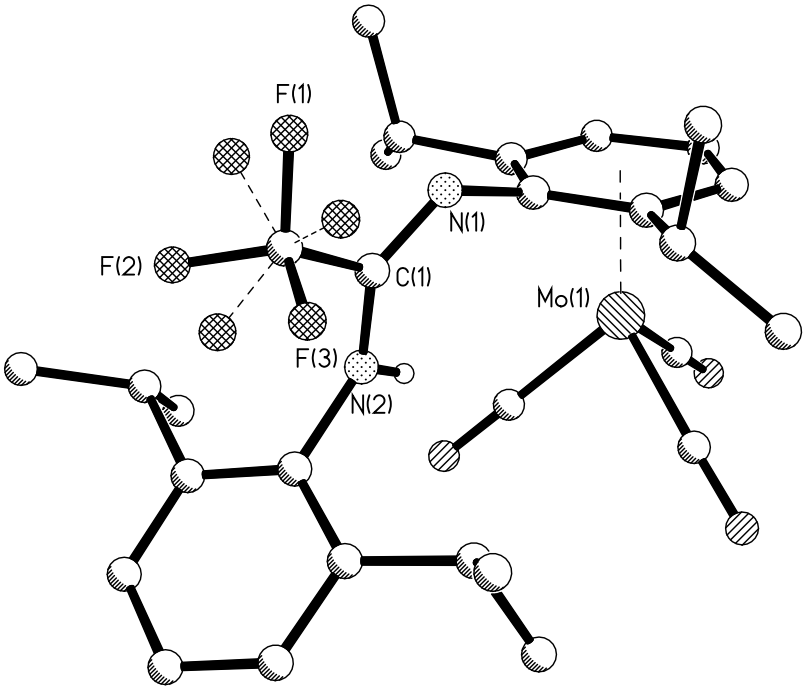
The University of Lethbridge

CHEMISTRY 3840 LABORATORY MANUAL

INORGANIC CHEMISTRY II



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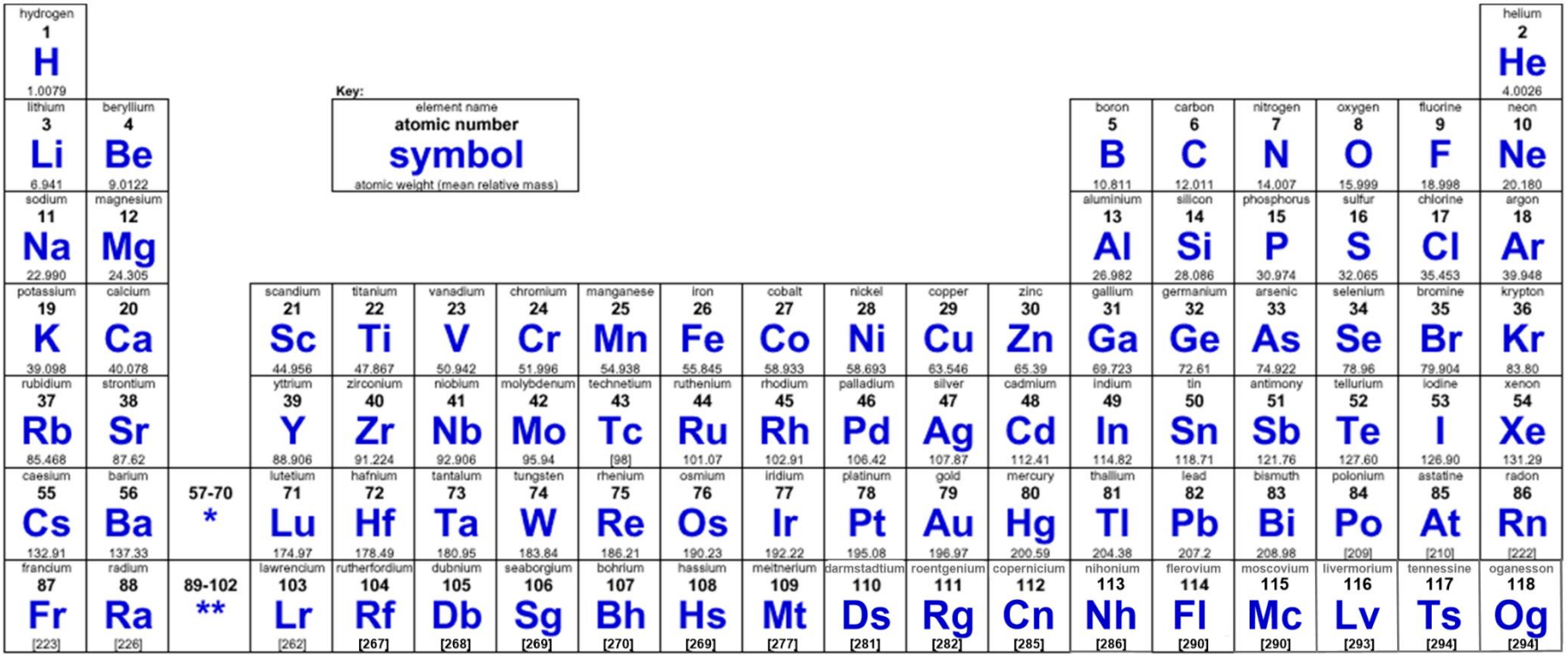
Department of Chemistry and Biochemistry


Key:
element name
atomic number
symbol
atomic weight (mean relative mass)
hydrogen 1 H 1.0079
helium 2 He 4.0026
lithium 3 Li 6.941
beryllium 4 Be 9.0122
boron 5 B 10.811
carbon 6 C 12.011
nitrogen 7 N 14.007
oxygen 8 O 15.999
fluorine 9 F 18.998
neon 10 Ne 20.180
sodium 11 Na 22.990
magnesium 12 Mg 24.305
aluminium 13 Al 26.982
silicon 14 Si 28.086
phosphorus 15 P 30.974
sulfur 16 S 32.065
chlorine 17 Cl 35.453
argon 18 Ar 39.948
potassium 19 K 39.098
calcium 20 Ca 40.078
scandium 21 Sc 44.956
titanium 22 Ti 47.867
vanadium 23 V 50.942
chromium 24 Cr 51.996
manganese 25 Mn 54.938
iron 26 Fe 55.845
cobalt 27 Co 58.933
nickel 28 Ni 58.693
copper 29 Cu 63.546
zinc 30 Zn 65.39
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germanium 32 Ge 72.61
arsenic 33 As 74.922
selenium 34 Se 78.96
bromine 35 Br 79.904
krypton 36 Kr 83.80
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yttrium 39 Y 88.906
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niobium 41 Nb 92.906
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rhodium 45 Rh 102.91
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silver 47 Ag 107.87
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indium 49 In 114.82
tin 50 Sn 118.71
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hafnium 72 Hf 178.49
tantalum 73 Ta 180.95
tungsten 74 W 183.84
rhenium 75 Re 186.21
osmium 76 Os 190.23
iridium 77 Ir 192.22
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Acknowledgments

Most of the experiments in this laboratory are derived from existing procedures at other Canadian universities. In particular, the following colleagues are acknowledged for providing details of experiments:

Prof. R.T. Oakley,	University of Guelph
Dr. D. Berry,	University of Victoria
Prof. N. Burford,	Dalhousie University
Prof. A. Hunter,	University of Alberta

Mr. Ben Ireland has done a great deal of work preparing high quality instrument user manuals.

To all Chem 3840 students: *This manual was prepared to aid you in learning the "how to" of inorganic chemistry, and to do so SAFELY and EFFICIENTLY. Please read this manual from cover to cover!*

Lethbridge, January 2025

Winter 2025 Lab Schedule

Monday	Wednesday†	Friday	Lab
Jan. 6	Jan. 8	Jan. 10	**No Lab period**
Jan. 13 **Last class before add/drop deadline (Jan. 13)**	Jan. 15	Jan. 17	**Lab Introduction & Check-in**
Jan. 20	Jan. 22	Jan. 24	**Lab 1a**
Jan. 27	Jan. 29 **Lab #1 Outline Due**	Jan. 31	**Lab 1b**
Feb. 3	Feb. 5 **Lab #1 Report Due** **Assignment #1 Due**	Feb. 7	**Lab 2a**
Feb. 10	Feb. 12 **Lab #2 Outline Due** **Midterm Exam #1**	Feb. 14	**Lab 2b**
Feb. 15 – Feb. 21 **Reading Week – No Labs or Classes**			
Feb. 24	Feb. 26 **Lab #2 Report Due**	Feb. 28	**Lab 3a**
Mar. 3	Mar. 5 **Lab #3 Outline Due** **Assignment #2 Due**	Mar. 7	**Lab 3b**
Mar. 10	Mar. 12 **Lab #3 Report Due** **Midterm Exam #2**	Mar. 14	**Lab 4a**

Mar. 17	Mar. 19 **Lab #4 Outline Due**	Mar 21	**Lab 4b**
Mar. 24	Mar. 26 **Lab #4 Report Due** **Assignment #3 Due**	Mar 28	**Multinuclear NMR Spectroscopy**
28Mar. 31	Apr. 2 **Last Day of Classes**	Apr. 4	**Lab cleanup & checkout**

† Lecture Assignments and Midterms have been added into the outline. They can be found in the **BLUE** font.

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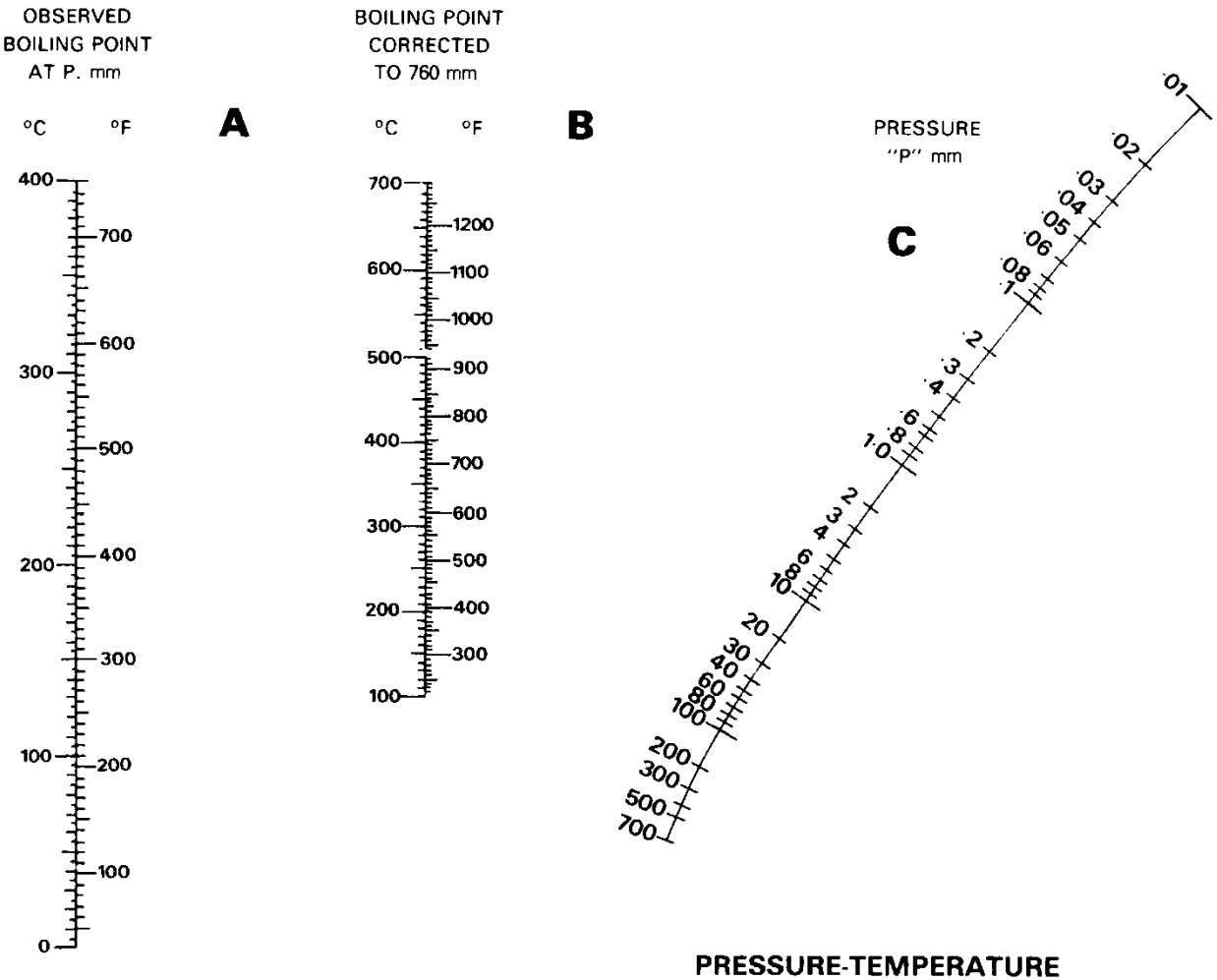
USEFUL DATA ON CONCENTRATED REAGENTS					
Reagent	%	Molar Mass (g/mol)	Molarity (M)	ρ (g/mL)	Aliquot*
Hydrofluoric acid HF	48.8	20.0	29.0	1.19	34.5
Hydrochloric acid HCl	37.2	36.5	12.1	1.19	82.5
Hydrobromic acid HBr	48.0	80.9	8.90	1.50	120
Hydroiodic acid HI	47	127.9	5.51	1.50	180
Perchloric acid $HClO_4$	70.5	100.5	11.7	1.67	86
Sulfuric acid H_2SO_4	98	98.1	18.0	1.84	55.5
Nitric acid HNO_3	70	63.0	15.9	1.42	63.5
Phosphoric acid H_3PO_4	85.5	98.0	14.7	1.70	69
Acetic acid CH_3COOH	99.8	60.0	17.4	1.05	57.5
Ammonia $NH_{3(aq)}$	29	17.0	14.8	0.9	67.5

* aliquot = mL of reagent which dilutes to 1 L of 1 M solution



PRESSURE-TEMPERATURE ALIGNMENT CHART

If literature b.p./pressure given; line up the 2 values in A & C. The theoretical b.p. @ 760 mm is read off in B. Line up this figure in B with another pressure in C and the approximate corresponding b.p. can be read off in A.

Laboratory operation and evaluation

Dress code:

In a chemistry laboratory, firm footwear and long pants that cover the entire leg must be worn at all times. Shorts, skirts, and sandals are not permitted, since they do not provide protection from spills. In addition, a lab coat and safety glasses (contact lenses are not permitted) must always be worn in the lab. You will not be allowed to proceed with the experiment if you are not following these safety guidelines (and the ones listed in section C). The dress code will be strictly enforced. You are responsible if you lose precious time and cannot complete experiments because of inappropriate attire.

Pre-labs

In the week before a new experiment is started, each student will have a short (10-15 minutes) meeting with the lab instructor. E*ach student will be asked about specific safety issues, the experimental procedure, anticipated time management and the theoretical background of the experiment. The* completed pre-lab questions found in the lab manual for each experiment must be handed in at this point. Working with a partner(s) on the pre-lab exercises is permitted, but they are to be completed individually and in one's own words. Any student who has not had a pre-lab meeting with the instructor will be barred from the lab for the duration of that experiment. Coming into the meeting, all students will be expected to have read the procedure for the upcoming experiment, as well as the MSDS's for the chemicals listed therein.

Assignment

(a) Complete a total of 4 experiments as follows:
- One experiment from each of Sections I, II, III and IV

Students will work **in assigned groups**, but must submit independent reports. ***Any evidence of passing-on portions of reports (including those from previous years), either between partners, or to others, will be treated as plagiarism and individuals will be prosecuted according to the rules of the University. There is a zero tolerance policy for any kind of plagiarism, duplication or cheating.*** Shared work in the pre-lab exercises is, however, permitted (though not required). Beyond this proviso, the utmost cooperation and collegiality in the laboratory portion of this course is strongly encouraged.

Evaluation

The lab is worth 25% of the total grade for Chem 3840. These 350 points are distributed as follows:

Pre-lab exercises and pre-lab discussion	(4x10 points)	40 points
Laboratory reports and results	(4x50 points)	200 points
Laboratory notebook	(4x10 points)	40 points
Lab Outlines	(4x10 points)	40 points
Instructor's evaluation		30 points
		350 points

Safety and Performance

The instructor's evaluation will be based on an assessment of the student's advance preparation and understanding of the experiment, industry, laboratory technique, safety consciousness, consideration of others, cleanliness and tidiness (particularly cleaining up of one's work area, and ensuring the experiment is clean and fully stocked before leaving the laboratory), and the quality of the results. A sample of each synthesized compound must be available for examination by the instructor.

Due Dates and Late Policy

Reports are due at **midnight** of the lab period one week after the completion of the experiment. *(For example: Report for lab 1 is due at **midnight** on Feb 5th)* If a report or assignment is handed in late, 20% will be deducted for the first 24-hour period that it is late. After 24 hours, the report or assignment will be awarded 0%. All reports and assignments must be submitted, even if it will receive a grade of 0%, in order to pass the lab.

Laboratory Notebook

A complete and accurate record is an essential part of chemical research. Although your Chemistry 3840 notebook is not a record of original research, an important objective of this laboratory is to provide training in keeping a research notebook. The record of any experiment should be sufficiently clear that another chemist reading it could understand **exactly** what was done, what results were obtained and, if necessary, repeat the work exactly as it was done. Your notebook will be judged primarily on how well it meets these criteria. Clarity and completeness are more important than neatness (although it must still be legible). It is not necessary to adhere to any particular format or organization as long as sufficient detail is provided. **It is very important to write down what you do as you do it.** Likewise, any observations should be recorded immediately – it is not acceptable to fill in your lab book after completing the entire experiment! It should also be noted that while the pre-lab exercises are both beneficial and mandatory, it is not acceptable to pre-record your *intended* experimental protocol. Changes in method are frequent, and readily forgotten when one has filled in a lab book prior to actually performing the experiment. In addition, this is very bad practice for those who will someday partake in original research where it is essential to write things down as they are done.

A bound, hard cover, lined notebook is required. Spiral or loose-leaf notebooks are unacceptable. The pages should be numbered consecutively and some blank pages left at the beginning for a table of contents. Begin each experiment on a new page and **write only in blue or black ink**. If you have read the entire procedure in advance you will have some idea how much information is to be recorded. Leave sufficient space to record the experiment on consecutive pages. Each experiment should be dated. When the experiment extends over more than one

laboratory period, a date should be entered at the beginning of the entries for each separate day's work or observations. (See Figure I-1.)

Include a short tabulation of the physical and chemical data of the compounds you are using, *i.e.* b.p. (remember to correct for altitude), m.p. (remember this is always a range), solubility, etc. (consult the CRC Handbook or the Merck Index for this information). Important equations (*e.g.* those developed for the pre-labs) should be included as well. All data are to be recorded directly into the laboratory notebook at the time they are obtained. Do not write data on a loose piece of paper for later copying. Nothing should ever be erased or removed from the notebook. If you make an incorrect entry, draw a line through the mistake and add a correction.

The laboratory notebook is also a good place to write down your thoughts and speculations as to the progress of your experiments. You may wish to include alternate methods and techniques in order to better achieve the end result. Finally, include any notes that may aid you in understanding and writing up the experiment (*e.g.* structures, references, equations, etc.). When writing scientifically (*e.g.* in your notebook) it is important to avoid first and second person (I, you, we, us, our). Also, your lab notebook should be written in **past tense** (unlike Figure I-1).

In summary, always include (as a minimum):

1) Date
2) A reference for the experiment, if one exists
3) A balanced equation with expected product
4) Weights, volumes and moles of reagents used
5) Estimated volumes used for solvents for all steps of a reaction (including recrystallizations)
6) Time between each manipulation or observation. Time of day works well.
7) Detailed observations, including, but not limited to, colour change, precipitate formation, gas evolution, exothermicity, etc.
8) Yield (Total and for each crop (when applicable))
9) A table of contents in the front of your book (reserve 3 – 5 pages for this) – keep it up to date
10) Key data collected (elemental analysis, IR peaks, NMR interpretation)
11) General conclusions reached

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September 20th 1990

Preparation of potassium trioxolatochromate(III)

$K_2Cr_2O_7 + C_2O_4H_2 + K_2C_2O_4 \cdot H_2O \longrightarrow K_4[Cr(C_2O_4)_3] + CO_2$

294.19 90.04 184.24

9.01 g of oxallic acid (100 mmol) is dissolved in 20 mL of d. H_2O, warming to 50°C

2.02 g of potassium dichromate (6.87 mmol) is added as a solid to the above solution in portions; vigorous effervescence occurs.

As the orange crystals of $K_2Cr_2O_7$ are added to the oxallic acid solution an instantaneous reaction occurs, leaving a very dark brown or black solution

After boiling this solution for about 2 min, 3.50 g (19.0 mmol) of potassium oxalate is added as a solid, rapidly. The solution soon turns a deep blue colour

After cooling the solution to R.T.

Figure I-1 Sample of notebook page

Laboratory Reports

You will be required to provide a short **typed** report on every experiment you perform. These reports should not be a regurgitation of the information provided in the laboratory manual, but rather a concise summary of the results obtained. Two or three pages will usually be sufficient.

A lab report should start with a **title** and a brief **introduction**, giving a short description of the background that is necessary to understand the goal of the experiment. A concise description of the **experimental procedure** (reference to the lab manual is not enough), including simple observations, such as times, colour changes, clarity, yield, melting points (remember clear and colourless are not the same concepts) is crucial. Always specify the number of moles of reactants, reaction conditions. A simple sketch of the apparatus is frequently useful. In the **results and discussion** section, discuss yields of products, melting points, and present and discuss (analyze) spectral results. References to background information, mechanisms, spectral or structural interpretation or any physical data, etc. should be included. The **references** should be listed under a separate heading at the end of the report, in the order in which they were cited. The format for such references varies from journal to journal; use the style of the American Chemical Society (*i.e. J. Am. Chem. Soc.*).

