Name: |  |
| Title: |  |

#### Grading Criteria

**Introduction: 2 points**
- Student clearly communicates proper context for the work
  
<table>
<thead>
<tr>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
</table>

**Organic Synthesis: 5 points**
- Student understands the reactions
  
  | 0 | 1 | 2 |
- Student clearly communicates the reaction sequence and results
  
  | 0 | 1 | 2 |

**Inorganic Synthesis: 5 points**
- Student understands the reactions
  
  | 0 | 1 | 2 |
- Student clearly communicates the reaction sequence and results
  
  | 0 | 1 | 2 |

**Characterization of Metal Complex: 10 points**
- Accurate and clear presentation and interpretation of the following methods:
  - IR
    
    | 0 | 1 |
  - Mass Spectrum
    
    | 0 | 1 |
  - Elemental Analysis
    
    | 0 | 1 | 2 |
  - Conductance
    
    | 0 | 1 | 2 |
  - Magnetic Moment
    
    | 0 | 1 | 2 |
  - Cyclic Voltammetry
    
    | 0 | 1 | 2 |
  - UV-Visible Spectrum
    
    | 0 | 1 | 2 |

**Mechanics of the Presentation: 3 points**
- Poster is clear and organized
  
  | 0 | 1 | 2 |
- Proper scientific tone is employed
  
  | 0 | 1 |

**TOTAL (Maximum = 25 points)**: ___

### Rubric for Written Report of Laboratory Project

| Name: |  |
| Title: |  |

#### Grading Criteria

**Abstract: 4 points**
- Student clearly communicates proper context for the work
  
  | 0 | 1 | 2 | 3 | 4 |

**Organic Synthesis: 10 points**
- Student understands the reactions
  
  | 0 | 1 | 2 | 3 | 4 | 5 |
- Student clearly communicates the reaction sequence and results
  
  | 0 | 1 | 2 | 3 | 4 | 5 |

**Inorganic Synthesis: 10 points**
- Student understands the reactions
  
  | 0 | 1 | 2 | 3 | 4 | 5 |
- Student clearly communicates the reaction sequence and results
  
  | 0 | 1 | 2 | 3 | 4 | 5 |

**Characterization of Metal Complex: 20 points**
- Accurate and clear presentation and interpretation of the following methods:
  - IR
    
    | 0 | 1 |
  - Mass Spectrum
    
    | 0 | 1 | 2 | 3 |
  - Elemental Analysis
    
    | 0 | 1 | 2 | 3 |
  - Conductance
    
    | 0 | 1 | 2 | 3 |
  - Magnetic Moment
    
    | 0 | 1 | 2 | 3 |
  - Cyclic Voltammetry
    
    | 0 | 1 | 2 | 3 |
  - UV-Visible Spectrum
    
    | 0 | 1 | 2 | 3 |
  - NMR
    
    | 0 | 1 |

**Mechanics of the Paper: 6 points**
- Writing is clear and organized
  
  | 0 | 1 |
- Writing follows proper format
  
  | 0 | 1 |
- Proper scientific tone is employed
  
  | 0 | 1 |

**TOTAL (Maximum = 50 points)**: ___
Desire2Learn On-Line Quiz for each chapter for a total of 35pts out of 210pts total
III. Outcomes

• Point Distribution (Fall 2009)
  – Ligand Synthesis Lab Reports: 2 @ 25 pts = 50 pts
  – Metal Complex Synthesis and Complexation
  – Lab Report = 50 pts
  – Textbook On-Line Quizzes: 7 @ 5 pts = 35 pts
  – Poster = 25 pts
  – Written Paper = 50 pts
  – TOTAL = 210 pts

• Grade Distribution

Aggregate 2006-2015 (n = 44)

Spring 2006 (n = 6)

Fall 2007 (n = 10)

Fall 2011 (n = 6)

Fall 2013 (n = 8)

Fall 2015 (n = 8)
### Course Evaluations by Students (n = 38)

#### Question 2: Initially, my interest in this subject was...

<table>
<thead>
<tr>
<th>Possible Responses</th>
<th>Number</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very High (1)</td>
<td>11</td>
<td>29%</td>
</tr>
<tr>
<td>High (2)</td>
<td>13</td>
<td>34%</td>
</tr>
<tr>
<td>Moderate (3)</td>
<td>14</td>
<td>37%</td>
</tr>
<tr>
<td>Low (4)</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Very Low (5)</td>
<td>0</td>
<td>0%</td>
</tr>
</tbody>
</table>

Total # Students Responding: 38

Aggregate Mean This Course: 2.08

#### Question 3: At this time, my interest in this subject is...

<table>
<thead>
<tr>
<th>Possible Responses</th>
<th>Number</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very High (1)</td>
<td>27</td>
<td>71%</td>
</tr>
<tr>
<td>High (2)</td>
<td>10</td>
<td>26%</td>
</tr>
<tr>
<td>Moderate (3)</td>
<td>1</td>
<td>3%</td>
</tr>
<tr>
<td>Low (4)</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Very Low (5)</td>
<td>0</td>
<td>0%</td>
</tr>
</tbody>
</table>