A key part of your write-up is your response to the points raised at the end of each experiment. The ideal case is to include them in your discussion, but do not forget to answer all of them. If you so choose, you can address each question separately after the general results and discussion section. These questions are designed to probe your understanding of the chemistry involved; you may well have to consult the literature cited in the manual in order to find an answer. *One or more questions on the final exam will probably be lifted from the material covered in the laboratory, so you are advised to study these points carefully.*

Each report will be due one week after the completion of the experiment. Hard copies must be handed directly to your instructor at the beginning of the lab period. It is important to remember that you must pass the laboratory component of Chem 3840 in order to receive credit for the course, regardless of your overall average. Likewise, all lab reports must be submitted (even if late) to pass the laboratory component (and thus, the entire course). Your lab note-books will be collected after the conclusion of the final experiment, and will be returned in the last lab period (check-out).

Attendance

Absences with a valid excuse (*e.g.* illness) will be accepted with documentation, and you will, at your instructor's discretion, be allowed to either make up the lab, or use your partner’s data to write your lab report. A valid excuse is a certified medical note or other extenuating circumstance acceptable to the instructor. If a student is absent without a valid excuse, they will still be allowed to make up the lab or use their partner’s data, but 20% will be deducted from the grade for that report. Similarly, if a student misses a pre-lab meeting, 20% will be deducted from the pre-lab mark.

General Tips for Lab Reports

Experimental:

- Use scientific units of time (minutes, hours, days, etc.). "Overnight" is not an acceptable period of time.
- Use appropriate American Chemical Society (ACS) style abbreviations: mg, g, mL, L, etc.
- Use significant figures.
- Report yields in both g and %.
- Melting points should always be reported as a range (mp xx – yy ºC) or (mp xx – yy ºC, dec).
- NMR: ^{1}H (C_6D_6, –35 ºC): δ 2.08 (s, 9H, $SiMe_3$), 1.16 (d, $^{4}J_{PH}$ = 2.5 Hz, 9H, $SiMe_3$), 0.32 (d, J = 7.2 Hz, 9H, CHMe_2).

Results:

- Avoid vague comments – give specific details, such as temperature, colour change, time, etc. whenever possible.
- If equations are inserted into the text, place them at the end of the first paragraph which mentions them.
- Number compounds, figures, schemes, etc. in the order they first appear in the text.

Discussion:

- Make a list of all remarkable or noteworthy results. Then go back and discuss each, trying to put it into perspective with known chemistry.
- Reserve broad, sweeping statements for the conclusions (or omit them completely).

Conclusions:

- This should be an analysis of the content of the experiment, focusing on implications and putting the work into perspective.

Tenses:

- Pay close attention to tenses. Use past tense for results which pertain to experiments and descriptions of results obtained. When describing spectral data, use present tense ("the spectrum reveals").

Pronouns:

- Do not use first and second person (I, you, we, us, our).

Miscellaneous Writing Tips:

- Formulas are not nouns. ("A resonance for the Me group" rather than "A resonance for Me").
- Use "exhibits" or "displays" rather than "shows".
- Within the text of the report, use numbers with units of times or measure (4 h, 8 g). For all else, use word for numbers less than 10 and numbers for 10 and above.
- Use a semicolon between independent clauses joined by conjunctive adverbs such as "that is", "however", "thus" and "therefore" (the intermediate is not easily observed; therefore, the final product is observed initially).
- Always begin a sentence with a word. Do not begin a sentence with a number or chemical formula.
- Always use complete sentences, even in the experimental section.

Common Abbreviations (as per the ACS format, unless noted, no periods are used):

av – average
mL – milliliters
ca. – approximately
cf. – compare
day – do not abbreviate
dec – decomposition
equiv – equivalent(s)
eq – equation
g – grams
h – hours
min – minutes
mmol – millimoles
mp – melting point
temp – temperature
s – seconds
THF – tetrahydrofuran
TMS – do not use; $SiMe_4$ or $–SiMe_3$
pyr – pyridine
vs. – versus

Suggestions

Your instructor appreciates feed-back and constructive criticism regarding the operation of the laboratory and the design and effectiveness of the experiments. Suggestions are welcome.

"The boss sort of keeps an open mind."

General Laboratory Procedures

Safety Equipment

The safe operation of any chemical laboratory is dependent upon the extent to which adequate safety measures are observed and practiced. As such, always be safety minded. This means that every student must do all they can to prevent accidents in their own work and they must be prepared for accidents by knowing in advance what emergency aids are available and how to use these aids.

The laboratory is equipped with several types of safety and first aid equipment. It is essential that you become familiar with the location and operation of these tools.

Shower There is an emergency deluge shower located in each laboratory. These are for use when corrosive liquids have spilled over large areas of clothes and skin, or when clothing is on fire.

Eye Wash Station Each laboratory is equipped with an eye wash station. These stations dispense tempered (luke-warm) water and provide thorough irrigation of the eyes and face in the event a person is splashed with an irritating chemical. The contaminated body part should be rinsed for a minimum of 15 minutes.

Fire Extinguisher Carbon dioxide fire extinguishers are in each laboratory. Know the location of these and how to operate them. They are very effective for fires involving organic liquids and electrical fires. Sand pails should be utilized for metal (*e.g.* sodium or potassium) fires. If a fire extinguisher is used even momentarily it must be given to the laboratory coordinator for recharging. Small fires in test tubes, beakers, etc. can usually be smothered by covering with a watch glass.

Use of Time

The efficient use of time is an asset not only to a student, but especially to a researcher. Plan your experiments so that you will profitably use time which would otherwise be spent watching, *e.g.* a distillation, a sublimation or a non-hazardous reaction that need not be attended. This course allows some latitude in the planning of experiments and you should be constantly looking for opportunities to use the available time effectively. Remember, if you manage to finish an experiment early you are free to leave.

Cleanliness

.....is next to Godliness. Since most of the experiments will involve the use of equipment which other students will use during the course, it is absolutely essential that all equipment be left in good condition at the end of each period. Any equipment which is broken should be reported to the instructor immediately so that a replacement may be found in time for the next class. Wash bottles of detergent, alcohol and acetone are provided at each sink, as well as scrubbers, sponges and rubber gloves. If you have particular difficulty cleaning a dirty piece of glassware, notify the lab supervisor. ***Since there are a variety of communal areas which make it difficult for the instructor to establish who is responsible for a given mess, the entire class will lose 10% of the value of their lab report if the laboratory is not left in satisfactory condition!***

Balances and weighing

A great many experiments in chemistry involve weighing at some stage. Much time can be wasted during weighing procedures, and one of the biggest time wasters is the habit of weighing to a degree of accuracy in excess of the requirements of the experiment.

For synthetic work, including parts of most of the experiments in this course, weighing to 0.1 g or 0.01 g is quite sufficient. Only for analytical work, such as in the characterization of some of the compounds prepared in this course, is greater accuracy required, on the order of 0.001 g or 0.0001 g.

Even if weighing is only carried out to the required degree of accuracy, time can be wasted in the actual process, and unless some method is used whereby weighing is carried out rapidly, many experiments cannot be done in the time normally available.

At no time are chemicals to be weighed directly onto the pans of the ANALYTICAL BALANCES. These include **all the balances located in the room** (SA-8406). *All of these balances will be irreparably damaged by exposure to the kinds of chemicals you will be handling in this laboratory.* For synthetic work, you will use only the top-loading balances located in the lab (SA-8406). Should you require a more accurate measurement than allowed by the top-loaders, follow the method of weighing by difference described in the following paragraphs. *Although they are more robust, even the top-loading balances are susceptible to corrosion. Make it a practice to clean up any spilled chemicals <u>on</u> or <u>around</u> the balances <u>immediately!</u> Balances used in these laboratories (all types) cost between $2000 and $4000, and must be treated with utmost respect.*

Accurate weighing technique: weighing by difference

To weigh an accurate amount of solid (*i.e.* to the nearest 0.001 g or better), place a **weighing bottle** (and cap) on a balance, tare it, remove the bottle from the balance, and place an estimated amount of material into the bottle. If the solid contains large crystals or lumps it should be lightly ground in a mortar before weighing.

The weighing bottle (with contents) is now capped, wiped clean and weighed using the correct procedure on the analytical balance (if the weight is significantly different from desired,

remove the bottle from the balance and repeat the above procedure until close (but there is no need to be exact)). *Immediately* record the weight in your notebook.

Return to the lab, and tip the solid into your flask, vessel or whatever is suitable, no attempt being made to remove the traces of solid which will cling to the weighing bottle. *Return to the balance room* and re-weigh the nearly empty bottle accurately. The loss in weight is the accurate weight of solid taken. This avoids the rather awkward process of washing all of the solid from the bottle and is quicker and more accurate.

This method is often used, as it is rarely necessary to weigh out an exact amount. It is bad practice to weigh out, for example, 1.25 g of a solid to make an exact 0.10 M solution. It is better to use the above method, finish up with a weight of 1.32 g and express the solution as:

$$(1.32 \text{ g}/12.6 \text{ L})\ M = 0.105\ M$$

This avoids the very messy practice of adding and removing odd crystals to try to get an exact weight.

By using the above method it is *never necessary* to have any loose chemicals near a balance, as only a closed bottle is used on the balance.

Setting up apparatus

When ground-glass joints are used, it is not necessary to lubricate them except when high temperatures or vacuum are involved or an inert atmosphere is required. If a joint becomes seized, try the following methods of loosening it: (a) rock the cone in the socket, (b) tap the joint gently with a block of wood, (c) warm the joint in a small flame, then tap gently, (d) soak the joint in penetrating oil, then try tapping. A common cause of seizure is a caustic alkali. Try to keep alkalis off the ground-glass, and if they do get on it, wash thoroughly as soon as possible. Seizures can usually be avoided by dismantling the apparatus immediately after use. Where required, the procedures call for lubricating the joints with silicone grease ("high vacuum grease"). *CAUTION: silicone grease may cause corneal damage. In order to avoid accidental transfer of grease to your eyes, be sure to thoroughly wash with soap and water to remove residual silicone grease from your skin.*

Care should always be taken, when glass apparatus is set up, to avoid **strain**. It is best to start with one piece, and build from there. Take a distillation apparatus as an example:

(a) Lightly clamp the flask at a height convenient for heating,

(b) Attach the still-head, screw-cap adapter and thermometer (no more clamps are needed for these),

(c) Attach the rubber tubing to the condenser, then position a clamp and stand so that the condenser will rest on the lower, fixed, side of the clamp. Attach the condenser to the still-head, and clamp lightly,

(d) Attach and support the receiver adapter and the receiver.

A similar procedure should be followed for the other assemblies.

Notes on individual assemblies

Reflux Clamp the flask and the condenser. If an air condenser is used, clamp it at the top.

Distillation Use a vented receiver adapter in the following circumstances:

(a) if a noxious gas or vapour is given off, and must be led off by rubber tubing to an absorption apparatus or a sink,

(b) if an inflammable vapour is given off (for example in ether distillation), and must be led off by rubber tubing to below bench level.

Where an air condenser is specified, it is frequently adequate to attach the receiver adapter directly to the still-head.

Fractional distillation Clamp the fractionating column only at the top. If a column is not available, a vertical air condenser or an ordinary condenser with an empty jacket can be used instead, though it will be less efficient.

Gas evolution A 250 mL flask, with a B24 joint, and a 100 mL dropping funnel are satisfactory for most purposes. If these are not available, it is convenient to prepare a number of standard rubber stoppers, each carrying a dropping funnel and a delivery tube, which will fit 250 mL wide-necked flasks.

Gas drying If ground-glass jointed apparatus is not available, a 250 mL conical flask with a rubber stopper is perfectly adequate.

Gas absorption If it is necessary to dissolve a gas in a liquid, the best method is to use a Büchner flask fitted with a wide glass tube in a rubber stopper. This overcomes the 'suck-back' problem by equalizing the internal pressure with that of the atmosphere.

Use of corks Even when apparatus with ground-glass joints is normally used, there are still occasions when corks are required. For efficiency corks must be rolled before use, and bored with care. A cork of the correct size should only just go into the neck of the flask. Soften it by rolling between the fingers, or between sheets of paper on the bench. Never try to roll a cork which already has a hole in it; it will almost certainly split.

To bore a cork, or a rubber stopper, choose a sharp borer slightly smaller than the tube or thermometer which is to go into the hole. Hold the cork in the hand, and push and rotate the borer until the hole is approximately half way through it. Now reverse the cork, and continue boring from the other end until the holes meet in the middle. Now use a rat-tailed file to increase the size of the hole until the tube or thermometer fits it with gentle pushing, but with no strain. Place the cork on the file, and rotate it with the hand or on the

bench; do not use a sawing action as this will cause an eccentric hole which is likely to leak.

When inserting tubes or thermometers into holes in corks, it is an advantage to moisten them with a little ethanol as a temporary lubricant. If a cork becomes stuck to a tube or a thermometer during use, it is best to cut it off, rather than risk breakage. *The majority of cuts which occur in the laboratory happen when pushing tubes through, or removing them from, corks.*

Reflux and distillation

Unlike ionic reactions, which are frequently extremely rapid, reactions between covalent substances tend to be slow. Particularly in main-group and organometallic reactions, it may be necessary to keep a reaction mixture hot for a matter of hours. This, coupled with the fact that volatile and inflammable solvents must be employed, makes it necessary for special equipment to be used.

Reflux The use of a reflux condenser is often necessary. It is used whenever a reaction mixture has to be kept boiling for an appreciable time and the solvent is volatile. A water condenser may be used for solvents boiling up to approximately 130 °C, and for higher boiling-point solvents an air condenser is adequate. The flask must never be filled more than half way; the size of flask should therefore be chosen by consideration of the total volume of the reaction mixture. A boiling stone or similar substance should be used to promote even boiling for all reflux procedures which do not employ magnetic stirring. The object of the apparatus is to keep the solution hot without loss of solvent. It is pointless to boil violently; the heating should be controlled so that the solution is merely simmering. The flask may be heated by an **electric heating mantle** controlled by a Variac **(NEVER plug a heating mantle directly into an electrical outlet!)**, or by using an oil bath on an electric hot plate.

Distillation The purpose of distillation is to purify a liquid, or to remove a solvent from a solution. The flask must never be more than half full, a boiling stone or magnetic stirring must always be used, and the choice of condenser is the same as for reflux work. The heating of the flask may be accomplished using any of the usual means. Purification of a liquid by distillation is best performed at a rate not exceeding 2 drops of distillate per second. Alternatively, removing a large quantity of solvent may be done much more rapidly.

Fractional distillation The purpose of fractional distillation is to separate two liquids of different boiling-point. As with other forms of distillation, the flask must never be more than half full, and a boiling stone or magnetic stirring must always be used. In order to get good separation of the liquids, it is essential that the distillation be carried out very slowly. The slower the distillation, the better the separation. A rate of 1 drop of distillate per second should be the aim.

Since the efficiency of the process depends on the fractionating column reaching thermal equilibrium (there should be a gradual increase in temperature from the top to the bottom of the column), best results are obtained if drafts are excluded. In addition, the source of heat should be steady.

Use of the separatory funnel

The separatory funnel is used for several important processes. Unless care is taken, its use can be one of the major causes of mechanical loss. The choice of size is particularly important and, as with flasks in distillation, the smallest which will properly do the job, is best.

Separating two immiscible liquids The liquid mixture is poured into the funnel, and the funnel is gently agitated to assist in the separation into layers. The funnel should always be stoppered, but if a particularly volatile substance, such as ether, is present, the funnel should be vented occasionally through the stopcock *(hold it slightly inverted while doing this)* to avoid the possible buildup of pressure.

When separation into layers has occurred, the stopper is removed and the lower layer drained into a small flask. Swirling the funnel and once again allowing separation to occur frequently provides a further small sample of the lower layer.

The top layer is poured from the top of the funnel into a second flask. It is a wise precaution to always keep both liquids, even if one of them is to be discarded. It is surprising how often the wrong layer is thrown away!

Washing a crude liquid One of the most common procedures consists of shaking a crude liquid product with an aqueous solution to remove some of the impurities. The reagents should always be used in small quantities, and the process repeated if necessary. Mechanical loss is always greater when large volumes of washing solutions are used.

Gases are often formed in considerable quantities during the cleaning process, thus, it is essential to release the pressure frequently. This is best done by inverting the well-stoppered funnel and opening the tap.

If the required substance is the top layer, then allowing the bottom layer to run off is quite simple. The entire bottom layer of waste should not be run off each time. It is better to leave a small quantity of the aqueous solution, and add further fresh reagent. Careful separation is completed only when running off the last of the various washing solutions. This avoids the risk of inadvertently losing a few drops of the treated product.

When the required substance happens to be the bottom layer, avoiding mechanical loss becomes more difficult. If the product is run off between each wash and then returned to the funnel for the next, the loss can become very great. The best compromise is obtained by using rather large volumes of washing solutions, and decanting the spent solution from

the top of the funnel. In this way the product never leaves the funnel until the final wash is over. It is then run out into its receiver, leaving the final washing solution in the funnel.

Liquid extractions The separatory funnel is often used to extract a solute from one solvent by means of a second solvent immiscible with the first. The removal of a solute from water by means of ether is one of the most common examples of this application.

The size of the funnel is chosen to accommodate the whole of the aqueous solution. This saves time which would otherwise be spent in repetition. A series of extractions with a small quantity of ether is much more effective than one with a large amount of ether. In practice the volume used is that which gives the smallest manageable top layer, bearing in mind that the ether solution must be decanted from the top of the funnel. If the layer is too small, decantation becomes difficult. The solution is usually extracted about three times with fresh quantities of ether, and all of the ether extracts are decanted into one flask. After the final extraction the aqueous layer is run off and the last ether layer decanted completely into the flask. The ether solution is then dried, and the solute obtained by distillation of the ether.

Filtration methods

There are a variety of techniques used for the separation of a liquid or solution from a solid.

Simple filtration The use of a filter funnel and a piece of filter paper folded into four is usually reserved for ionic substances (*e.g.* NaCl) precipitated from aqueous solution. Precipitates obtained in qualitative analysis and inorganic problem work are often rather fine, and cannot be efficiently filtered using a pump. Covalent solids, however, are usually separated from a volatile solvent, and the comparative slowness of simple filtration brings in complications caused by evaporation.

It is essential in simple filtration to ensure that the paper is carefully folded. The paper must be fitted carefully into the funnel and wetted thoroughly with water, or the appropriate solvent, prior to the start of the filtration.

The contents of the filter paper should remain at least 1.5 cm from the top of the paper. These simple precautions can make a dramatic difference in the time required for a filtration to reach completion, and should never be neglected.

Filtering of organic liquids This is usually done to remove solid impurities which are not in a very fine state of subdivision. A normally folded filter paper will work for this purpose, but the 'fluted' filter paper gives a faster rate of filtration. A fluted filter paper is essentially one that is folded to give a corrugated effect which allows the whole of the paper to be active rather than only half, as is the case with simple filtration.

There are a variety of ways of folding such a paper; one of the easiest is as follows:

The paper is carefully folded in half, opened out, and then folded in the same direction at right angles to the original fold. The paper is then folded twice more, the folds

being all in the same direction and mutually at 45°. Each section is now individually folded in the opposite direction. The result is a fluted paper with sixteen faces. The paper is then placed in a suitable sized funnel and pushed down so that all of the ridges touch the side of the funnel. Since all of the paper is being used, only one layer thick, filtration is appreciably faster.

When filtering a small amount of liquid to free it from a drying agent it is best to use a very small piece of cotton wool, pushed lightly into the top of a funnel stem, or even into the narrow part of a disposable Pasteur pipette. The mechanical loss entailed by absorption on a filter paper is thus obviated, and much higher yields of product are obtained.

The Büchner funnel and filter pump This system of filtration is the most widely used when dealing with recrystallized substances. The Büchner funnel may be attached to the flask by means of a cork, but a much more useful device consists of a flat piece of rubber with a hole in the centre capable of receiving the funnel stem and making a good seal.

The disc of rubber allows, within reason, any size funnel to be fitted to any size flask. If this method is adopted, then the size of the funnel chosen is the smallest that will hold the solid, and the flask is similarly chosen to be the smallest that will hold the liquid, if both solid and liquid are required. If the solid is to be discarded, than a large funnel can be used to increase the rate of filtration. Alternatively, if the liquid is to be discarded, then the flask may be large enough to hold all of the liquid as well as the washings. The choice of size is very important, as mechanical loss during filtration can be significant.

The filter-paper disc is placed in the funnel, and wetted with the solvent present in the solution to be filtered. It is essential that the funnel and flask be perfectly dry. If the solvent concerned is ethanol, then the paper may be wetted with water. If available, connect the suction flask to a Woulff bottle (ask the instructor how to use a Woulff bottle). The pump is then turned on and the paper pressed into place. During filtration the pump must never be turned off, as this may cause water from the pump to be drawn back into the filtrate. When all of the material has been filtered, open the stopcock of the Woulff bottle to ambient pressure (or disconnect the pump from the flask) while the pump is still running. If some of the solid has not been transferred to the funnel, a portion of filtrate can be retrieved and used for swilling the residue into the funnel. The solid is washed free of filtrate by pouring a small portion of chilled fresh solvent into the funnel while the pump is disconnected. Finally, the solid is drained as dry as possible using suction from the pump while applying pressure with a clean glass stopper.

Gravimetric filtration In quantitative work it is essential that all of the solid be transferred and retained in the filter funnel. A **filtering crucible** with a porous sintered-glass bottom is the most convenient apparatus to use. Porosities from 0 (coarse) to 5 (very fine) are available,

although for most purposes a porosity of 3 is best; a few fine precipitates will require a porosity of 4.

The sintered-glass crucible is dried in an oven, cooled, and accurately weighed before use. To collect the solid the pre-weighed crucible is set in the mouth of the Büchner flask by means of a firm rubber cone. The pump is turned on, and as much supernatant as possible is decanted off through the crucible. The liquid should be directed into the crucible via a glass rod.

The solid is then transferred, using a gentle jet of the appropriate solvent to swill out all particles. If solid clings to the apparatus, it can be collected using a glass rod protected with a **rubber 'policeman'**. The pump suction at this stage should be as gentle as possible; otherwise the porous glass may clog. Finally, the solid and crucible are washed repeatedly to remove all soluble materials, and dried to constant weight.

Drying methods

The drying of liquids In the majority of cases with organic liquids extreme drying is not necessary and drying agents such as *anhydrous calcium chloride* or *anhydrous sodium sulfate* are adequate. Of the two, calcium chloride is the more efficient, but also the more messy.

As calcium chloride will remove water and ethanol, it is employed when both need removing. If, however, the drying only needs to remove water; anhydrous sodium sulfate is generally employed. Sodium sulfate will only work at temperatures below 30 °C and should generally be used at room temperature. It is capable of removing its own weight of water, but the use of too much drying agent should be avoided at all times as this will cause the drying agent to become 'wetted' with the product and a large mechanical loss will be entailed.

In order to dry an organic liquid, whether a product or a solution containing the product, the liquid should be placed in a suitable sized conical flask, fitted with a good stopper or cork, and the drying agent added. The corked flask should be shaken at intervals, and left for at least five minutes, preferably longer.

If sufficient drying agent has been used some should remain unchanged in appearance: *i.e.* a fine opaque powder of sodium sulfate or firm granules of calcium chloride.

The drying of solids Various methods exist for drying solid materials. When deciding which method to use it is important to know something about the physical properties of the material. For example, if dehydration of a hydrate or melting of an organic solid occurs, recrystallization will have to be repeated resulting in further loss of time and material.

Although the method of air drying takes longer than the others, it is one of the most safe for non-deliquescent solids. The damp solid, drained as dry as possible on the filter, is transferred to a watch-glass and spread out evenly. The solid can then be left to dry overnight in a location free of dust and drafts. As an added precaution against dust, a

second, larger watch-glass should be placed over the product in such a fashion that free evaporation remains possible.

Though the desiccator is ideal for drying many solids, care must be taken when drying hydrates. It is quite possible to lose some water of crystallization if the dehydrating agent is too effective. Thus, samples to be dried should be spread out on a watch-glass and labeled with their name and date.

The desiccator must be regularly recharged with fresh desiccant, and the ground-glass seal kept greased with a minimum quantity of silicone grease, so it appears transparent. Several desiccants are listed in Table I-1 with comments on their relative usefulness.

Table I-1 Common drying agents

Desiccant	**Remarks**
Phosphorus (V) oxide	Expensive, fast and efficient.
Concentrated sulfuric acid	Cheap, hazardous, fast and efficient. If $BaSO_4$ is dissolved in the acid, it precipitates when the drying capacity is exhausted.
$CaCl_2$	Cheap, moderate effectiveness. Use if ethanol was the solvent.
Soda-lime	Use if acidic vapours need to be absorbed.
Silica gel	Readily regenerated, but limited effectiveness. Changes colour when exhausted if stained with $CoCl_2$.
Drierite	(Anhydrous sodium sulfate) Commonly stained with $CoCl_2$; Blue when fresh, red when exhausted. Very inert; use for most applications.
$MgSO_4$	Ensure it is anhydrous! Used to dry organic liquids, especially ethers.

It is important to remember that after opening, a desiccator takes at least two hours to re-establish a dry atmosphere.

A vacuum desiccator is used to speed the drying of a sample. The sample must be covered with a second watch-glass and the desiccator evacuated and filled slowly to avoid blowing the sample about. In order to guard against implosion, a vacuum desiccator must be covered with strong adhesive tape, or be enclosed in a special cage when being evacuated and de-evacuated.

Recrystallization and purification of solids

Inorganic solids, when first prepared, are rarely pure. The original solid must be recrystallized from an appropriate solvent. If the solvent is a flammable liquid, as it often is, it is better to carry out a recrystallization under reflux, until more experience has been gained. With

ethanol, a very common solvent, it is quicker and neater to use a conical flask, but this does entail a risk of fire.

Reflux method The solid is placed in a suitable sized flask, preferably a conical flask as it can be easily put aside to cook, and a condenser attached. A small volume of solvent is poured down the condenser and the mixture is raised to its boiling point. If all of the solid has not dissolved, a bit more solvent should be added after removing the mixture from the hot plate. Repeat this process until the solid just dissolves at the boiling-point. If there are no insoluble solid impurities, the solution will be clear. The mixture should then be removed from the hot plate and slowly allowed to cool to room temperature. Once the solution reaches room temperature, it may be necessary to gently swirl the flask in order to initialize crystallization. The solid usually crystallizes upon cooling, but, if crystallization is slow to start, scratching the inside of the flask with a glass rod frequently helps crystals to form. The flask should be cooled to at least room temperature, or preferably lower, by placing it in either iced water or a refrigerator.

The pure product is filtered off at the pump. It is essential for both the filter flask and funnel to be clean and dry, except for the solvent concerned. The mixture to be filtered is poured on to the filter paper and the solid remaining in the flask is washed out with the filtrate. This is important. The filtrate is, of course, a saturated solution of the required solid, and so the filtrate cannot reduce the yield by dissolving some of the crystals. The filtrate should be used for washing out the flask several times, until all of the solid has been transferred to the filter. On no account should fresh solvent be used for transferring the solid to the filter. The recrystallized solid is then dried in a suitable manner, bottled and labeled.

Open flask method This is essentially the same as the previous method, but is carried out directly on the hot plate with an open conical flask. The solvent is only just allowed to come to a boil and then the flask is removed from the heat. At this point, it should be possible to see the vapour condensing inside the flask, and there should not be a risk of fire if care is taken. The obvious advantage of this method is speed. This approach is not suitable for low-boiling solvents such as ether or pentane.

Recrystallization requiring hot filtration If, during a recrystallization, there is an insoluble solid impurity, it becomes necessary to filter the hot solution. Care must be taken that no crystallization occurs during the process as this would block up the filter funnel and cause great difficulty. To avoid this, the following procedure is used:

The crude solid is dissolved in the solvent in the normal way, and when all of the solute has just dissolved at the boiling-point, a further small quantity of solvent is added. This ensures that the solution is not quite saturated. This solution is kept hot while a separate sample of solvent is heated to boiling and then poured through the prepared

Büchner funnel. This procedure heats up the funnel and flask. The filter paper, which must be in position, is held in place by a glass rod. The selected funnel should be reasonably large as this will retain the heat better and the filtration will be faster.

The hot solution is rapidly filtered with the pump on full. As soon as all of the solution is through the funnel, the pump is disconnected and the funnel removed.

At this stage the solute will almost always have begun to crystallize in the receiving flask. To save mechanical loss, the solution should be kept in the flask and cooled in the normal way. The final filtration to collect the crystals therefore requires another flask.

The use of activated charcoal

Sometimes there are coloured impurities present in the crude material to be recrystallized. These are removed from the solution while hot by adsorption onto activated charcoal.

The recrystallization is carried out normally until the crude material is dissolved. At this point, a little extra solvent is added, and the mixture cooled slightly. A small amount of activated charcoal is added to the cooled solution. It is important to cool the solution before adding the charcoal, as this material tends to promote boiling. If the solution is not sufficiently cooled prior to the addition of the charcoal, the entire mixture will usually boil over violently.

The mixture with the charcoal is allowed to boil gently for a few minutes, and is then filtered hot, using the method described above. It is important to ensure that the paper is well fitted or charcoal may get around the edges and contaminate the product. As in hot filtration, the funnel should be large so that the filtration is as rapid as possible. The flask should be of a suitable size for the volume of purified solution obtained.

Column chromatography

Chromatography using columns of adsorbent material is useful for separations on the preparative scale because gram quantities of material are readily purified. Many adsorbents are available, but these experiments all use aluminum oxide (alumina) or silica gel.

Packing the column Clamp the glass tube upright and check that the tap is closed. Wash the walls of the column by pouring ~20 mL of solvent down the inside walls. Half fill the column with the chosen eluting solvent. Push a pad of non-absorbent cotton-wool or glass-wool to the bottom of the tube; be careful not to ram it down too hard and make sure that there are no air bubbles trapped in the glass or cotton-wool.

Method 1: Dry Packing:

Now slowly pour in roughly 25 g of chromatographic aluminum oxide or fine silica gel. Use a filter funnel to guide in the powder and, if a blockage occurs (*e.g.* just above the solvent level), rock the tube gently. You can also tap the tube gently with your fingers to settle the powder uniformly and release any trapped air bubbles.

Push a second pad of cotton-wool down the tube to protect the upper surface of the column from disturbance. Drain off the excess solvent until the level falls to the upper cotton-wool pad; never let the solvent level fall lower, otherwise the uniformity of the column will be ruined by trapped air bubbles. The column is now ready for use.

Method 2: Slurry Method:

Add a sufficient quantity of solvent to the weighed out chromatographic aluminum oxide or fine silica gel so that when you swirl the flask, the contents move freely (make sure that no air bubbles are trapped in the slurry). Pour the slurry into the top of the column while you drain solvent out the bottom (save this solvent to use when running the column). Be sure to close the stopcock when the solvent is approximately 0.5 cm above the absorbant. Finally, push a second pad of cotton or glass-wool down the tube onto the top of the column. The column is now ready for use.

Loading the column Dissolve your sample in the minimum volume of solvent required to make a homogeneous solution. Using a pipette, place the sample directly on top of the column. Allow the column to drain slowly and wash in the sample by adding small portions of fresh solvent. The sample should now be adsorbed as a narrow band at the top of the column.

Developing the column Develop the column by running solvent through it. Fill up the tube with solvent being careful to pour the solvent down the wall of the tube. This is important to ensure the top of the column is not disturbed. Allow the solvent to pass through the column at a rate of approximately 5 mL per minute. Keep the tube topped up, as the liquid pressure will encourage a good flow rate and there will be less danger of letting the column run dry (which will make it virtually impossible to achieve proper separation). If the flow rate is too slow, pressure can be applied by attaching a small hand bellows to the top of the tube (flash chromatography).

Collect equivolume fractions of solvent draining from the column. Coloured materials are readily seen as they are eluted from the column, but colourless substances must be found by evaporating the fractions to dryness, or by running t.l.c. on each fraction.

Thin-layer chromatography

In thin-layer chromatography (t.l.c.) a suitable adsorbent is spread on a glass plate. After activation of the adsorbent by heat, the plate is spotted with a dilute solution of the material under study and then developed with a suitable solvent. When the solvent has risen a convenient distance up the thin film, the plate is dried and treated with a detecting agent. Commercial plates with plastic or foil backing are also available, and are extremely convenient.

Silica gel is the preferred adsorbent for t.l.c., although cellulose and alumina thin films can also be readily prepared. In all cases the adsorbent must be specially manufactured for t.l.c. work, and it is simpler to use materials free of special additives or binders. T.l.c. is generally faster than

other techniques and sharper separations are possible, but to master the method you will have to work with care and ensure your apparatus is properly cleaned.

Preparing the plates

(a) Silica Gel A slurry of roughly 30% w/v of silica gel in chloroform is kept in a well-sealed wide-mouthed bottle, and microscope slides are coated by dipping them into the slurry. The slurry bottle should be placed on a large sheet of blotting paper in a fume cupboard. Shake the slurry bottle and then dip in two well-cleaned microscope slides, held together at the top by crucible tongs. Dip in and lift out the slides in a continuous movement; do not coat the top 1 cm of the slides. Allow to drain briefly. Handling the edges only, ease the slides apart and lay them, thin film uppermost, on the blotting paper for five minutes to dry. Activation is not necessary. If the film is not uniform, the microscope slide was not clean.

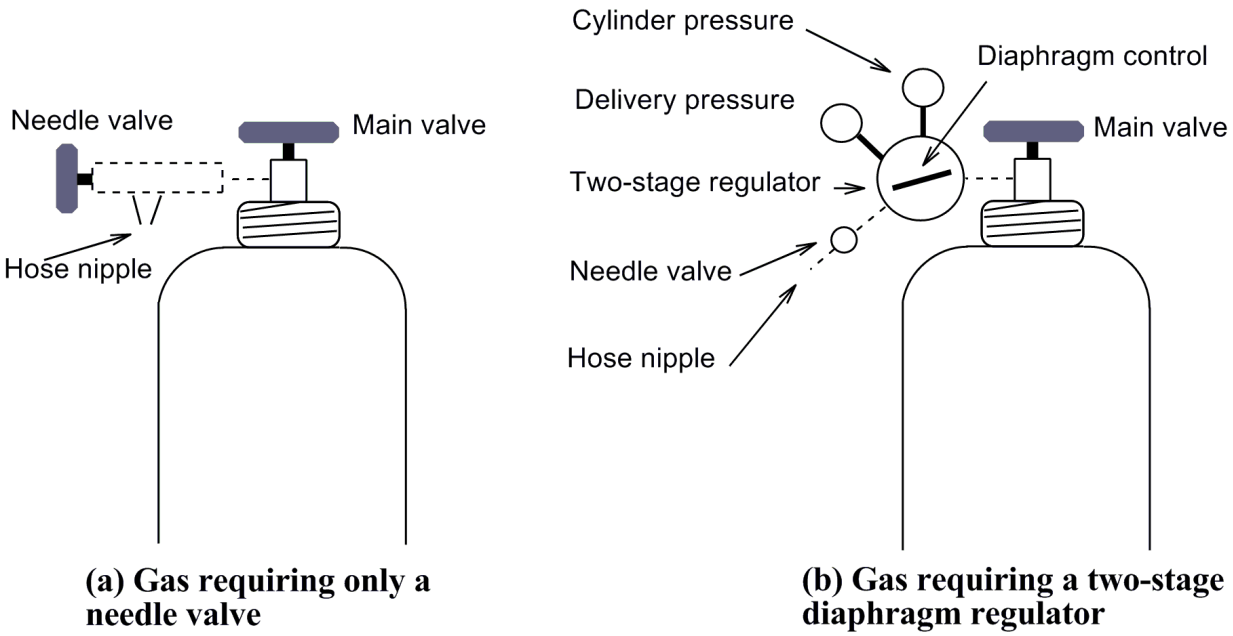
(b) Prepare a slurry of 1 g of cellulose in 5 mL of acetone by mixing well in a small glass mortar. Hold a 15 cm x 5 cm glass plate over a sheet of blotting paper and pour the slurry on to one end of the plate. By gently rocking the plate, spread the thin film uniformly over the plate, and then lay it down for five minutes to dry. Activation is not necessary. By use of the same technique it is possible to spread on 15 cm x 5 cm plates slurries of alumina or silica gel (1 g in 2.5 mL of 85% aqueous ethanol; if the slurry proves too thick or too thin, slightly vary the volume of solvent). Allow to dry at room temperature, then activate in an oven at about 120 °C for thirty minutes.

Spotting the plates Thin films must be handled and spotted with extra care because of their fragile nature. Spot the plates with a maximum of 0.002 mL of 0.01 – 0.1 M solutions from a capillary or fine wire loop. If possible, solutions should be prepared in the same solvent that will be used for development of the chromatogram.

As many as three separate spots can be placed on a microscope slide, if channels are scratched in the thick film with the edge of a spatula and surplus material is cleaned from the edges of the slide.

Compressed Gas Cylinders

Several experiments make use of gases which are commercially available in compressed gas cylinders. They come in a variety of sizes with several valves and regulators. The metallic content of the values is dictated by corrosive properties of the gas. The facile reaction of N_2O_4 with copper, for example, requires that the cylinder and valve contain very little copper. Many cylinders contain a safety valve or nut which is designed to rupture if the pressure inside exceeds the specifications of the cylinder. Under no circumstances should anyone tamper with the safety nut.



(a) Gas requiring only a needle valve

(b) Gas requiring a two-stage diaphragm regulator

Figure I-2 Details of the two main types of compressed gas cylinders used in the lab

The main valve (Figure I-2) on a cylinder is simply an on-off valve which allows no control of the gas flow; it should always be used with some type of control valve. A needle valve permits such control but if the cylinder contains a compressed gas, the cylinder pressure will decrease as the cylinder is used and the gas flow will likewise decrease. Thus, for compounds which exist as gases (*e.g.* CO, N_2, BF_3) in a cylinder, a given flow rate cannot be maintained without continuous adjustment. Compounds which condense to form liquids under pressure exert their natural vapour pressure so long as any liquid remains in the cylinder. For these gases (*e.g.* MeBr, NH_3) a continuous flow rate can be obtained with a needle valve.

To achieve a constant flow rate for gases which do not condense under pressure in a cylinder, a pressure regulator is required. (Figure I-2b) First, open the main valve; the gas pressure in the cylinder is given on the right hand gauge. Next, open the regulator valve by turning the knob counterclockwise. Such regulators should not be operated with the valve partially open; it is best to open it completely and then close it a quarter of a turn. Finally, adjust the flow rate to the desired level by opening the needle valve. The pressure between the needle valve and the regulator is given on the left-hand gauge. The regulator will maintain this pressure. During the experiment, the flow can be halted by closing the needle valve, but when you are finished with the cylinder for the day, close the main valve to prevent loss of the gas in case the regulator leaks slightly. Do not empty a cylinder completely; leave approximately 25 psi so that the cylinder does not become contaminated with air or other gases before it is returned to the supplier for refilling.

In several experiments, N_2 gas will be used to flush air from a reaction system, as shown below. Before the reaction is begun, the N_2 flow is sometimes turned off with the stop-cock. This

normally produces a pressure build-up which could result in the rupture of the Tygon tubing connecting the apparatus to the nitrogen cylinder. To prevent this, it is convenient to connect an oil or mercury bubbler to the nitrogen line to act as a pressure release valve for the excess nitrogen (Figure I-3).

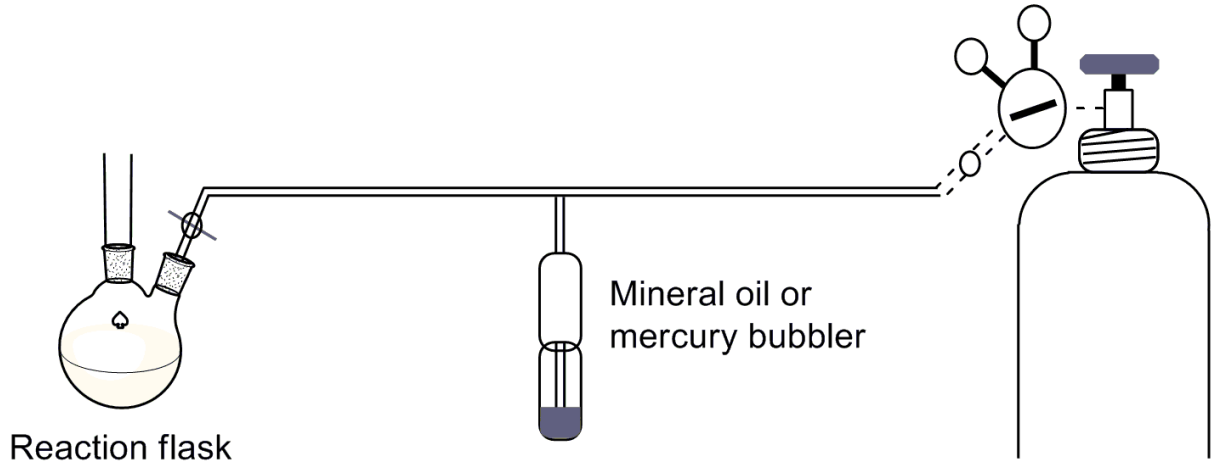


Figure I-3 In-line connection of a gas-bubbler

Handling Air-Sensitive Reagents

A large variety of air-sensitive reagents is available commercially. Specific examples include solutions of boron complexes, organoboranes, borohydrides, Grignard reagents, organoaluminums, organolithiums, and organozincs. Since all of these reagents react with water or oxygen or both (sometimes violently), they must never be exposed to the atmosphere.

Most modern synthetic chemists are familiar with the utility of these versatile organometallic reagents. However, because the compounds are air-sensitive or pyrophoric, some workers hesitate to make use of the remarkable chemistry of these reagents. Some chemists still believe that very specialized equipment and complicated techniques are required for handling these materials. This is often not the case.

Air-sensitive reagents available from Aldrich Chemicals are packaged in special bottles. The Aldrich Sure/Seal packaging system (Figure I-4) provides a convenient method for storing and dispensing research quantities of air-sensitive reagents. With this bottle, reactive materials can be handled and stored without exposure to atmospheric moisture or oxygen. The reagent comes into contact only with glass and Teflon, yet it can be readily transferred using standard syringe techniques.

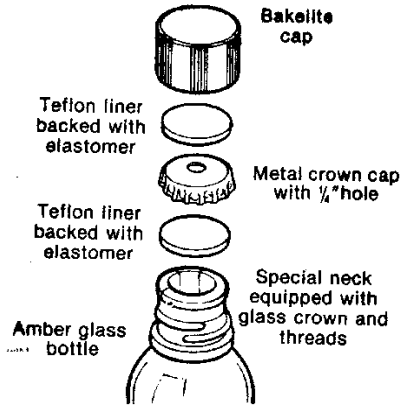


Figure I-4 The Aldrich Sure/Seal packaging system

The Bakelite cap on a Sure/Seal bottle can be removed because the crown cap, with its teflon-elastomer liner, is already crimped in place. The reagent can then be dispensed using a syringe or double-tipped needle (cannula) inserted through the hole in the metal crown cap. After the needle has been withdrawn from the bottle, a small hole will remain in the Teflon/elastomer liner. Under normal circumstances, the hole in the liner will self-seal and the reagent will not deteriorate. However, the possibility exists that once an elastomer is punctured, it may leak on long-term storage. This possibility is virtually eliminated with the Sure/Seal system because when the Bakelite cap is replaced, the Teflon/elastomer liner in the cap forms a seal against the top of the metal crown. Thus, the contents are effectively protected from moisture and oxygen in the atmosphere.