Total # Students Responding: 38

Aggregate Mean This Course: 1.32

#### Question 6: Course required meaningful work and study.

<table>
<thead>
<tr>
<th>Possible Responses</th>
<th>Number</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly Agree (1)</td>
<td>31</td>
<td>82%</td>
</tr>
<tr>
<td>Agree (2)</td>
<td>6</td>
<td>16%</td>
</tr>
<tr>
<td>Sometimes Agree (3)</td>
<td>1</td>
<td>3%</td>
</tr>
<tr>
<td>Disagree (4)</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Strongly Disagree (5)</td>
<td>0</td>
<td>0%</td>
</tr>
</tbody>
</table>

Total # Students Responding: 38

Aggregate Mean This Course: 1.21

#### Question 9: Course expanded my knowledge, comprehension, and/or skills

<table>
<thead>
<tr>
<th>Possible Responses</th>
<th>Number</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly Agree (1)</td>
<td>35</td>
<td>92%</td>
</tr>
<tr>
<td>Agree (2)</td>
<td>2</td>
<td>5%</td>
</tr>
<tr>
<td>Sometimes Agree (3)</td>
<td>1</td>
<td>3%</td>
</tr>
<tr>
<td>Disagree (4)</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Strongly Disagree (5)</td>
<td>0</td>
<td>0%</td>
</tr>
</tbody>
</table>

Total # Students Responding: 38

Aggregate Mean This Course: 1.11

#### Question 16: Instructor demonstrated enthusiasm for the course subject.

<table>
<thead>
<tr>
<th>Possible Responses</th>
<th>Number</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strongly Agree (1)</td>
<td>36</td>
<td>95%</td>
</tr>
<tr>
<td>Agree (2)</td>
<td>2</td>
<td>5%</td>
</tr>
<tr>
<td>Sometimes Agree (3)</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Disagree (4)</td>
<td>0</td>
<td>0%</td>
</tr>
<tr>
<td>Strongly Disagree (5)</td>
<td>0</td>
<td>0%</td>
</tr>
</tbody>
</table>

Total # Students Responding: 38

Aggregate Mean This Course: 1.05

### Aggregate for Questions 6-20

- Mean of the Means Items 6-20: 1.15
- Hubin Mean F2005-F2012: 1.37
- Chemistry/Physics Mean: 1.59
- University Mean: 1.63

---
Student Evaluation Comments

• “This has been the best lab I have ever been in... I really liked how the lab was one long experiment.”
• “I really found this course to be a great exposure to synthetic chemistry. I have learned many useful skills that I will continue to use.”
• “This lab has been great. It feels like I am accomplishing a lot more. I am learning how to prepare a journal article. It has been a very good experience.”
• “I have enjoyed the way the lab is set up. Lab feels like I am accomplishing something instead of just doing an experiment and throwing it away.”
• “The lab portion of the course was a very helpful mini research experience.”
• “I love Inorganic Chemistry Lab. Sometimes it is tough, but everything is interesting. We have fun in lab and learn a lot...”
• “Great lab. Required application of knowledge and skills while expanding on both.”
• “Excellent teaching, fantastic techniques, and clear, concise work meaningful & relevant to subject.”
• “This lab made me enjoy Inorganic. It actually made me like Chem. Labs again.”
• “This lab required a lot of effort. Dr. Hubin is a very nice instructor but the course work is really tough.”
Publishable Work?

**SPRING 2006**


**FALL 2007**


- “Chloro(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)copper(II) chloride”
Fall 2009 (In Preparation)
• “Dibromo(4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane)cobalt(III) hexafluorophosphate”

Fall 2011 (in Preparation)
• “1,8-Dimethylcyclam complexes of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II)”

Fall 2013 (in Preparation)
• “1,8-Dibenzylcyclam complexes of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II)”

Fall 2015 (In Preparation)
• “1,4,7,10,13-pentaazacyclopentadecane complexes of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II)”
Methyl or benzyl substitution results only in mononuclear complexes, even in the $\text{M}^0$ (Hubin et al., 2001, 2003) or $\text{M}^4$ (Yin et al., 2006) oxidation state, while oxidation of the unsaturated ligand complexes results in $\mu$-oxo iron(III) dimers (Hubin et al., 2003).

Structural characterization of an Fe$^{2+}$ mononuclear complex has not been achieved prior to the present study, which (i) demonstrates that even upon oxidation the methyl-substituted ligand does not allow dimerization to occur and (ii) provides a structure for the lower valent analogue to the unsaturated analog's iron(III) $\mu$-oxo dimer. Comparison of the Fe$^{2+}$ with the Fe$^{3+}$-complexes of the same ligand shows that the smaller Fe$^{2+}$ ion is more fully encapsulated by the cavity of the bicyclic ligand. The Fe$^{2+}$-complexes of the same ligand show that the smaller Fe$^{2+}$ ion is more fully encapsulated by the cavity of the bicyclic ligand. The Fe$^{2+}$-complexes of the same ligand show that the smaller Fe$^{2+}$ ion is more fully encapsulated by the cavity of the bicyclic ligand.
Lessons Learned

• This is a lot of work

• Things will go wrong. Will you be able to “fix” them?
  – Re-extracting five water layers over the weekend
  – Re-making two cobalt complexes because of an unexpected oxidation outcome

• Consider your project carefully before diving in
  – Semester-long project vs. several week project as part of “normal” lab
  – Scope of project and equipment needed may make it impractical

• Rewarding for students and instructor
  – Confidence
  – Understanding
  – Publications