Laboratory glassware contains a thin film of adsorbed moisture which can be easily removed by heating in an oven (125 °C/12 hours or 140 °C/4 hours). The hot glassware should ideally be cooled in an inert atmosphere by assembling the glassware while still hot and then flushing with a stream of nitrogen or argon. Keck clips or rubber bands are required to secure all joints during the flushing process.

Small quantities (up to 50 mL) of air-sensitive reagents may be transferred with a syringe equipped with a long needle (8 – 16"). The long needles are used to avoid having to tip the reagent bottles. The reagent may be introduced into the reaction vessel via a rubber septum. These rubber septa slowly degrade upon contact with organic vapours, and therefore will only provide a positive seal for a limited number of punctures, depending on the needle size. The lifetime of the septum may be extended by always reinserting the needle through the same hole and by replacing the septum with a glass stopper immediately upon completing the addition. If a glass syringe and plunger are utilized, they should be oven-dried before use. The syringe and plunger should not be assembled before being placed into the oven, and should be cooled afterwards before assembly. If a plastic disposable syringe is to be used, it should not be placed in the oven, as it will warp upon exposure to prolonged heat.

The syringe transfer of liquids can be readily accomplished by first pressurizing the Sure/Seal bottle with dry nitrogen. This can be achieved by inserting a hose attached to a nitrogen

cylinder, as illustrated in Figure I-5. A much more safe, and thus, preferred method, however, is to inject a slightly greater volume of nitrogen gas into the Sure/Seal bottle as liquid that will be removed. This maintains a constant neutral pressure inside the bottle and can be carried out by flushing (withdraw a full syringe of nitrogen gas from an appropriate source and then expel it) the needle and syringe with nitrogen gas three times prior to injecting the desired quantity of nitrogen. The nitrogen pressure is used to slowly fill the syringe with the desired volume of the reagent. Note that the nitrogen pressure pushes the plunger back as the reagent enters the syringe. As such, the plunger should be pulled back only if needed, and in these cases only very slowly, since rapid movements tend to cause leaks and creates gas bubbles. Once the desired quantity of reagent is in the syringe (remember that a small amount is still in the needle!), reorient it such that the plunger is pointing downward toward the floor. Gently create a small "head space" by pulling the needle out of the solution (but keep it in the bottle) and withdrawing several milliliters of nitrogen gas into the syringe. The needle can now be pulled completely out of the bottle and the reagent quickly transferred to the desired vessel by puncturing the rubber septum on the reaction flask or addition funnel. Be sure to keep the syringe upside down until after the needle punctures the rubber septum. This process will ensure that absolutely none of the potentially dangerous reagent is lost during transfer.

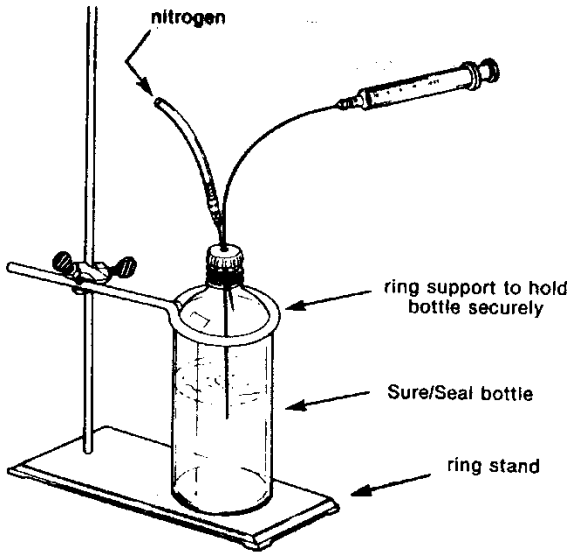


Figure I-5 Filling syringe using nitrogen pressure

When handling air-sensitive materials, it is important that the user be thoroughly familiar with the basic chemistry of the reagent. Also, the user should be prepared for unexpected problems. For example, at least one extra set of clean, dry syringes and needles should always be available in case the first set becomes plugged.

Chemistry Laboratory Rules and Safety Precautions

1. Wear appropriate clothing in the laboratory:
   (a) a lab coat has to be worn at all times
   (b) no sandals or open shoes are allowed
   (c) no shorts or skirts are allowed inside the laboratory

2. If you have any possible conflicts between the lab environment and any acute and/or chronic medical conditions (epilepsy, diabetes, allergies, etc.) please consult your lab coordinator/instructor prior to any scheduled lab work. Likewise, if you are pregnant, or are trying to conceive you should consult your instructor to ensure that you are not unknowingly exposed to teratogenic materials.

3. Never work alone in the laboratory.

4. Smoking and eating are not permitted.

5. Unauthorized experiments are strictly prohibited.

6. Know the location and use of the fire extinguisher, safety showers and first aid kit.

7. It is required that you wear **prescription glasses** or **safety glasses** at all times in the laboratory for your own protection. Contact lenses are particularly dangerous and they **must not be worn** in the laboratory.

8. Report all injuries to your instructor at once.

9. Never taste chemicals or solutions.

10. Use the fume hoods at the sides of the laboratory for all poisonous reactions or any reactions which produce noxious gases.

11. When diluting concentrated acid or base *always add the concentrated acid or base to water* (never the reverse), while stirring the solution. Be very careful with sulfuric acid.

12. Keep an orderly, clean laboratory desk. Return glassware to the lab drawer when finished using it to keep the work area from becoming cluttered.

13. Leave unneeded books, etc. outside of the laboratory. Never block aisles with personal effects, or leave clothing, etc. on the benches.

14. Waste crocks are provided for the disposal of all solid chemicals and paper, etc.
   (1) Non-chlorinated solvents
   (2) Chlorinated solvents
   (3) Sulfur chlorides

15. Stock reagent bottles are placed on the side bench or beside the balances; leave them at that position.

16. Always read the label twice before taking any chemical from a bottle. If you are not sure if you have the right chemical, ask!

17. Properly label all chemicals or reagents, including newly prepared samples.

18. When pouring reagents, hold the bottle so the label points upwards facing the palm of the hand. The accumulation of reagent on bottle lip may be removed by touching the bottle lip to the rim of the receiving vessel.

19. Avoid using an excess of reagent. If you happen to have measured out too much, see if someone else can use the excess.

20. Due to possible contamination of the contents of a whole stock bottle, never return unused chemical to the stock bottle.

21. Always check your glassware before you use it. If it is broken or cracked, exchange it for a new one.

22. There is one container reserved for broken glass. All broken glassware should be placed in this crock and no other.

23. If corrosive chemicals or liquids come in contact with the skin or clothing, flood with copious amounts of water for an extended period of time.

24. Spilled chemicals should be wiped up immediately; spilled acid or base should be rinsed with plenty of water and wiped up with a sponge and the sponge rinsed after.

25. Inserting glass tubing or thermometers through a rubber stopper – first lubricate the tube and stopper with glycerol or water, then holding the tube near the end to be inserted insert slowly while rotating the tube. BE VERY CAREFUL!

26. When you are ready to leave the laboratory, your bench area should be rinsed off with a wet sponge and the water, gas, and air valves shut off.

27. The chemistry store room is out of bounds to students. If you require apparatus, ask your instructor for it.

28. Disposable polyethylene gloves are provided; other glove materials may not protect you against the chemicals handled in this lab.

29. Never pipette by mouth.

30. Material Data Safety Sheets (MSDS) are available for all chemicals and reagents. Consult your instructor for access to this information.

Consent Form

This form must be completed, signed, and submitted to the laboratory instructor before any laboratory work is begun.

* * * * * * * *

I have read and understood both the general procedures and the safety rules within this manual that appear on pages B-1 – B-19 and C-1 – C-3 respectively, recognize that it is my responsibility to observe them, and agree to abide by them throughout this course.

Name (please print) _____

Date _____ Signature _____

Mel-Temp 3.0 for Melting Point Determination

Preparing Your Sample:

1.) Solid samples may be loaded directly into provided m.p. tubes by pressing the open end of the tube into the sample, inverting the tube then gently tapping it on a solid surface to move the sample to the bottom of the tube.

NOTE: If the tube is overloaded, the temperature of the sample will not be fully homogeneous during m.p. determination and the obtained m.p. range will be quite broad. In practice, the ideal amount of material to use for m.p. determination is the smallest practical amount that can be loaded into the m.p. tube while remaining clearly visible through the eyepiece of the m.p. unit.

ALSO NOTE: It is possible (with slight modification) to use a m.p. unit for b.p. determination (not discussed here). If this is required, ask your instructor for assistance in modifying your procedure to determine the boiling point of a liquid sample.

Setting Up:

1.) If the instrument is powered off, press the power switch. This will activate the light so your sample is visible through the eyepiece. The current temperature of the unit will be displayed on the digital readout on the front of the instrument.
2.) Check through the eyepiece to see if previous users have broken m.p. tubes off inside the instrument and notify your instructor if this is the case. Slide your sample into any open sample slot on the top of the instrument. Your sample should be well-lit and clearly visible as you will need to watch it closely. If necessary reposition the sample prior to heating.
3.) Set the temperature range that you wish to examine (low and high end) and the rate at which you would like the instrument to heat. This is done by pressing "Set" ("start" will be visible on the lower readout) and using the up/down arrows to set the low end of the temperature range that you wish to examine by pressing "Set" again. The "end" prompt should be visible on the lower readout. Increase the temperature using the up arrow until you reach the upper end of the range of interest and press "Set." "rate" should now be visible on the lower readout. Set the rate at which you wish to heat (in °C/min) using the up/down arrows. Pressing "Set" again will initiate the heating protocol (see "Recording a melting point", step 1).

NOTE: For any known materials, you should have an approximate idea of the melting point before you come arrive at the lab. Examining a temperature range of 5 to 10 °C about the expected value and heating at a rate of 1 °C/min is recommended.

If you have no idea what the m.p. is (*e.g.* a novel compound has been prepared), start at room temperature and end at the highest limit of the instrument (400 °C) scanning at the maximum rate (10.0 °C/min). Watch the sample and record an approximate m.p. value when it begins to melt. At this point, a more accurate m.p. range may be determined by preparing a new sample and closely

observing its behavior within 5 to 10 °C about the approximate value. For the more accurate m.p. range, set the instrument to heat at a rate of 1 °C/min.

Recording a Melting Point:

1.) Once you have set up the instrument, press "Set" one final time to begin heating the sample. The instrument should rapidly heat to a point below the set temperature range and continue heating at the set rate. If the instrument remains well below your temperature range of interest for an extended period of time, the "Ramp" button will allow the user to temporarily override the programmed rate and manually increase the temperature. The heating element will be active while the button is depressed. Note that holding the "Ramp" button down for extended periods of time will cause the instrument to heat rapidly, potentially overshooting the desired melting point.
2.) Watch your sample closely and record the temperature from the digital readout when you reach the melting point.

NOTE: Remember that all melting "points" should be recorded as ranges beginning when the sample shows visible signs of melting (appearing damp or "sweating") and ending when the sample is completely liquid. A narrow m.p. range (< 2 °C) is generally indicative of high purity, though exceptions do exist. Record your observed melting point in your lab book in ink. If you have recorded an approximate m.p. or have conducted multiple trials (recommended) please highlight the values you wish to submit in your lab report and briefly note a rationale if replicate trials are inconsistent with each other (poor precision often results from improper instrument usage or poor sample homogeneity) or with literature values (poor accuracy often results from low purity or differences in instrumentation used. If possible, use other characterization techniques to identify any impurities present).

ALSO NOTE: Some samples do not melt; but rather, decompose below their respective melting points. If your sample undergoes a clear transition without melting (often a colour change to black) record your "melting point" as "m.p. = ___°C (dec)." A single value, rather than a range, may be appropriate if the decomposition is abrupt.

FINALLY, NOTE: Some samples may neither melt nor decompose below the maximum limit of the Mel-Temp 3.0 (400.0 °C). If you observe a material to be stable up to 400.0 °C, simply record "m.p. > 400.0 °C."

Cleaning Up:

Dispose of any used m.p. tubes in the provided containers. If a m.p. tube breaks off in the instrument, please notify your instructor so the problem may be corrected.

Bruker Tensor 37 IR Spectrometer

Setting Up (ignore if you are not the first user of the day):

The main power switch for this instrument is located on the back. If the instrument is powered off prior to use, it will take about one minute to warm up before it is ready to use.

1.) Start the instrument control software (OPUS 6.5) using the desktop icon and log in using the following account:

    Username: ftiruser
    Password: user

    The software will take about one minute to initialize.
2.) Click "OK" on the "about OPUS" window if it opens.
3.) From the "measure" menu at the top of the screen, select "setup measurement parameters." From the new window, load the dataset "FIR.xpm" (for far IR) or "MIR.xpm" (for mid IR) which can be found in the C:\OPUS65\XPM directory.
4.) Click "Save and Exit" to apply your changes.

Preparing Your Sample:

A wide variety of techniques exist for preparing a sample for IR collection. By default, the instrument will be set up for neat solid samples. Some of these techniques will require reconfiguration of the spectrometer hardware – please ask your instructor for assistance if needed.

1.) Neat solid samples on crystal plates: A sample of a solid is pressed onto a reusable crystal plate. The IR spectrum is recorded directly. Conceptually, this is very similar to solid sample preparation for the Alpha FT-IR spectrometer.
2.) Neat liquid samples or solutions on salt (NaCl, KBr or CsI) plates: A (non polar) solution or liquid may be placed on an appropriate salt plate (CsI are recommended) and either allowed to dry (in the case of solutions), creating a film of the sample, or sandwiched between two plates, creating a thin uniform layer of the fluid. Please verify that your solvent or sample will NOT dissolve or corrode the plates (consult you instructor if necessary). * Requires installation of a special sample holder. Consult your instructor for any necessary hardware changes.
3.) Nujol mull on salt plates: Similar to above, but a solid sample is prepared in nujol (an inert mineral oil), which is then sandwiched between salt plates. * Requires installation of a special sample holder. Consult your instructor for any necessary hardware changes.
4.) KBr pellets: A small amount of a solid sample is ground into excess KBr (generally 1 mg of sample to 100 mg of KBr), which is then pressed into a plate or pellet using a sample press. KBr pellets are discarded after use. * Requires installation of a special sample holder. Consult your instructor for any necessary hardware changes.
5.) Neat gaseous samples: A gaseous sample is held in a specially-designed sample container. Crystal (or any non-IR-absorbing material) windows in either end are aligned such that the path of IR radiation proceeds unobscured through the sample. * Requires installation of a gaseous sample holder. Consult your instructor for any necessary hardware changes.

Using the Instrument:

Note: If OPUS 6.5 is not open when you arrive at the instrument, please start at setup step 1.

1.) BEFORE loading your sample, click on the "advanced data collection" icon. Give your sample a name in the appropriate field and click "start background measurement." This will collect a background spectrum (of air) that will be subtracted from your sample spectrum.

NOTE: Depending upon the nature in which the sample has been prepared it may be necessary to run a background spectrum of the medium which contains your sample (*e.g.* nujol or KBr).

2.) The exact nature of the instrument preparation will vary according to the method which you have used to prepare your sample. For the standard neat solid preparation, place a small amount of solid onto the crystal plate of the sample holder then lower the top anvil until it clicks into place. Place the holder into the sample chamber of the spectrometer. For alternate methods of sample preparation, consult your instructor for assistance.

3.) Click "start sample measurement." Wait a few moments until the collection is complete and your spectrum appears.

4.) If your spectrum appears too weak (peaks are of low intensity and not well separated from the baseline) or too strong (the detector is saturated and your peaks are not resolved) right click on the spectrum, select "remove from display," and restart at step 2, adjusting the amount of material used accordingly.

Preparing Your Spectrum:

1.) Once your spectrum has been collected, a number of tools are available. If your spectrum is poorly centered on the screen, the "spectrum adjustment" tool will allow you to correct it.

2.) You may need to adjust your baseline (using "baseline correction" tool) if it deviates substantially from level. Otherwise, proceed directly to "peak picking."

3.) The automatic peak picking tool (activated by clicking the "peak picking" icon) will label the major peaks in the spectrum.

4.) If you would like more or less detail, the minimum peak height may be set using the "interactive peak picking" tool (activated by clicking the drop-down arrow on the side of the icon, then selecting the "interactive peak picking" option). Click and drag on the arrow tool to set the desired peak height.

5.) Once you are satisfied with your spectrum, print it using the "Quick Print" tool (the "Print" tool should only be selected by advanced users).

Cleaning Up:

Cleanup will vary according to the experiment type. Neat samples on crystal plates must be wiped clean using *iso*propanol.

1.) If NaCl, KBr or CsI plates have been used they will need to be removed from their holders and wiped clean using acetone. NEVER clean any salt plates with water or alcohol – they will dissolve! Please return salt plates to their respective containers/dessicators promptly to preserve them for future use.

2.) KBr pellets should be removed from holders and discarded into an appropriate solid waste container. Residual KBr may be rinsed off of metal holders using water. If rinsed, dry holders thoroughly or rinse with acetone (non-plastic holders only) and allow to air dry before returning them for other users.
3.) It is generally sufficient to allow neat gas chambers to ventilate in a fume hood to remove gaseous samples. The process may be expedited by flushing the chamber with nitrogen or air. Any corrosion or staining caused by the sample should be noted and cleaned if possible.

Bruker Alpha FT-IR Spectrometer

Setting Up (ignore if you are not the first user of the day):

If the indicator light in the top right corner is blinking green, the instrument is not on. Press the small green button on the rear left (near the power cord) to start the instrument. Warm-up takes approximately 8 minutes. When the indicator light is solid green, the instrument is ready to use.

1.) Start the instrument control software (OPUS 6.5) using the desktop icon and log in using the following account:

    Username: ftiruser
    Password: ftir

    The software will take about 1 minute to initialize.
2.) Click "OK" on the "about OPUS" window if it opens.
3.) From the "measure" menu at the top of the screen, select "setup measurement parameters." From the new window, load the dataset "basic ftir.xpm" which can be found in the C:\OPUS65\XPM directory.
4.) Click "Save and Exit" to apply your changes.

Preparing your sample:

This instrument will collect IR spectra of neat solid and liquid samples. Most samples will work provided that they are not air sensitive or highly corrosive – consult your instructor if you are uncertain. Samples are loaded directly onto the crystal plate and no specific preparation is required.

Using the instrument:

Note: If OPUS 6.5 is not open when you arrive at the instrument, please start at setup step 2.

1.) Check that there is no visible debris on the crystal plate or beneath the ATR arm. If there is, first complete cleanup step 2.
2.) BEFORE loading your sample, click on the "advanced data collection" icon. Give your sample a name in the appropriate field and click "start background measurement." This will collect a background spectrum (of air) that will be subtracted from your sample spectrum. If you wish to use a blank, load your blank material onto the crystal plate (see next step for loading instructions) before taking a background scan and clean it off before adding your sample (see cleanup step 2).
3.) Load the instrument by placing a very small amount (a few milligrams at most) of your sample on the crystal plate in the centre of the instrument and lower the anvil by pressing down on the ATR arm until it clicks into place. A red dot should now be visible on the front of the arm – if not, consult your instructor.
4.) Click "start sample measurement." Wait a few moments until the collection is complete and your spectrum appears.
5.) If your spectrum appears too weak (peaks are of low intensity and not well separated from the baseline) or too strong (the detector is saturated and your peaks are not resolved) right

click on the spectrum, select "remove from display," and restart at step 2, adjusting the amount of material used accordingly.

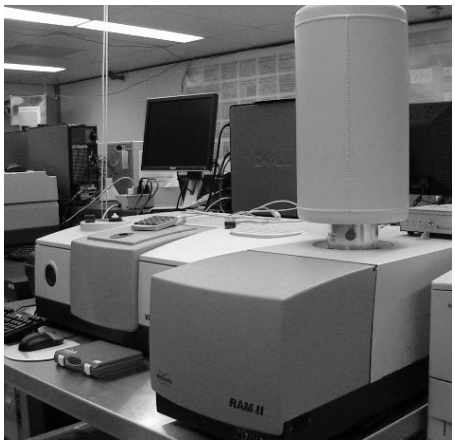
Preparing your Spectrum:

1.) Once your spectrum has been collected, a number of tools are available. If your spectrum is poorly centered on the screen, the "spectrum adjustment" tool will allow you to correct it.
2.) You may need to adjust your baseline (using "baseline correction" tool) if it deviates substantially from level. Otherwise, proceed directly to "peak picking."
3.) The automatic peak picking tool (activated by clicking the "peak picking" icon) will label the major peaks in the spectrum.
4.) If you would like more or less detail, the minimum peak height may be set using the "interactive peak picking" tool (activated by clicking the drop-down arrow on the side of the icon, then selecting the "interactive peak picking" option). Click and drag on the arrow tool to set the peak height.
5.) Once you are satisfied with your spectrum, print it using the "Quick Print" tool (the "Print" tool should only be selected by advanced users).

Cleaning Up:

1.) If you do not wish to save your work, right click on the spectrum and select "remove from display." If you wish to save your work, consult your instructor. You will likely be asked to place your work in a specific directory.
2.) Lift the ATR arm and clean the crystal plate and the bottom of the arm thoroughly using a kimwipe and *iso*propanol. Allow the instrument to air-dry for a few minutes before the next reading.

Bruker Ram II / Vertex 70 FT-IR/Raman Spectrometer



NOTE: The RamII/Vertex 70 is capable of functioning as either a Raman or standard IR spectrometer, though only one mode may be active at a given time. Explicit discussion of the IR mode will not be covered in this guide; however, note that operation of the Vertex 70 IR spectrometer is highly similar to operation of the Bruker Tensor 37, discussed previously.

ALSO NOTE: The Raman spectrometer is extremely sensitive to vibration. Do not place any items related to sample preparation directly on the instrument bench top (as with any instrument) and avoid using the instrument bench top as a writing surface. Be very cautious not to bump the instrument or do anything else which might cause nearby vibrations (*e.g.* stomping or dropping items on the floor) while spectra are being collected.

Setting Up:

1.) *To be done well in advance of instrument usage (3 to 4 hours)*: Ensure that the 4L liquid nitrogen storage tank contains at least 1L of liquid nitrogen (preferably, fill the tank – provided that subsequent users will need the instrument in the near future). Verify that the liquid nitrogen tank is capped to minimize loss of coolant or contamination of the storage tank. This step must be done well in advance to allow for temperature equilibration. A large plastic funnel is useful for filling.

NOTE: All remaining setup steps may be completed immediately prior to data collection.

2.) If the control computer is offline, turn it on and log in to the account using:

Username: ftiruser
Password: user

3.) Turn on the laser source (the small peripheral device located behind the liquid nitrogen storage tank) by first switching the power supply to "on" at the back of the device, then turning the key in the lock at the front of the device to the "on" position. At present (spring, 2009) the security key is simply kept in the instrument. If it has been removed for security reasons, consult your instructor or a department technician regarding its whereabouts.

4.) Open the beam splitter compartment (on the top of the Vertex 70 component, behind the sample compartment) and check that the CaF_2 beam splitter (labeled "SI") is in place in the central slot. The KBr beam splitter is used only for mid-IR collection and may be stored in the spare beam splitter slot on the far right of the compartment. Close the beam splitter compartment.

5.) Start the instrument control software (OPUS 6.5) using the desktop icon and log in to the account using:
Username: ftiruser
Password: user

The software will take approximately 1 minute to initialize.

6.) Click "OK" on the "about OPUS" window if it opens.

7.) Click the "advance data collection" tool on the main toolbar. You should start at the "basic" tab of the new window. In the "Experiment" field, load the dataset "raman.xpm" which can be found in the C:\ProgramFiles\OPUS65\XPM directory.

NOTE: Fields within this window are colour-coded according to the set parameters. All fields should appear white (normal), yellow (caution), or red (danger). The instrument will operate safely if all parameters are depicted with a white "normal" or yellow "caution" background but the obtained data may not be ideal if key fields are set to "caution" values. If, at any stage in the setup procedure, you observe a field with a red "danger" background, immediately notify your instructor as this may indicate a problem with the instrument.

8.) The laser power may also be set from the "basic" tab of this window. Set it to 100mW unless another power level is specifically noted in your experiment. Record the laser power and report it along with all other relevant instrument parameters.

9.) Under the "advanced" tab, set the desired number of scans for your spectrum collection (64 scans are generally sufficient).

10.) Set the desired resolution for your final spectrum. Note that higher resolution (lower values as measured in cm^{-1}) collection will take longer periods of time and necessitate a smaller aperture setting for the source radiation, which in turn reduces the intensity of the observable signal. Resolution at 4 cm^{-1} is generally sufficient for coursework; however, resolution to 2 cm^{-1} may be accomplished under normal conditions using this instrument. Once your desired resolution is set, navigate to the "optic" tab and check the background colour of the "aperture" field. If you have increased the resolution relative to the last user, this field will likely be yellow (caution). Increase or decrease the aperture size such that the value in the field is as large as possible without triggering the "caution" background (the background for your final value should be white). This will set the incident radiation to be as intense as possible (giving maximum signal) within the restraints of the set resolution level. Setting the aperture size too high will lower the resolution (the "caution" background warns you of this) so if more power is needed, as is the case with a weakly diffracting sample, first return to the "advanced" tab, lower the resolution, then increase the aperture size to the maximum allowable value from the "optic" tab.

11.) Under the "optic" tab, verify that the beam splitter is correctly set to "CaF_2." Also verify that the "accessory" field is set to "XYZstage."

NOTE: Some additional setup is required, and is specific to each sample. See "Using the Instrument" for sample-specific parameters.

Preparing your sample:

A number of sample preparation methods are available depending on the state of your sample. Regardless, sample holders are located in a small blue case generally kept on top of, or near the

instrument. Raman spectroscopy requires only small quantities of material, so use of neat solid holders or capillary tubes will minimize waste. NMR tube and cuvette sample holders are available, but should only be used if these types of samples have already been prepared for other characterization purposes.

1.) Small quantities of solid may be directly pressed into solid sample holders using the press included with the sample case. Note that one such holder contains a standard sample, and may not be washed out or re-used (it is sealed to prevent this).
2.) Solid or liquid samples may be placed within a capillary tube (kept next to the melting point instruments) which may then be fitted into an appropriate holder (found in the sample case) which may in turn be placed into the instrument. Sealed capillary tubes are preferred to minimize the chance of spillage, but open tubes are acceptable if the user is cautious to properly orient the tube within the sample compartment of the instrument.
3.) Liquid or solution samples may be placed in an NMR tube for which a sample holder is provided (as is the case with capillary tubes). For solution samples, be aware the solvent may possess vibrational modes which may obscure those of the material of interest. In such cases the solvent should be carefully chosen.
4.) Larger quantities of liquids or solutions may be placed in the provided mirrored cuvette. For solution samples, be aware the solvent may possess vibrational modes which may obscure those of the material of interest. In such cases the solvent should be carefully chosen.

Using the instrument:

NOTE: The Raman spectrometer is extremely sensitive to vibration. Do not place any items related to sample preparation directly on the instrument bench top (as with any instrument) and avoid using the instrument bench top as a writing surface. Be very cautious not to bump the instrument or do anything else which might cause nearby vibrations (*e.g.* stomping or dropping items on the floor) while spectra are being collected.

ALSO NOTE: This section is a continuation from "Setting Up" (above). The previously outlined setup steps may be appropriate for sequential users with similar samples; however, it is important to note if any special settings have been made by the previous user. If you are the first group to use the instrument, consult your instructor to verify that setup has been completed. If you are following another group, verify that their instrumental settings are appropriate for your sample.

1.) Open the compartment at the front of the Ram II (below and in front of the liquid nitrogen tank). Open the sample holder by pulling back on the plunger, then set your sample into the sample holder. Solid sample holders should be oriented with the sample toward the detector. Liquid and solution samples in a cuvette should be placed such that the mirrored surface on the cuvette faces the detector (the darkened outer surface faces away from the detector). Any samples in unsealed capillary tubes should be oriented such that the tube is in an upright position to avoid spillage. Gently release the plunger to hold your sample in place. DO NOT allow the sample holder to snap shut as this will cause certain sample holders (particularly solid sample holders) to eject sample toward the detector. This will necessitate cleaning of the instrument. Close the sample compartment.

2.) Open the "advanced" tab of the "advance data collection" window. Enter a file name for your spectrum in the appropriate field and verify that the designated path is within your class directory (C:\DocumentandSettings\CHEM3840).
3.) Return to the "basic" tab and enter a sample name, (including your initials to minimize confusion) and a brief description to help identify your sample, in the appropriate fields.
4.) Navigate to the "check signal" tab and select "spectrum" from the list of options on the left. The preview window should show a weak spectrum (see note below if not). Toggle "store mode" on. This will track changes to the spectrum and facilitate maximization of the signal. Any signals visible in the spectrum should be maximized by centering the sample physically using the XYZ stage. Buttons to adjust the alignment are found within the "check signal" tab, but the same procedure may be accomplished using either the keypad attached to the instrument, or the number pad of the keyboard. The keypad is preferable as it may be held in the hand above the instrument bench to minimize vibration, though all three methods are acceptable. Adjust X (left/right), Y (up/down), and Z (toward/away from the detector) parameters to maximize the intensity of the signal observed in the preview window. Clicking and dragging to select a region will adjust the view (by zooming in on the selected region) if certain peaks are of interest. To zoom out, right click on the preview window.

    Each directional parameter (X, Y, and Z) must be independently optimized. It is often useful to begin at the setting X = 100, Y = 100, Z = 100 to 130, independently optimizing X, Y, and Z in that order. Once each parameter has been independently optimized, vary each by a few increments to check that the sample is indeed centered (the signal should decrease if the location is changed in any direction from optimal).

    NOTE: If a spectrum is not observed in the preview window, the sample is likely badly out of alignment. Reset the physical location to X = Y = Z = 100. The "interferogram" setting may be used as a rough centering tool. In this mode, the amplitude of the observed signal should be maximized using the same procedure outlined above. Once a peak is clearly visible, final centering should be conducted using the "spectrum" setting.

5.) Click "Sample Raman Spectrum" to begin spectrum collection.
6.) Progress may be tracked along the lower portion of the spectrum screen. When the indicated number of scans has been completed, a spectrum will appear in the main window.

Preparing your Spectrum:

1.) Briefly inspect your spectrum to verify that the peaks are clearly distinguishable from the baseline. If your signal appears weak, your sample may be improperly centered (see "using the instrument," step 4) or weakly diffracting. In the former case, centre the sample and repeat the collection procedure. In the latter, either increase the number of scans collected to enhance the signal:noise ratio ("setting up" step 9) or decrease the resolution and increase the aperture size ("setting up" step 10). Repeat the spectrum collection.
2.) Once your spectrum has been collected, a number of tools are available. If your spectrum is poorly centered on the screen, the "spectrum adjustment" tool will allow you to correct it.

3.) You may need to adjust your baseline (using "baseline correction" tool) if it deviates substantially from level. Otherwise, proceed directly to "peak picking."
4.) The automatic peak picking tool (activated by clicking the "peak picking" icon) will label the major peaks in the spectrum.
5.) If you would like more or less detail, the minimum peak height may be set using the "interactive peak picking" tool (activated by clicking the drop-down arrow on the side of the icon, then selecting the "interactive peak picking" option). Click and drag on the arrow tool to set the desired peak height.
6.) Once you are satisfied with your spectrum, print it using the "Quick Print" tool (The "Print" tool should only be selected by advanced users).

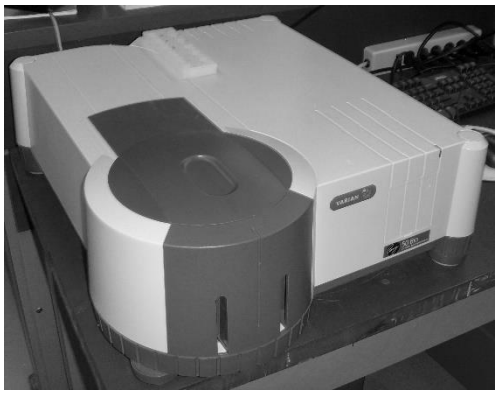
Cleaning Up:

Cleanup will vary according to the sample preparation method used.

1.) Solids pressed into neat solid holders must be rinsed out using a suitable solvent. The holders must be dried prior to returning to the sample case. Please check that no residue remains, as this will interfere with future users of the sample holder.
2.) Capillary tubes may be disposed of in the labeled containers along with m.p. sample tubes.
3.) NMR tube samples should be cleaned as one would normally clean an NMR tube. To clean your NMR tube, rinse the contents into the appropriate waste container. If any solids have formed, brush them out using a small test tube brush or pipe cleaner and rinse the tube with acetone and/or water. If clean, caps may be rinsed and reused. If damaged, caps may be discarded.
4.) If a cuvette is used, empty it into an appropriate organic or heavy metal waste container and rinse it thoroughly using acetone.

Varian Cary 50 Bio UV/Vis Spectrometer

Setting Up:



To access this instrument, one must log on to the accompanying computer (FISCEK-HSC06) using the following account:

Username: cary50
Password: user.

A variety of programs are available from the desktop; however most have highly similar interfaces. For collection of simple absorption spectra, "Scan" is recommended for beginning users. If the nature of your experiment requires only absorption values for one particular wavelength of radiation, "Simple Reads" is the recommended interface.

1.) Open the collection program of your choice from the desktop. Detailed instructions for "Scan" and "Simple Reads" interfaces are given below.
2.) Set up parameters for data collection by clicking the "Setup" button located toward the upper left corner of the interface.

a.) "Scan" mode: It is usually sufficient to only set parameters using the general settings tab (the first one which opens with the "Setup" menu). Set the range of wavelengths you wish to scan under the "X mode" heading. This instrument is capable of scanning a maximum range of 900 nm to 190 nm.

The level of detail which the instrument collects may be set using "Scan controls" (beginners should use the "simple" option for setting scan controls). This will allow selection from a range of preset scanning parameters which range from "Slowest" to "Survey" (very fast). Simply put, these preset options present a trade-off between quality of data and time required to collect. "Slowest" will collect a high quality spectrum, but take relatively more time to do so. "Survey" will only take a few moments, but the resultant spectrum will be of lower quality. All other presets range between these two extremes. For course purposes, the "Medium" to "Fast" settings are generally sufficient.

One other setting of note is found under "Display Options" and has to do with the manner in which spectra are displayed. If you will be collecting a limited number of spectra of the same or closely related materials, it may be more simple to show all traces on one plot (this saves paper and is more concise). To do so, simply select "Overlay Data."

Finally, note that absorbance is plotted on the Y-axis by default. If you wish to plot another parameter or change the default range, this may be done using the "Setup" menu as well. Click "Ok" to apply your settings.

b.) "Simple Reads" mode: Set up is far more simple for this mode. If the nature of your experiment requires only information on the absorbance of a solution at a given

wavelength, set this wavelength in the "Read at wavelength" field of the setup menu (remember, the accessible range is 900 to 190 nm). Click "Ok" to apply your settings.

Preparing your sample:

1.) Prepare a dilute solution of your material of interest in an appropriate solvent. Since UV absorbance is often highly dependent on the nature of the material, the concentration required will vary according to the sample. Ideally, the peaks of a collected spectrum will range from near-zero absorbance to just below A = 1.0 on the Y-axis. Peaks slightly higher than A = 1.0 may be acceptable but if the majority of the spectrum is above approximately A = 0.8 on the Y-axis or if stronger peaks appear truncated, a more dilute solution should be prepared. If the collected spectrum is weak (the highest peak is below approximately A = 0.4) a more concentrated sample is necessary. If you do not know the nature of your material of interest, a solution with a concentration between 1.0×10^{-5} mol/L and 1.0×10^{-4} mol/L is often a good starting point. If you are constructing a calibration curve, your lab manual may suggest a range of concentrations to use.

2.) Obtain UV absorbance quartz cuvettes from your instructor. The cuvettes for this instrument are transparent on two opposing sides and frosted on the remaining two sides. The cuvette should be handled wearing gloves or only using the frosted sides (preferably both) to prevent depositing any skin oils or debris in the path of the UV radiation, which may alter the collected spectrum.

NOTE: The cuvette should always be placed in the instrument such that the UV radiation passes through the transparent sides of the cuvette. Facing the instrument, the path length is oriented perpendicular to the user's line of sight (so the frosted sides should be facing directly toward and away from the user).

ALSO NOTE: the cuvettes for the UV fluorimeter look quite similar to those for the Cary50, but are transparent on all 4 sides. These cuvettes should be reserved for users of the fluorimeter, as the fluorimeter cannot use absorbance cuvettes.

3.) If you have been supplied two cuvettes, fill one (approximately 80% full – overfilling accomplishes little and is likely to create a mess) with the solvent which you have used to prepare your sample and one with the sample solution itself. If only one cuvette is available, fill it with solvent and empty/refill it with sample prior to spectrum collection. Cap your cuvettes to minimize spillage. If the transparent sides of the cuvette have fingerprints or debris on them, polish them gently with a kimwipe.

NOTE: Many organic solvents are potentially damaging to the instrumentation or control computers. Never place or pour solvents on the instrument bench unnecessarily. A fume hood is available in the instrument room for sample preparation. Always fill cuvettes on a separate bench top or in a fume hood, as opposed to inside the instrument itself.

Using the instrument:

1.) A zero absorbance value must be set for the instrument to give accurate results. Slide the top of the sample chamber open and place your solvent cuvette (frosted sides toward the front and back) in the instrument's sample holder. Close the cover and click "Zero" (just

below "Setup"). All collections should be made with the sample chamber covered to minimize interference by ambient light and UV radiation.

2.) OPTIONAL: If you suspect that your solvent has any substantial UV absorbance, a baseline collection may help eliminate solvent absorption peaks. This option is available in the "Scan" program, but not in "Simple Reads." It may be selected from the "Setup" menu. The background collection should be performed at this time by clicking "Baseline." All baseline data is stored in the program until it is closed or until the baseline is overwritten with a new one. To verify that another user's baseline data is not applied to your spectrum (if the program was open when you arrived at the instrument), check that no baseline correction is selected in the "Setup" menu. Alternately, you may collect a blank spectrum by clicking "Start" to verify that your solvent does not absorb substantial amounts of UV radiation.

3.) Remove the solvent cuvette from the instrument and replace it with a sample cuvette.

4.) Click "Start" (top of the window in the middle). If you have not previously saved your data, you should be prompted to do so now. Locate your class' subfolder within C:/Data/ and give your file a name which indicates your identity (user initials) and the experiment which you are conducting. Click "OK."

5.) Name your sample when prompted and click "OK".

a.) For "Simple Reads" mode, you will simply see a list of absorbance values taken at the desired wavelength. To take additional readings, click "Start" again. One reading is taken each time "Start" is clicked. For simple reads, three to five collections are recommended as averaging these values can slightly improve accuracy.

b.) For "Scan" mode, a spectrum will now be collected. If the sample is too concentrated or too dilute, make the necessary adjustments and repeat "Preparing your sample" steps 1 and 3.

Preparing your spectrum:

1.) No spectrum preparation is needed for "Simple Reads" – proceed to step 2. For "Scan" mode, spectrum preparation is largely automated, but a visual inspection should be made to verify that the appropriate peaks have been identified. The spectrum may be modified using a variety of tools in the toolbar at the top of the spectrum window. Absorbance values for all labeled peaks will be automatically tabulated and are displayed below the printed spectrum. If you have several overlapping spectra, these values will be sorted according to sample name.

2.) Print your data from the "File" menu. The default printer is located in the instrument room next to the NMR processing computer.

3.) Save your data if you would like to keep it.

4.) Clear all traces from the window (scan mode) by right-clicking the spectrum and selecting "clear all traces" to prepare the instrument for the next user. If using simple reads mode, simply close the program.

Cleaning up:

Empty the quartz cuvettes into an appropriate organic or heavy metal waste container and rinse them thoroughly using acetone.

NOTE: Other facilities may use less expensive plastic cuvettes for UV absorbance. Never wash a plastic cuvette with acetone unless you know the nature of the material used – acetone may etch or corrode certain types of plastic.

Bruker Avance II 300 MHz NMR Spectrometer

NOTE: Due to high demand, use of the NMR spectrometer is only permitted during previously-scheduled times which may vary from semester to semester. Refer to the posted regulations for up-to-date information. Please consult your instructor to make special arrangements if you require access to this instrument outside of your regularly scheduled laboratory time.

Setting Up:

1.) If the control computer in the NMR room is powered off or locked, log in to the account:

Username: nmr user
Password: nmr

2.) If Bruker Biospin is not active, it may be started from the desktop. The lock display window (on the right screen) and BSMS control suite may be opened by clicking the corresponding options on the "NMR step-by-step" menu.

Preparing your sample:

1.) Place a 5 – 10 milligrams of the sample of interest (for a solid) or *one* drop (for a liquid) into an NMR tube and dissolve in approximately 0.75 mL of your chosen deuterated solvent. This will most likely be $CDCl_3$ but other solvents such as C_6D_6 or D_2O may be available depending upon the nature of your experiment.
2.) Cap, mix and label your NMR sample.

Using the instrument:

IMPORTANT NOTE: Please ask for assistance if you have never loaded a sample into the NMR spectrometer before. Improper loading may cause serious damage to the instrument.

ALSO NOTE: All NMR spectrometers generate powerful magnetic fields. As such, it is important that one never approaches a spectrometer while carrying any large metal objects (tools, etc.) or magnetic media (credit cards, magnetic storage media, etc.). In addition, one should not use an NMR spectrometer if they have a pacemaker or large metal plate within their body. While the Avance II is well-shielded, one should still keep metallic objects outside the area indicated by the yellow cones.

1.) Under "NMR Step-By-Step" menu, click "Create Dataset." Verify that the directory that you are working in corresponds to your course (ask for help if needed) and give your experiment a unique sample name. Include your name or initials in the sample name to help minimize confusion.

Also note the fields labeled "EXPNO" (experiment number) and "PROCNO" (procedure number). These may be used to help organize your experiments. The organizational scheme the program uses is as follows: maindirectory > yourclassdirectory > your experiment > EXPNO > PROCNO. For example, a Chem 3840 student with initials "BI" may set up an experiment "BIexperiment2" and wish to run one ^{1}H spectrum and one $^{13}C\{^{1}H\}$ spectrum

for each of three separate samples. All six spectra could be stored within the experiment "CHEM3840/BIexperiment2/…" if each dataset was given a unique EXPNO. You may use any organization scheme you wish, but each spectrum should be appropriately titled and all spectra from a single laboratory experiment should be within one sub-directory to keep clutter in the class directory to a minimum.

2.) If you wish to navigate between multiple open experiments, your datasets will become visible in the folder list on the left of the main window. If it is not found within the list, close and then re-open your course directory folder to refresh the list.

3.) Check that the top of the instrument is not capped (if it is, the sample lift will not initiate) and open the BSMS control suite (found in the NMR Step-By-Step menu, if it is not already open. It may be brought to the front by clicking the corresponding colour-coded tab on the top right of the main window). Select the "Main" control tab. Under sample, click "Lift." The button should turn green and the sample location indicator (at the very bottom of the control screen) should display "Up." You should hear gas flowing out of the top of the instrument.

4.) The tube height guide (at right) has both a blue plastic component (the "spinner") and a colourless glass component (the "guide"). Place the spinner into the top of the guide as shown, then carefully load your sample tube into the spinner so it touches (but is *no lower than*) the bottom of the glass guide. ***If your sample tube is too low when it is placed into the instrument, it will cause damage*.** Your solution should be approximately centered about the horizontal line on the side of the guide.

5.) *Without* removing your NMR tube from the blue spinner, lift it out of the colourless glass guide. Release your sample tube (along with the spinner) slowly over the top of the sample port *without* allowing it to drop. The sample should float on the stream of compressed air at the top of the sample port. If the flow rate is not high enough to support the sample without holding it, inform your instructor so that the necessary adjustments can be made.

6.) Using the BSMS controller, click "Lift" again. The sample location indicator should display "Missing" momentarily, followed by "Down." Your sample should be slowly lowered into the instrument. You may also notice an increase in the lock level, shown on the secondary monitor.

7.) Cap the sample port.

8.) Click on "NMR Step-By-Step" then "Lock." This will bring up a menu prompting you to select your solvent. Click on the solvent that you are using, then "OK." The instrument will automatically undergo a locking procedure. Once the "lock: finished" message appears at the bottom of the screen, proceed to the next step. This will likely take approximately one minute.

9.) Set up the experiment you wish to run using the appropriate "1D Experiments" or "2D Experiments" option under the "NMR Step-By-Step" menu. Some common 1D experiments you may wish to use are: 1d_proton (^{1}H), 1d_carbon_decoup (^{13}C{^{1}H} – time permitting), 1d_P31_decoup (^{31}P{^{1}H}), or 1d_19F_wide (^{19}F, the "wide range" experiment is recommended for any inorganic or organometallic species containing fluorine). Loading

the default experiment parameters will likely be sufficient, though a number of customization options exist for each experiment. Consult your instructor if you would like to run a non-standard experiment.

10.) Tune and match the probe by clicking "Tune and Match" on the step-by-step menu. Allow the automated procedure to run until the "atma: finished" message appears. This will likely take 2 – 4 minutes, depending on the nucleus you wish to run and the instrument's previous settings. You may skip this step if the preceding user had the instrument tuned to the nucleus which you are interested in.

NOTE: the Bruker Avance II may be simultaneously tuned to two nuclei on two separate channels. One channel exists for collection of ^{1}H data while all non-H nuclei are run on the "x channel". In other words, you do not need to re-tune between running ^{1}H and ^{31}P spectra provided that you tune both to begin with. You do however need to re-tune between ^{31}P and ^{13}C. Selecting "Tune and Match" from within an "x channel" experiment (any non-H nucleus) will automatically tune the x channel to the selected nucleus and the proton channel. Selecting "Tune and Match" from within a ^{1}H experiment will not tune the "x channel."

11.) Click "Gradient Shimming" on the step-by-step menu and allow the automated shimming procedure to run until the "gradshimau: finished" message appears. This will likely take several more minutes. At this stage, the lock signal may have disappeared from the lock window. If this is the case, return to the BSMS control Suite. Under "Lock" click "Gain" then under "Value" click "Step –" or "Step +" as needed until the lock signal is visible. The signal should now approximate a horizontal line and should not fluctuate significantly over time.

12.) Click "acquire" to begin collecting your spectrum. The length of time this takes will vary from a few moments to several hours depending on the nature of your experiment (a simple 1D proton experiment should take no more than 3 minutes).

NOTE: At this stage you may wish to complete the section below ("Preparing Your Spectrum") before ejecting your sample. If you are not satisfied with your finished spectrum you may make adjustments to your experimental parameters and restart step 11. If you eject your sample and wish to collect a new spectrum, you must start again at step 1. If other users are waiting, you may briefly inspect your data but should relocate to the processing computer to generate your final spectrum.

13.) Uncap the sample port and click "LIFT" under "SAMPLE" on the BSMS control suite. Retrieve your sample then click "LIFT" again to stop the gas flow and re-cap the sample port. Remove your sample tube and replace the spinner into the guide.

Preparing Your Spectrum:

1.) If other users are waiting to use the NMR spectrometer, please relocate to the processing computer to prepare your spectrum. The processing computer is located immediately outside the NMR room (within the instrument room). The topspin program is available on this computer along with access to all data stored on the NMR harddrive. Note that files are stored in the Z:/ directory (as opposed to C:/) as they are accessed remotely – your class

directory should still be accessible from the left sidebar, but it will be a sub-folder of "Z:/". Also note that in order to protect original data, changes to spectra made from the processing computer will not overwrite any original files.

2.) Most basic spectral preparation and interpretation tools are found under the "NMR Step-By-Step" menu in the order that they should be completed. To visualize your spectrum once it has finished running, click "Exponential Multiplication" then "Fourier Transform." Beginning users should accept the default parameters in the subsequent pop-up windows.

3.) You should now see your spectrum, but it may not be completely in-phase. The most simple procedure for correcting this is the "Auto Phase Correct" tool, which is also in the "NMR Step-By-Step" menu.

4.) Locate your residual solvent peak or peaks and verify that the chemical shift(s) is(are) correct. If not, reset the shift of the most well-refined solvent peak to the correct value (see the supplied table next to the NMR control computer if you are unsure) by clicking the "Spectrum Calibration" tool (located on the main toolbar) then left-clicking the peak of interest. A popup window will appear allowing you to set the correct chemical shift for the peak.

    NOTE: You can change the view of your spectrum using the tools on the bottom row of the main toolbar (beginning with *2, /2, etc.). You can also zoom in on your spectrum by left-clicking the spectrum and dragging across the region of interest (this will not work if you are using the "Spectrum Calibration" tool or any other tool requiring you to click on the spectrum). Remember that there are tools on the aforementioned toolbar to reset your spectrum to the full collected width or to the default height.

5.) Next, select "Peak Picking" from the "NMR Step-By-Step" menu. This will activate peak picking mode, which will limit your ability to make other modifications to the spectrum until you have closed it. The toolbar in the peak picking window contains a number of options for defining new peaks and ranges; however, the most straightforward tool is called "Define New Peak Picking Range." This tool should toggle on once peak picking mode is activated and can be toggled on or off using the appropriate icon on the peak picking toolbar. When this option is toggled off, clicking and dragging on the spectrum will zoom as it does outside of peak picking mode. Other spectrum viewing and resizing tools remain active in peak picking mode.

    To define a peak picking range, toggle the appropriate tool on and click/drag to define a square around the top of any peaks of interest. Once drawn, peak picking regions may be deleted by right clicking on the region itself and selecting the appropriate "delete" command. Once you have selected all peaks of interest their markers (along with labels) should be visible on the spectrum. Save your changes by clicking the "Return, save changes" icon on the peak picking toolbar. This will return you to the main spectrum window and your peak labels should now be visible.

6.) Next, integration may be performed where appropriate. Enter integration mode from the "NMR Step-By-Step" menu. Integration mode is much like the peak picking mode in that it limits the manipulation options that are available. The icon for "Define New Region Using Cursor" will appear in place of "Define New Peak Picking Range" and is toggled on

or off similarly. Use this tool to define your integration regions as you defined your peak picking areas.

NOTE: Integration ranges are one-dimensional so one need only to define a region along the baseline. It is not necessary to draw a box around the peak of interest, as it was for Peak Picking.

Select a peak to serve as the "calibration" peak and right-click on the corresponding region. Select "calibrate" and set the value in the pop-up window to the known or expected integration value of that peak. The integration values for all other regions will adjust automatically. Right-clicking an integration region will also give the option to delete that region, analogous to deleting a peak picking region. Click "Return, save changes" to exit integration mode.

7.) Your spectrum should now appear essentially complete. If you wish to modify any peak picking or integration regions, you will have to re-enter the appropriate mode(s). Re-size the spectrum using the appropriate tools. You can print a spectrum using default display parameters from the file menu, or prepare your spectrum using the "Plot Editor" tool from the "NMR Step-By-Step" menu. Clicking "Plot Editor" will open a new program and load your spectrum automatically.

8.) If you choose to use the plot editor you may use a variety of tools such as region expansions, plot stacking, font and colour changes, and so on. These tools will not be discussed explicitly in this manual, but note that right clicking on a spectrum and clicking "1d/2d edit" from the main plot editor window will open a control window which allows for many of the same manipulations that you will have seen in the Bruker Biospin software (on the bottom row of the main toolbar). If you are interested in any more advanced spectral preparation tools, your instructor may be able to advise you further. When you have finished with the plot editor, print your spectrum from the "file" menu.

Cleaning Up:

NMR spectroscopy requires minimal cleanup – just be sure to leave the room at least as tidy as you found it. If you would like to save your NMR sample for future study, label it and keep it in the provided holder (lower left shelf of the cabinet) for short-term storage, or with your lab materials for longer periods of time. To clean up your NMR tube, rinse the contents into the appropriate waste container – acetone is often helpful here. If any solids have formed, brush them out using a small test tube brush or pipe cleaner and rinse the tube with acetone and/or water. If clean, caps may be rinsed and reused. If damaged, caps may be discarded.

Varian 431GC-210MS Gas Chromatograph – Mass Spectrometer

Setting Up:

1.) Verify that the main power supply to the GC-MS is on and start the control computer if this has not already been done. Log in to the computer using the following account:

    Username: Varian
    Password:

2.) Logging in to windows will automatically open the GC-MS control toolbar from which all necessary programs may be launched. Click "System Central" to open the main program and connect to the peripheral via the IP address 10.2.128.1.
3.) Open the "method builder" program by selecting "new method" from the main toolbar or by selecting "view/edit method" from the active method displayed (most likely Dailychecks.mth). From within the method builder program, open the method "CHEM3840default.mth" from the "methods" directory. You may wish to alter parameters for your experiment at this stage. If you wish to make changes to the CHEM 3840 default method, select "File" > "Save As" and save your method file in the "methods" directory with a name identifying your course number (be sure to include the user's initials and the date).
4.) Select "MS acquisition method" from the list of options at the left of the method builder. This will allow you to set the range of charge-to-mass ratios that the MS will survey. The maximum allowable range is 45 to 650. Surveying the full range is recommended unless you are interested in only a small, known region of the mass spectrum.
5.) Select "GC control" from the list within the method builder window. Set the time increments and desired temperature ranges using the provided spreadsheet. When run, the GC will adjust to the desired temperature, remain at this temperature for the indicated amount of time (not including the time required to reach this temperature), then increase to the next desired temperature. An estimate of the total time (including that required to adjust the temperature) is provided in the far right-hand column.
6.) Many other instrumental parameters may be set using the method builder tool; however, this should only be attempted by advanced users. Save your method file and exit from the method builder.

Preparing your sample:

It is important to analyze only samples which are highly volatile and completely free of salts. If this is not the case the column, which is very expensive, may become blocked and need to be replaced.

All samples should be dissolved in an appropriate non-reactive organic solvent (*e.g.* hexane, toluene, dichloromethane, etc.). Please note that aqueous solvents (*e.g.* alcohols, water) are not compatible with the column and will cause irreversible damage.

Mass spectrometers are extremely sensitive and only a very small amount of sample is required. While detection limits vary somewhat from sample to sample, a good starting concentration (to avoid overloading the detector) is 0.5 to 1.5 mg of sample/mL of solvent. At suitable concentration signal intensity should be between 1 tand 9 megacounts. If the signal intensity is significantly outside of this range, adjust the concentration accordingly and re-run the sample. Please note that if the detector is overloaded, subsequent runs may be contaminated with peaks from that sample.

All samples must be sealed within appropriate containers for the GC autosampler. These sample vials will be provided by your laboratory instructor at the beginning of the lab. The auto-sampler is only compatible with liquid (solution) samples.

Using the instrument:
Single sample injection may be run when only one sample is required. If numerous samples must be run on a single day, a batch run is most efficient. Both approaches will be briefly discussed.
Running a single sample:

1.) Place your sample (in a sealed sample holder) in the auto-sampler tray.
2.) Once your method has been set up, select "inject" > "single sample". When prompted, title your sample, identify the slot in the auto-sampler which holds it and indicate the method you wish to use (this will be CHEM3840default.mth if you have not set up your own method).
3.) When initiated, the auto-sampler will undergo a programmed sequence of actions which include rinsing the syringe and introduction of your sample to the GC column. Do not interfere with any moving parts or move any vials while this sequence is taking place.
4.) Allow the automated procedure to finish. A timer in the central "GC" window of the control software will indicate the amount of time remaining in the procedure. You will be able to watch the GC output in real time as your method is running. Once the procedure is complete, proceed to "Preparing your spectrum."

Running a batch of samples:
To begin a batch of samples, verify that all users have placed their sample containers in the autosampler and that the desired sample list is active in the "system central" window (see step 1 below). From the "Automation" menu, select "Begin Sample List". This will automatically sample and run each vial identified in the sample list according to the parameters outlined in the corresponding "methods" file.

1.) From the "system central" window, open the sample list by selecting "File" > "open sample list". Check which holder in the autosampler corresponds to your sample and name the corresponding field. In the last field, select "Daily Checks" method. This will run a routine diagnostic test once your sample run has completed. *Running the "Daily Checks" method at the end of each sample run is essential for the maintenance of the instrument and proper logging of GC-MS usage. Please do not neglect this step.*
2.) To begin the sample batch, select "Automation" > "Begin Sample List". The automated procedure described above will take place for each sample in the sample list.

Preparing your Spectrum:

1.) Once your sample has run, you may locate the corresponding GC-MS output in the …/VarianWS/data/ directory. To do this, launch the "Review/Process" program from the main toolbar and navigate to your dataset.
2.) A number of methods for visualizing output will be available. Select the GC output to display it in the main window. GC output will be automatically grouped into regions. Left click on a peak to view the corresponding mass spectrum for the region.
3.) You may resize your mass spectrum by clicking and dragging in the spectrum window (lower right by default). The "full scale" option will resize the spectrum to the full m/z range.
4.) Once your mass spectrum is appropriately sized, right click on the spectrum and select "Print". A new window will pop up; select "Print Active".
5.) This will output your file to a new window, from which you may review it, save it, or send it to the printer.

    NOTE: At present (Spring, 2009) hard copy printing has not yet been configured for the GC-MS computer. To output your file in a standard image format, select "export" > "to clipboard" from the print preview window. Paste the image into another program (*e.g.* MS paint) which is capable of saving in a standard image format (.jpg, .gif, etc.) and save it to the hard drive or to any portable data storage device. This can also be accomplished directly by selecting "export" > "to file"; however, the available format types are fairly limited.

Cleaning Up:
Once your sample has been run, rinse any residual material from your sample container into an appropriate waste container. Return the sample container to your laboratory instructor.

Ionization Isomers: Pentaamminebromocobalt(III) Sulfate and Pentaamminesulfatocobalt(III) Bromide

Introduction

Isomers are important in both organic and inorganic chemistry, especially transition metal complexes. Historically, isomerism was foundational in the extended controversy between the camps of Blomstrand-Jørgensen and Werner as to the correct formulation of coordination compounds. Without the aid of modern spectroscopic and structural techniques, the two groups of researchers prepared multiple isomers of compound after compound to try and substantiate their own interpretations of the correct structures. As an example of their widely different interpretations of the same empirical data, consider the two interpretations put forward for the compound $CoCl_3(NH_3)_6$, known then as luteocobaltic chloride (after its colour).

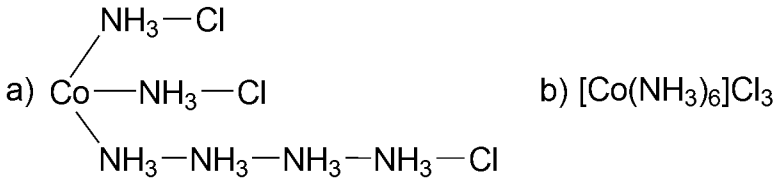


Figure I-1 Jørgensen (a) and Werner (b) formulations of $CoCl_3(NH_3)_6$

The ease of precipitation of the three chloride ions by aqueous silver nitrate was explained away by both camps: Werner had the correct idea, that the chloride ions were ionic and no covalent bond needs to be broken when solutions of this compound react with Ag^+. Jørgensen argued that chloride bound via the nitrogen chains was easily displaced, but chloride directly bound to the metal was more difficult to displace. It is easy in retrospect to ridicule Jørgensen's ideas, but they were fully consistent with much of the evidence, and were patterned on the successful chain interpretation of hydrocarbon compounds.

Where the two theories differed was in the formulations of isomers. Jørgensen accounted for isomerism by altering the chain-lengths of the ammine groups, as in the hydrocarbons. Werner argued for isomerism based on the relative arrangement of groups around the central metal ion, what we now know as stereoisomerism. Werner's theory predicted that there should be two isomers of $[CoCl_2(NH_3)_4]Cl$. One of these, the *praseo* form had been known since 1857. The other proved very difficult to pin down, due to the fact that it is unstable and easily reverts to the *praseo* form. The eventual isolation of the *violeo* isomer by Werner in 1907 led to Jørgensen's final admission of the defeat of his theory.

Since these early controversies, in which a completely unanticipated type of chemical structure was deduced using only chemical techniques and the one physical technique of conductivity measurements, Werner's theories have been unambiguously corroborated by X-ray crystal structures of coordination complexes. A wide variety of isomerism has been identified in coordination complexes. In this lab we consider an example of ionization isomerism, and use IR, spectral and conductivity evidence to distinguish the isomers.

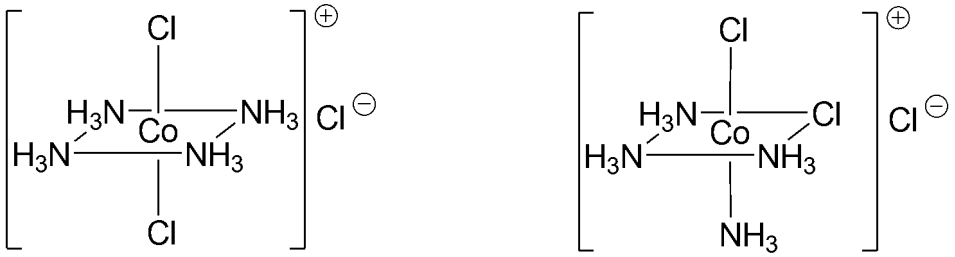


Figure I-2 Stereoisomers of $[Co(NH_3)_4Cl_2]Cl$

Instructional goals:

Properties of the following elements are highlighted: Co, N, O, S and Br

(1) Experience with a classic synthetic sequence for a coordination complex, making use of inert and labile ligands, and the trans influence.
(2) Understanding of ionization isomerism, and why it caused so much confusion before Werner's theory was available.
(3) Experience with the use of infrared spectroscopy to distinguish ionization isomers.
(4) The use of group theory arguments to interpret infrared spectral bands in coordinated small molecules.

Pre-lab exercise

1. Write balanced equations for all steps in parts 1-3 of the synthetic procedure.
2. Define precisely what is meant by ionization isomerism. Sketch out the structures of the two ionization isomers to be prepared in this lab. Why is the Werner theory so important in distinguishing these ionization isomers?
3. To what point groups do the structures drawn in Question 2 belong? Consider only the complex cations.
4. How will IR spectroscopic data distinguish between the two isomers? What chemical tests could one perform to distinguish the two, if IR spectroscopy was not available?
5. What range of IR frequencies do you need to record to get the data required for this experiment?
6. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Concentrated HCl is corrosive and releases vapours of the acid. Handle only in a fume hood.
2. Concentrated aqueous ammonia is corrosive and releases unpleasant vapours. Handle only in a fume hood.
3. Sulfuric acid is extremely corrosive and can burn both the skin and respiratory tract. Use with care and only in a fume hood.
4. The solvents ethanol, and especially diethyl ether, are highly flammable liquids.

Procedure

Preparation of $[Co(NH_3)_5Cl)]Cl_2$ and $[Co(NH_3)_5Br]Br_2$

Dissolve 8 g of $CoCl_2 \cdot 6H_2O$ in 10 mL of water. Add this solution to an evaporating dish containing a slurry of 25 g of NH_4Cl in 50 mL of concentrated aqueous ammonia and stir well using magnetic stirring. Add 5 mL of 30% H_2O_2 dropwise (at this point the colour of the solution should be chocolate brown).

After all of the peroxide has been added, place the evaporating dish on a hot plate in the fume hood. Heat with occasional stirring for 15 – 30 minutes (do not allow to dry). The contents should be a thick brown slurry. Rinse the paste into a 250 mL beaker containing 100 mL of 3 M HCl and heat the solution while stirring for 10 min. Allow the mixture to cool and filter the precipitate using a Büchner funnel and trap. Wash the precipitate with three 10 mL portions of cold water, followed by three 10 mL portions of acetone.

Divide the precipitate into two parts, in 2:1 proportions. Place the smaller portion into a 250 mL beaker containing 100 mL of 2 M ammonia (solution A), and the larger portion into another 250 mL beaker containing 200 mL of 2 M ammonia (solution B). With constant stirring heat both beakers to 50 – 60 °C (no higher). After a short time all of the precipitate will dissolve giving a deep red solution which should be hot filtered (Büchner funnel) through fine filter paper. Transfer each solution to a 1 L beaker and reheat to 50 – 60 °C. Add three 50 mL portions of concentrated HBr in 5 min intervals to solution B, and three 25 mL portions of HCl in 5 min intervals to solution A. (Be careful to maintain the temperature at 50 – 60 °C.) Continue to heat and stir for an additional 15 min, then cool the mixture to room temperature. Filter and wash product B with three 10 mL portions of dilute (2 M) HBr, followed by three 5 mL portions of acetone. Filter and wash product A with three 10 mL portions of cold water, followed by three 5 mL portions of acetone. Label both precipitates and allow them to dry in a desiccator for several days (over KOH).

Note: Work on the following two syntheses simultaneously.

Preparation of pentaamminebromocobalt(III) sulfate

Saturate 250 mL of warm (40 – 45 °C) water with $[Co(NH_3)_5Br]Br_2$. Using a Büchner funnel filter the warm mixture and slowly add it to 40 mL of concentrated HCl. Cool the solution in ice and filter the product, $[Co(NH_3)_5Br]Cl_2$, using a Büchner funnel. Wash the precipitate with three portions of cold 3 M HCl, followed by ethanol until the washings are acid-free. Leave the product to air dry. Dissolve the dry $[Co(NH_3)_5Br]Cl_2$ in concentrated H_2SO_4 by slowly adding small quantities of solid at a time. The evolution of gaseous HCl should be apparent. When no more gas evolves, add 10 mL of cold water to the rapidly stirring semi-liquid mass. Heat the mixture at 70 °C using a hot plate until most of the material dissolves. Filter the hot solution using a glass frit (not filter paper) as quickly as possible and cool the supernatant in an ice bath. Isolate the small quantity of violet crystals by filtration and wash the product with ethanol until the washings are acid-free. Dry the product at approximately 100 °C for two hours.

Preparation of pentaamminesulfatocobalt(III) bromide.

Dissolve 1.0 g of the previously prepared $[Co(NH_3)_5Cl]Cl_2$ in 2.5 mL of concentrated H_2SO_4, (the amount of H_2SO_4 should be almost 6 times the amount of $[Co(NH_3)_5Cl]Cl_2$) and heat the mixture on a steam bath for 10 min. Transfer the solution to a beaker containing 30 mL of cold water, and slowly add a mixture of 5.2 mL of HBr in 20 mL of water to the stirring solution. Let the resulting red solution stand for 5 min at room temperature, then very slowly, with stirring, add 95% ethanol until a faint permanent turbidity (approximately 80 mL of 95% ethanol is required) can be seen. Add a further 10 mL of 95% ethanol to precipitate the desired compound, then filter (using fine filter paper) and wash the solid with ethanol until the washings are acid-free. Air dry the product.

Characterization

Measure the melting point of all four products. Calculate the percent yields and obtain IR spectra. Compare the data with literature values. Record the visible spectrum of each product from 800 to 350 nm in distilled H_2O.

Report

Hand in your product as well as all original spectra. Discuss the IR spectra with respect to the identification of the ionization isomerism. Your discussion should address the following points:

1. What is the structure and point group of each isomer?
2. Which ligands are observed in the IR spectra of the four complexes you have prepared? What are the symmetries of the ligands in each compound?
3. Use group theoretical arguments to support your assignment of the ionization isomers.
4. Discuss the base-hydrolysis mechanism as it relates to the purification step in Part I. Discuss the chemical principles used in the conversion of the purified complexes from Part I into the products of Part II. Explain the origin of any mixtures observed in the products.
5. Why do many cobalt complexes display isomerism?

References

1. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987, Vol 1, p. 1, 31; Vol. 2, p. 23; Vol 4. p. 817.
2. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989.
3. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
4. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, 4th Ed.*; HarperCollins: New York, 1993.
5. Meissler, G. L.; Tarr, D. A. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Inc.: Upper Saddle River, 2004.
6. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Ltd.: Uppers Saddle River, 2008.
7. Shimanouchi, T.; Nakagawa, I. *Inorg. Chem.* **1964**, *12*, 1805.
8. Schlessinger, G. G.; Britton, D.; Rhodes, T.; Ng, E. *Inorg. Synth.* **1967**, *9*, 160.
9. Diehl, H.; Clark, H.; Willard, H. H.; Bailar, J. C., Jr. *Inorg. Synth*. **1939**, *1*, 186.

Linkage Isomers: Nitritopentaamminecobalt(III) Chloride and Nitropentaamminecobalt(III) Chloride

Introduction

For a general introduction to isomerism in transition metal coordination compounds, see the introduction to Experiment 1 on page *1*-1 of this manual.

Certain types of isomerism could not have been foreseen by the classical methods used by Jørgensen and Werner during their long-standing dispute over the coordination theory. Often these could only be determined by modern spectroscopic and structural methods, although these in themselves have some serious pitfalls. An example of such a phenomenon is the linkage isomerism of the nitrite ligand, NO_2^-. This bent ion has lone pairs of electrons on the oxygen and nitrogen atoms, and can coordinate to metals via either type. With metals of suitable intermediate hardness, both forms of coordination may be observed to the same metal fragment. The structures of the two complexes prepared in this laboratory are depicted in Figure II-1.

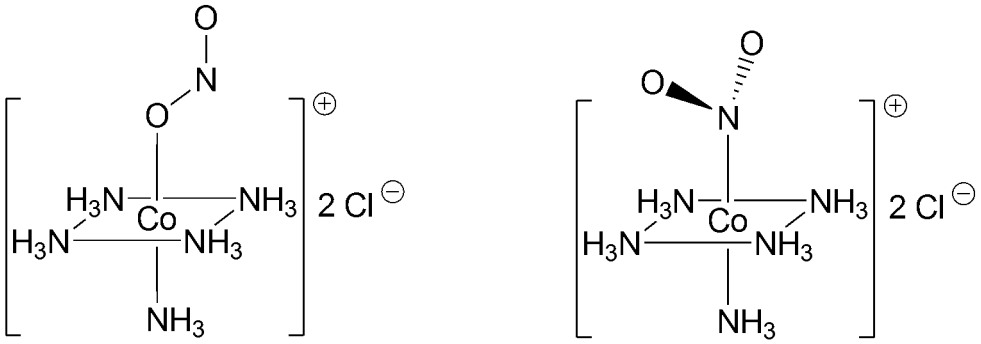


Figure II-1 Linkage isomers $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$

Instructional goals:

Properties of the following elements are highlighted: Co, N, O, and Cl

(1) Experience with a classic synthetic sequence for a coordination complex, making use of inert and labile ligands, and the trans influence.
(2) Understanding of linkage isomerism, and why it caused so much confusion before Werner's theory was available.
(3) Experience with the use of infrared spectroscopy to distinguish linkage isomers.
(4) The use of group theory arguments to interpret infrared spectral bands in coordinated small molecules.

Pre-lab exercise

1. Write balanced equations for of all the steps in parts 1 and 2 of the synthetic procedure.
2. What are the point groups of the structures in Figure II-1?
3. Draw the Lewis structure of the nitrite ion, identifying the lone pairs used in the two coordination modes.
4. What range of IR frequencies do you need to record to get the data required for this experiment? How will IR distinguish the two isomers? Give specific details.
5. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Concentrated HCl is corrosive and releases vapours of the acid. Handle only in a fume hood.
2. Concentrated aqueous ammonia is corrosive and releases unpleasant vapours. Handle only in a fume hood.
3. The solvents ethanol, and especially diethyl ether, are highly flammable liquids.

Procedure

Part 1: Preparation of $[Co(NH_3)_5Cl)]Cl_2$

Dissolve 8 g of $CoCl_2 \cdot 6H_2O$ in 10 mL of water. Add this solution to an evaporating dish containing a slurry of 25 g of NH_4Cl in 50 mL of concentrated aqueous ammonia and stir well using magnetic stirring. Add 5 mL of 30% H_2O_2 dropwise (at this point the colour of the solution should be chocolate brown).

After all of the peroxide has been added, place the evaporating dish on a steam bath in the fume hood. Heat with occasional stirring for 15 – 30 minutes (do not allow to dry). The contents should be a thick brown slurry. Rinse the paste into a 250 mL beaker containing 100 mL of 3 M HCl and heat the solution while stirring for 10 min. Allow the mixture to cool and filter the precipitate using a Büchner funnel and trap. Wash the precipitate with three 10 mL portions of cold water, followed by three 10 mL portions of acetone.

Transfer the impure precipitate to a 600 mL beaker containing 300 mL of 2 M aqueous ammonia and a large flat magnetic stir bar. With constant stirring heat the solution to 50 – 60 °C (no higher!). After a short time all of the precipitate will dissolve giving a deep red solution which should be hot filtered (Büchner funnel) through fine filter paper.

Transfer the solution to a 1 L beaker and reheat to 50 – 60 °C. Add three 75 mL portions of 12 M HCl in 5 min intervals. The solution should be stirred continuously between, and especially vigorously during, the addition of the acid. (Be careful to maintain the temperature at 50 – 60 °C.) Continue to heat and stir for an additional 15 min, then cool the mixture to room temperature. Filter and wash the product with three 10 mL portions of cold water, followed by three 5 mL portions of acetone. Label the precipitate and allow it to dry in a desiccator for several days (over KOH).

Part 2: Preparation of nitritopentaamminecobalt(III) chloride

Dissolve 1.5 g of $[Co(NH_3)_5Cl]Cl_2$ in a mixture of 5 mL of conc. NH_4OH in 25 mL of distilled water. Warm the mixture for 30 min on a steam bath (watch for the onset of decomposition – it may not be necessary to heat for the entire 30 min) and remove any small quantities of undissolved starting material by filtration. CAUTION: It is a common mistake to stop well before a saturated solution is obtained; filtering off the solids too early will lead to poor yields or even complete failure in the next step! Carefully add 6 M HCl until the solution is neutral (pH 7) when tested with long-range pH strips. Cool the mixture in an ice bath. Add 1.5 g of sodium nitrite and keep the mixture in an ice bath for 1 – 2 hours. Filter the precipitate, and wash with ice water, followed by 95% ethanol, and finally, diethyl ether. **Note that IR spectra on the nitrito isomer MUST be collected within approximately one hour of initial preparation!**

Part 3: Preparation of nitropentaamminecobalt(III) chloride

Dissolve 1.0 g of $[Co(NH_3)_5ONO]Cl_2$ in a mixture of 10 mL of hot water containing several drops of concentrated ammonia. While cooling, add 10 mL of concentrated HCl. Cool the solution thoroughly and filter off the $[Co(NH_3)_5NO_2]Cl_2$. Wash the product with 5 mL of 95% ethanol, followed by diethyl ether. Air dry at room temperature for several hours.

Characterization

Measure the melting point of all three products. Calculate the percent yields and obtain their IR spectra. Since chloride ions give no IR signals, and the Co–Cl bond only a weak stretching band, the spectrum of the chloropentaammine complex can be used to distinguish the bands due to the nitrite group from those due to the ammine ligands. Compare the data with literature values.

Study the effects of (i) time, (ii) heat and (iii) ultraviolet light on the solid samples of the two isomers. This can be conveniently done with KBr pellets (if sufficient care is taken with them). For example, prepare two KBr pellets of each of the ONO and the NO_2 complexes. After obtaining the initial spectra, leave one of each in a desiccator for 1 week. Heat the others in an oven at 100 °C for about one hour between measurements. Continue this process until no further changes in the spectral patterns are observed.

For (iii), several hours of exposure to an intense UV light source may be required in order to see significant changes. HINT: It is a waste of paper to print all of the spectra you measure; use the multiple spectra option to compare sequential spectra on the computer screen. Print only definitive spectra, or combine several spectra which indicate the growth and decay of peaks, on a single sheet of paper.

This study should be done with sufficient care that you can unequivocally describe the effect of all three processes on the two isomers. Use IR spectroscopy to monitor the changes. N.B.: It is not necessary to print out all of the IR spectra you measure, *e.g.* if heating the sample causes only a partial change, return it to the oven longer and re-record the spectrum at a later time.

Report

Hand in your product as well as all original spectra. Discuss the IR spectra with respect to the identification of the linkage isomerism. Present the results of your solid-state reaction studies, documented by appropriate IR spectra. Your discussion should address the following points:

1. What is the structure of each isomer?
2. Which ligand is observed in the IR spectrum? What is the symmetry of this ligand in each compound? Use group theoretical arguments to assign the spectral bands of the two isomers.
3. Discuss the base-hydrolysis mechanism as it relates to the purification step in Part I. Discuss the chemical principles used in the conversion of the purified complexes from Part I into the products of Part II. Explain the origin of any mixtures observed in the products.
4. Discuss the formation of the two isomers in this experiment in terms of possible thermodynamic and kinetic control.
5. Discuss the photochemical reaction observed in this experiment. Background on photochemistry of transition metal compounds is available in the course text.

References

1. Wilkinson, G.; Gillard, R. D.; McClevery, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987, Vol. 1, p. 1 & 31; Vol. 2, p. 23; Vol. 4, p. 666.
2. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989.
3. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
4. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, 4th Ed.*; HarperCollins: New York, 1993.
5. Meissler, G. L.; Tarr, D. A. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Inc.: Upper Saddle River, 2004.
6. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Ltd.: Uppers Saddle River, 2008.
7. Adell, B. *Z. Anorg. Allg. Chem.* **1955**, *279*, 219.
8. Wendlandt, W. W.; Woodlock, J. H. *J. Inorg. Nucl. Chem.* **1965**, *27*, 259.
9. Balzani, V.; Ballardini, R.; Sabbatini, N.; Moggi, L. *Inorg. Chem.* **1968**, *7*, 1398.
10. Grenthe, I.; Nordin, E. *Inorg. Chem.* **1979**, *18*, 1109.
11. Grenthe, I.; Nordin, E. *Inorg. Chem.* **1979**, *18*, 1869.
12. Nakamoto, K.; Fujita, J.; Murata, H. *J. Am. Chem. Soc.* **1958**, *80*, 4817.

Preparation of 1,2-Bis(diphenylphosphino)ethane in Liquid Ammonia

Introduction

Liquid ammonia is produced commercially on a large scale via the Haber process; its importance lies in its use as a fertilizer and as a precursor for nitric acid. In chemical laboratories, liquid ammonia is widely used as a non-aqueous solvent, particularly as a medium for reductions. Upon addition of many electropositive metals to liquid NH_3, a deep blue colour characteristic of solvated electrons is produced. Although the liquid range (m.p. = –77.8 °C, b.p. = –33.4 °C) is seemingly inconvenient, the large heat of evaporation (1.37 kJ g^{-1} at the b.p.) ensures easy handling in ordinary glassware.

In this experiment you will prepare a solution of solvated electrons by dissolving a measured quantity of sodium metal in liquid ammonia. This solution will be used to effect the reductive cleavage of a phenyl group from triphenylphosphine to form sodium diphenylphosphide, which will precipitate from the solution as a canary yellow solid. Subsequent addition of 1,2-dichloroethane will afford 1,2-bis(diphenylphosphino)ethane, or "diphos" as it is affectionately known. This compound is widely used in organometallic chemistry as a chelating bidentate ligand capable of stabilizing low-valent transition-metal centres. The coordination properties of diphos will be illustrated through the preparation of a simple Ni(II) complex.

Instructional goals:

Properties of the following elements are highlighted: Na, N, P and Ni

(1) Gaining familiarity with the use of liquid ammonia as a solvent.
(2) Synthesis of an important organophosphorus compound.
(3) The use of diphos in forming coordination complexes.
(4) Use of high-field ^{1}H and ^{31}P NMR spectroscopy in the characterization of these compounds.

Pre-lab exercise

1. Write down balanced chemical equations for the synthesis of "diphos" and the preparation of $[NiCl_2(Ph_2PCH_2CH_2PPh_2)]$.
2. What is the structure of $Ph_2PCH_2CH_2PPh_2$? Create a HyperChem model of this molecule and optimize it in MM+.
3. What are the possible structures of $[NiCl_2(Ph_2PCH_2CH_2PPh_2)]$? How could you distinguish between the possibilities?
4. When Na is dissolved in $NH_{3(l)}$ what is the resultant blue colour due to?
5. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Metallic sodium is extremely hazardous. It reacts with moisture to release H_2, which readily ignites, leading to explosions. Follow directions explicitly, especially proper cleaning of ANY equipment (including gloves, paper towel, etc.) which comes into contact with sodium. Always wear gloves when handling sodium.
2. Anhydrous ammonia is a gas at room temperature, and is extremely toxic. It must be handled only in enclosed apparatus in a fume hood.
3. 1,2-dichloroethane can react explosively with ammonia. Do not add prematurely! It is moderately toxic by inhalation, and is a suspected carcinogen.
4. DUE TO THE EXTREME HAZARD OF THIS EXPERIMENT, STUDENTS MUST WEAR A FULL FACE SHIELD UNTIL ALL OF THE NH_3 HAS EVAPORATED.
5. The solvents methanol, *n*-propanol and especially diethyl ether and acetone, are highly flammable liquids.
6. Dry ice is very cold (–78 °C) and cause severe tissue damage. This is particularly true if skin comes into contact with a dry ice solvent bath. Always wear gloves accordingly.

Procedure

Preparation of 1,2-bis(diphenylphosphino)ethane

Note: This experiment must be done in a fume hood. Wear safety goggles and gloves!

Weigh a Petri dish or small (100 mL) beaker containing approximately 30 mL of xylene on a top loading balance. Add a chunk of sodium metal (1 to 1.5 g); this can be cut and transferred from the main supply using a spatula.

Note: Sodium metal reacts violently with water. Use extreme caution when handling. Do not expose to air for long periods.

Assemble the apparatus as depicted in Figure III-1. Use a 3-neck, 250 mL RB flask containing a teflon coated magnetic stir bar. (N.B. It is helpful to add a line on the outside of the RB flask to indicate 75 mL.) Fill the dewar with a dry ice/acetone mixture and ensure the flask is well inside this dewar to keep the ammonia in the liquid phase during collection. Ensure the stir bar turns freely. Fit the condenser with a drying tube containing fresh potassium hydroxide pellets. Insert the gas inlet tube into the side-arm of the flask and close the other side-arm with a glass stopper. Attach the tygon tubing leading from the ammonia cylinder to the gas inlet tube (**ensure the cylinder is a siphon cylinder which releases ammonia as a liquid**).

Fill the condenser ¾ full with dry ice and add approximately 25 mL of acetone. Add more dry ice as necessary throughout the experiment to maintain this level (before continuing, ask the instructor to inspect the apparatus for proper setup). Open the ammonia cylinder valve slightly and allow the gas to flow in until approximately 75 mL (1.5 inches) have condensed into the bottom of the flask, then close the valve.

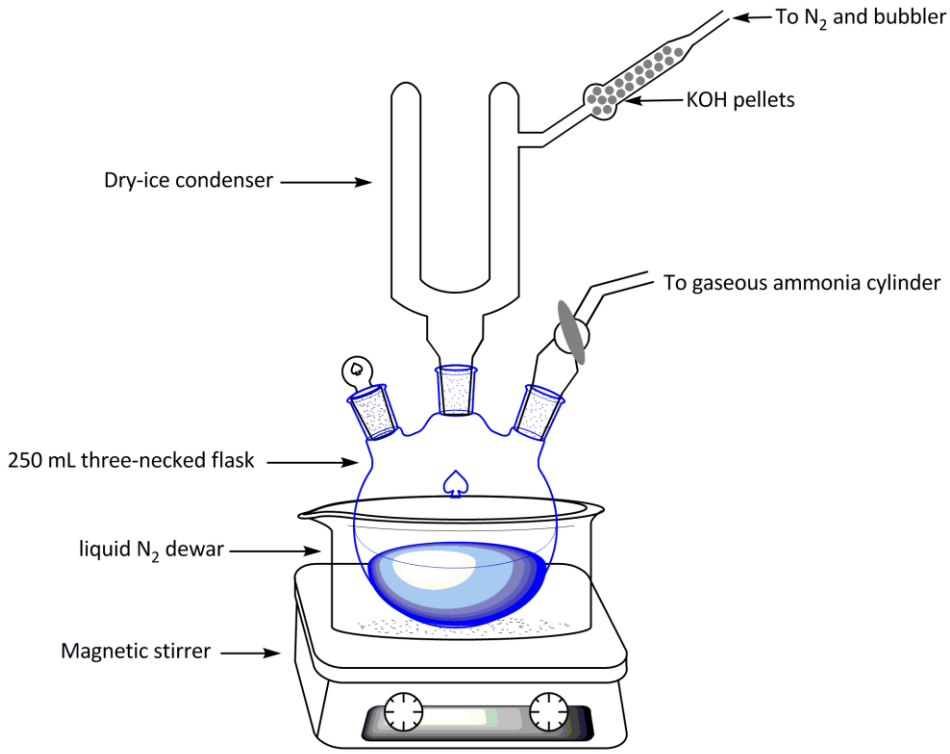


Figure III-I Apparatus for preparation of sodium diphenylphosphide in $NH_{3(l)}$

Adjust the rate of stirring to be slow, but steady. Carefully scrape the surface of the previously weighed sodium chunk down to the shiny metal. Cut pieces of sodium and transfer them (using the spatula) to the reaction flask through the stoppered side-arm (be sure to have a positive pressure of nitrogen when the stopper is removed). Replace the stopper when not making an addition to prevent atmospheric water from condensing in the mixture. The sodium chunk should be added in about 10 separate pieces. Any residual sodium in the Petri dish is decomposed by the **careful** addition of ethanol. Leave this ethanolic mixture standing at the back of the fume hood until the end of the laboratory period, and then cautiously add a small quantity of water to complete the decomposition.

While using a funnel (to avoid material adhering to the ground glass joint), add 5.7 g of triphenylphosphine via the same side-arm used for the sodium addition. Allow the mixture to react for 5 – 10 min with constant stirring. Add approximately 6 g of 1,2-dichloroethane to 1 mL of diethyl ether and cautiously (it may spit back!) add the solution dropwise (use a disposable Pasteur pipette) to the RB flask. As the addition proceeds, the yellow colour should be discharged with concomitant formation of a thick white solution. After 5 – 10 min, remove the condenser and allow the ammonia to boil off. (This will take about 30 min but may be accelerated using a warm water bath (consult your instructor prior to doing this). Alternatively, the flask may simply be left overnight in the fume hood and the reaction worked-up the following day.)

Add 25 mL of water once the flask has reached room temperature. Stopper and shake the flask. This washes away sodium chloride and facilitates the removal of the product. Pour the mixture into a Büchner funnel. Rinse the flask with an additional 25 mL of water and pour the contents

into the funnel. Wash the crude white product with 4 – 2 mL portions of methanol. Transfer the product and filter paper to a 250 mL beaker, add a minimum amount of *n*-propanol and heat on a hot plate to boiling. Hot filter the mixture by gravity and cool the resulting filtrate in an ice-bath. Filter off the crystals of 1,2-bis(diphenylphosphino)ethane in a Büchner funnel and allow them to air dry.

Preparation of [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride

Dissolve 0.16 g of $NiCl_2 \bullet 6H_2O$ in a warm mixture of 10 mL of methanol and 10 mL of 2-propanol. Add this mixture to a warm solution of 0.25 g of 'diphos' in 25 mL of 2-propanol. Filter out the orange needle-like crystals and wash them with diethyl ether. Record the yield and obtain the IR and Raman spectra of your product.

Characterization

Obtain the m.p. of both products. Record the IR spectrum of both products. Record the ^{1}H, ^{13}C and $^{31}P\{^{1}H\}$ NMR spectra (as appropriate) of your products. The purity can be assessed from the integration of the phenyl (δ = 7.0 – 8.0 ppm) and methylene (δ = 1.5 – 2.5 ppm) regions.

Report

Hand in your product as well as all original spectra. Discuss the IR spectrum with respect to the Ni–Cl bands. Provide a full interpretation of the NMR spectra, including chemical shifts, coupling constants and intensities of all signals observed. Explain the phenomenon of "deceptively simple NMR spectra", with specific reference to the ^{1}H NMR spectrum of $Ph_2PCH_2CH_2PPh_2$. At the end of your report, address the following additional questions:

1. Explain the fate of the phenyl sodium co-produced in the reductive cleavage of triphenylphosphine.
2. In what way can the blue colour of solvated electrons be related to the electronic structure of the hydrogen atom?
3. Addition of Fe^{3+} ions in small quantities rapidly discharges the blue colour of $Na/NH_{3(l)}$ solutions. Why?
4. What is the "chelate" effect, *i.e.* why do bidentate ligands have larger binding constants to metals than monodentate ones?

Molecular Modeling

1. Draw out your diphos ligand (without H atoms) in HyperChem and select “Add H and Model Build” from the menu.
2. You will notice that HyperChem adds two extra hydrogen atoms to each phosphorus to make P(V) atoms. Since we want P(III) atoms you must erase the extra hydrogens.
3. Now add the $NiCl_2$ fragment. (Do not “Add H and Model Build” again!)
4. Optimize the structure of the complex using MM+. Is the structure square planar or tetrahedral?

5. Optimize the structure of the complex using PM3. (This may take 15 – 20 min) Is the structure square planar or tetrahedral? Record the Ni–P and Ni–Cl bond lengths as well as the P–Ni–P, Cl–Ni–Cl and Cl–Ni–P bond angles.
6. Which structure is more reasonable, PM3 or MM+? Explain.

References

1. For information on liquid ammonia as a solvent, see: Porterfield, W. W. *Inorganic Chemistry*; Addison Wesley Publishing Company: Reading, 1984, Sections. 7-5 and 7-8.
2. For information on the chelate effect, see Porterfield, W. W. *Inorganic Chemistry*; Addison Wesley Publishing Company: Reading, 1984, Section. 10-4.
3. Carty, A. J.; Harris, R. K. *J. Chem. Soc., Chem. Commun.* **1967**, 234.
4. Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1982, p. 222-223.
5. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989.
6. Meissler, G. L.; Tarr, D. A. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Inc.: Upper Saddle River, 2004.
7. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Ltd.: Uppers Saddle River, 2008.
8. Van Hecke, G. R.; Horrocks, W. D., Jr. *Inorg. Chem.* **1966**, *5*, 1968.
9. Browning, M. C.; Mellor, J. R.; Morgan, D. J.; Pratt, S. A. J.; Sutton, L. E.; Venanzi, L. M. *J. Chem. Soc.* **1962**, 693.
10. Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

Studies on Ligand Field Strength: Chromium Complexes with Ligands of Different Δ_o

Introduction

Chromium(III) is a common example of a d^3 ion, and its electronic spectra have been extensively studied. In this experiment the visible spectra of several complexes of Cr^{3+} will be studied in order to observe the spectral changes produced by varying ligands. Some typical values of Δ_0, the crystal field splitting parameter, for a series of octahedral Cr^{3+}complexes will be determined. For a d^3 ion in an approximately O_h environment, the position of the lowest energy absorption maximum gives a reasonably good value of Δ_0. Furthermore, the ratio of the first two bands (due to $^4A_2 \rightarrow {}^4T_2(G)$ and $^4A_2 \rightarrow {}^4T_1(F)$ transitions) can be used to estimate the B value. Figure IV-1 reproduces a Tanabe-Sugano diagram suitable for Cr(III).

Some of the complexes that will be examined are available, but some are not and must first be prepared. In the first part of this lab the required complexes will be synthesized. The complexes that you will prepare are potassium trioxalatochromate(III) and tris(ethylenediamine)chromium(III) sulfate. Potassium chromium(III)sulfate (chrome alum) and *trans*-$[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$ are commercial products. The latter compound is sold as $CrCl_3 \cdot 6H_2O$, but is known to have the indicated *trans*-structure. You will record the spectrum of this complex, and also aquate it to $[Cr(OH_2)_5Cl]^{2+}$, and record the new spectrum. Finally, the visible and IR spectra of a chromium thiocyanate (thiocyanate = NCS^-) complex will be recorded and the spectral data will be used to determine whether this ligand is attached via the N or S atoms.

Instructional goals:

Properties of the following elements are highlighted: Cr, N, O, Cl and S

(1) Experience with the synthesis of typical chelate complexes of a first-row transition metal.

(2) Experience with the use of IR spectroscopy to characterize transition-metal complexes.

(3) Use of a UV-visible spectrophotometer to characterize transition-metal complexes in aqueous solution.

(4) Experience with the determination of Δ_0 and B constants from electronic spectra of metal complexes.

(5) Use of spectral criteria to distinguish the coordination modes of ambidentate ligands.

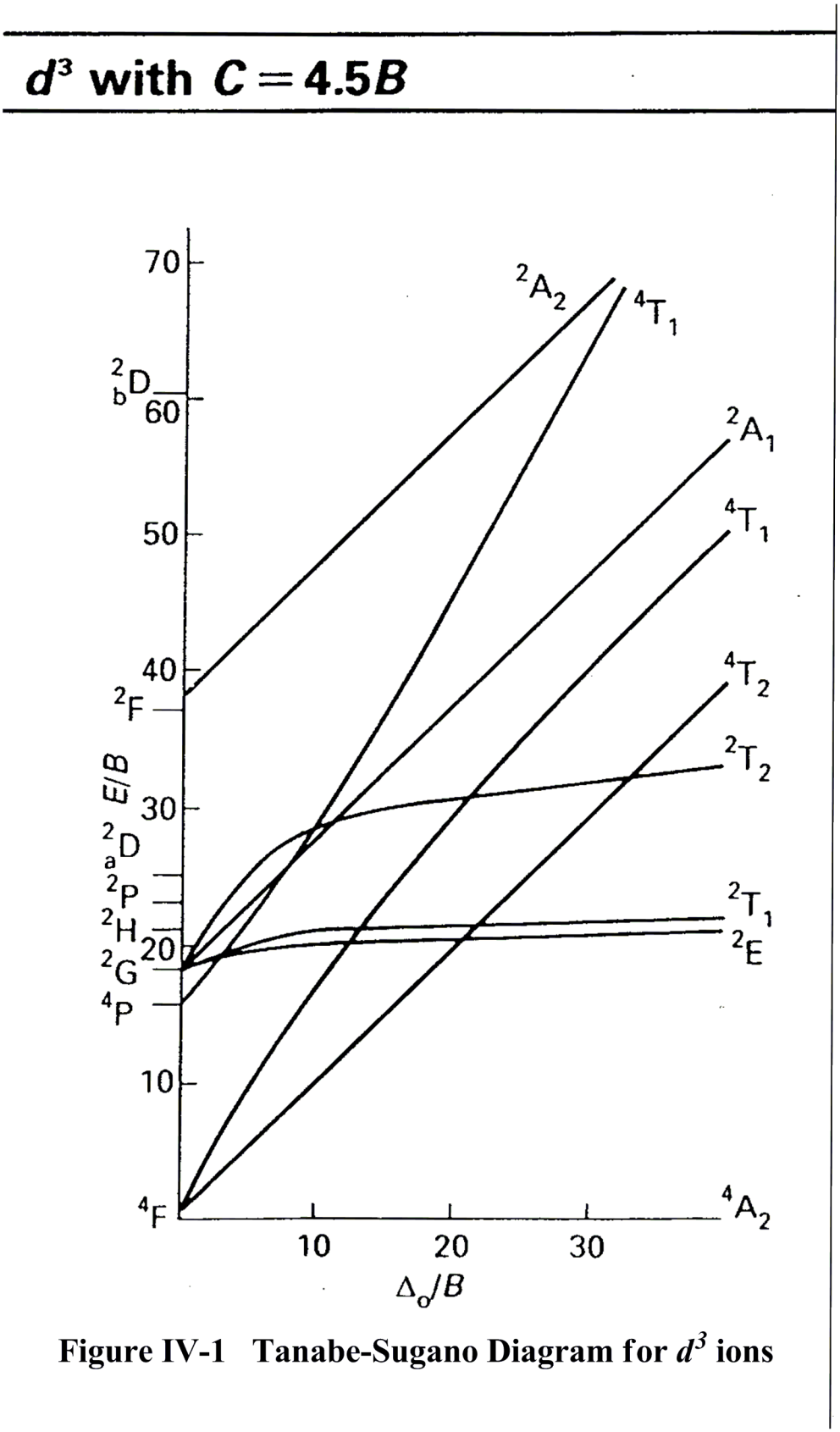


Figure IV-1 Tanabe-Sugano Diagram for d^3 ions

Pre-lab exercise

1. Sketch the structure of each complex prepared in this lab, and assign their point groups.
2. Write balanced equations for the synthesis of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and $[Cr(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$.
3. What is meant by the term alum? What ion is produced in solution by dissolving chrome alum? Why is this salt used as the source of this ion?
4. What spectral criteria will you look for to determine the mode of attachment of NCS^- in $K_3[Cr(NCS)_6]\cdot 4H_2O$?
5. What range of IR frequencies will you record?
6. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Ethanol is a highly flammable liquid and should be handled accordingly.
2. Ethylenediamine emits a strong, foul odour. Use only in a fume hood.
3. Perchloric acid is extremely hazardous and must ONLY be used in the dedicated perchloric acid fume hood located in D-770. Keep away from all oxidizable materials, *e.g.*, paper, organic solvents, clothing. Dry perchlorates of such materials can be vicious explosives!!

Procedure

Preparation of potassium trioxalatochromate(III)

Dissolve 9 g of oxalic acid dihydrate in 20 mL of warm water. Add 3 g of potassium dichromate in small portions. When vigorous effervescence ceases, boil the solution and dissolve 3.5 g of potassium oxalate monohydrate in it. Allow the mixture to cool to room temperature, then add 4 mL of 95% ethanol. Continue cooling the mixture in an ice bath. Collect the blue-green crystals in a Büchner funnel and wash them with 2 – 25 mL portions of 50:50 ethanol:water, followed by 2 – 25 mL portions of 95% ethanol. Air dry the product.

Preparation of tris(ethylenediamine)chromium(III) sulfate

Place 5 g of anhydrous chromium(III) sulfate (previously ground to a fine powder and dried at 110 °C for a day) and 10 mL of 99% ethylenediamine in a 100 mL RB flask (with a ground-glass joint) equipped with an air condenser. Heat the mixture on a steam bath. Within an hour the sulfate will begin to lose its green colour and powdery character. If this does not occur, a drop of water may be added to catalyze the reaction.

Once the reaction is initiated, shake the flask at intervals so that any unreacted sulfate becomes exposed to the amine. Leave the brown mass on the steam bath for at least twelve hours (*e.g.* overnight). Break up the orange product and grind it into powder. Wash the powder with alcohol, and air dry the purified product (tris(ethylenediamine)chromium(III) sulfate).

Spectroscopic study

Prepare 25 mL of a 0.008 M aqueous solution of potassium trioxalatochromate(III), as well as 25 mL of both 0.005 M tris(ethylenediamine)chromium(III) sulfate and 0.005 M potassium chromium(III)sulfate (chrome alum). Record their visible spectra in the range 350 to 800 nm. In this range you can use plastic cuvettes. Note that the tails of the UV bands will be well off-scale at this concentration. Ignore these. The exact concentrations can vary somewhat, but must be known to at least 2 significant figures so that the molar absorption coefficients can be calculated for each absorption maximum.

Commercial $CrCl_3 \cdot 6H_2O$ is, in fact, *trans*-$[Cr(H_2O)_4Cl_2]Cl$. A solution of this compound will slowly aquate to give $[Cr(H_2O)_5Cl]^{2+}$ and $[Cr(H_2O)_6]^{3+}$. Prepare 50 mL of a 0.07 M solution of $CrCl_3 \cdot 6H_2O$ in 0.002 M $HClO_4$. Immediately take 10 mL of this solution, dilute it with 10 mL of 0.002 M $HClO_4$, and run the spectrum of this solution in the range 350 to 800 nm. Use quartz UV cells. **WARNING: Perchloric acid is hazardous and must ONLY be used in the dedicated perchloric acid fume hood located in D-770. Keep away from all oxidizable materials, *e.g.*, paper, organic solvents, clothing. Dry perchlorates of such materials can be vicious explosives!!**

Warm 10 mL of the original solution in a 55 °C water bath (*i.e.* a beaker on a hot plate or burner, checked with a thermometer) for 2 minutes. Immediately add 10 mL of ice-cold water and record its spectrum. This should be $[Cr(H_2O)_5Cl]^{2+}$.

$[Cr(H_2O)_6]^{3+}$ is present in the solution made from chrome alum. However, you are free to see if you can further aquate the complex, which should lead to an identical spectrum.

Record the visible spectrum of $[Cr(SCN)_6]^{3-}$ as a 0.005 – 0.01 M aqueous solution. A small quantity of $K_3[Cr(NCS)_6] \cdot 4H_2O$ is supplied.

Characterization

Record the melting points and yields of the compounds prepared in parts 1 and 2. Record their infrared spectra. Also record the IR spectrum of $K_3[Cr(NCS)_6] \cdot 4H_2O$.

Report

Tabulate all of the spectral data. Using the Tanabe-Sugano diagram (Figure IV-1) and your UV spectra calculate the octahedral crystal field splitting parameter Δ_0 for the ligands water, oxalate, chloride and ethylenediamine. Determine the Racah parameters for each ligand using the supplied Tanabe-Sugano diagram. From a qualitative examination of the spectra for the mixed chloro/aqua complexes, deduce which gives the greater *d*-orbital splitting. Construct a short spectrochemical series for the ligands used. Your discussion should address at least the following points:

1. Which selection rules govern the spectra you have recorded? Discuss with reference to your data.

2. Explain briefly why chromium(III) complexes give more than one d–d band in the electronic spectrum.
3. What effect do the ligands have on the electronic spectra? Discuss the field-strength effects observed in your data.
4. What factors affect the breadth of the observed spectral bands?
5. What effect does chelation have on the symmetry of the ligand fields for chromium(III) complexes?
6. Is the NCS^- ligand in $[Cr(NCS)_6]^{3-}$ bound via the sulfur or nitrogen atom? Base your argument on the spectra you have recorded and by comparison with the other complexes studied in this laboratory.
7. Discuss all IR spectra.

References

1. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, 4th Ed.*; HarperCollins: New York, 1993.
2. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006.
3. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989.
4. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987, Vol 1, p. 213, 250; Vol. 2, p. 772.
5. Meissler, G. L.; Tarr, D. A. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Inc.: Upper Saddle River, 2004.
6. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Ltd.: Uppers Saddle River, 2008.
7. Johnson, H. B.; Reynolds, W. L. *Inorg. Chem.* **1963**, *2*, 468.
8. Dance, I. G.; Freeman, H. C. *Inorg. Chem.* **1965**, *4*, 1555.
9. Espenson, J. H.; Birk, J. P. *Inorg. Chem.* **1965**, *4*, 527.
10. Salzman, J. D.; King, E. L. *Inorg Chem.* **1967**, *6*, 426. (See also *4***,** 532 and *6*, 906).
11. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.

Preparation of Titanocene Pentasulfide, A Sulfur Chain Compound

Introduction

Sulfur can exist in several allotropic forms. The monoclinic and rhombic modifications both consist of crown-shaped eight-membered ring structures. Other ring sizes are known, with n in S_n ranging from 6 to 20; however, these are all thermodynamically less stable than the 8-membered ring, to which they revert if dissolved in any organic medium. For both aesthetic and practical reasons considerable interest has been displayed in the study of these less stable (and more reactive) ring sizes. As a result a number of extremely elegant synthetic routes have been devised to prepare these different rings. These reactions involve the use of a variety of organic and organometallic sulfur transfer agents, *i.e.*, compounds that facilitate the incorporation of specific chain lengths of sulfur units into open chain or cyclic molecules.

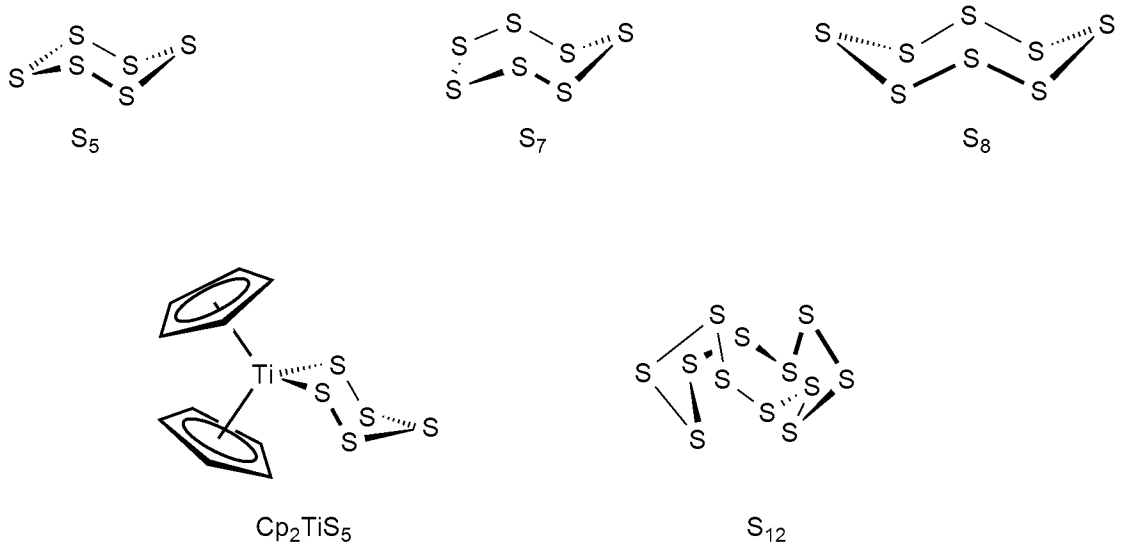


Figure V-1 Structures of representative sulfur chain compounds

In the present experiment the organometallic sulfur-transfer agent bis(cyclopentadienyl)titanium pentasulfide, $(C_5H_5)_2TiS_5$, a versatile compound which has been used to synthesize a wide range of sulfur-containing rings, will be prepared. The preparation involves the use of lithium polysulfide and $(C_5H_5)_2TiCl_2$. The former reagent is generated *in situ* by the action of lithium triethylborohydride ($LiEt_3BH$), known affectionately as **superhydride**, on sulfur (S_8).

The above reaction is extremely efficient in terms of the yield of the product, but care must be taken to ensure the correct stoichiometry, otherwise a brown tar is produced. The superhydride reagent is available commercially, but is extremely air-sensitive. The compound must be transferred via a syringe under an atmosphere of nitrogen. For full discussion of the methods used to perform such a transfer, see the section on air-sensitive compounds in the "General Laboratory Procedures" portion of the lab manual.

Instructional goals:

Properties of the following elements are highlighted: B, S and Ti

(1) Experience with air-sensitive reagents and syringe techniques.
(2) Use of a rotary evaporator.
(3) Understanding and use of ^{1}H NMR and UV-VIS spectroscopy.
(4) Interpretation of mass spectra.

Pre-lab exercise

1. What happens in the reaction of superhydride with cyclic S_8? Write a balanced chemical equation for this reaction. Why is it so important to control the stoichiometry of this addition accurately?
2. Write a balanced chemical equation for the reaction of the sulfur anion with $(C_5H_5)_2TiCl_2$.
3. What are the structures of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2TiS_5$? What are their point groups?
4. Create molecular models of both compounds in HyperChem using the following procedure. The cyclopentadiene molecule is attached to the titanium by drawing a five membered ring, making it aromatic, and then drawing five bonds to the metal atom. When you invoke Add Hydrogens and Model Build, there will be no H atoms added because there are already four bonds to carbon. Turn on Allow Ions, then manually add hydrogen atoms to all five carbons. With Explicit hydrogens turned on, invoke Model Build to improve the 3-D model. Alternatively you may go directly to the MM+ method to optimize the structure. Build $(C_5H_5)_2TiCl_2$ first, as it is more simple and has higher symmetry. Then modify this structure by converting the two Cl atoms to S, and drawing in the remaining three sulfur atoms to make a ring. Note that for these transition metal compounds you can only Geometry Optimize with MM+.

5 Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in time allotted for each operation!

SAFETY NOTES

1. Lithium triethylborohydride in THF solvent is a flammable solution, which can release hydrogen gas, with all of the attendant hazards, if it comes into contact with water or moist air.
2. THF is a highly flammable liquid. It is mildly toxic by inhalation, and has an unpleasant odour. Old bottles of THF can be contaminated with explosive peroxides.
3. Syringe transfer of flammable liquids is hazardous if excess pressures develop. WEAR FULL FACE SHIELD WHILE TRANSFERRING THE SUPERHYDRIDE.
4. The toxicity of the product is unknown, but it has an irritating odour, which can cause headaches in some people. Keep the product isolated from yourself and others!

Procedure

Note: This entire experiment should be done in the fume hood because of the offensive smell of the sulfur compounds that are used and prepared in this experiment. Use acetone to rinse all of the residues from the flask, cuvettes, etc. directly into the solvent waste container IN THE FUME HOOD. Only then should the glassware be removed for cleaning.

Weigh 0.65 g of sulfur and add it to a 250 mL side-arm RB flask with an attached nitrogen bubbler. Put a stir bar into the flask. Add 75 mL of **dry** tetrahydrofuran (THF).

Now set up the superhydride bottle as described in the manual (see air-sensitive compounds) and draw out 8.0 mL of the reagent solution (it is sold as a THF solution). Immediately inject it into the reaction vessel (ask the instructor for assistance with the manipulation of the syringe).

Discharge the contents of the syringe into the flask, extract the syringe, and replace the stopper. Working as quickly as possible, add 1.00 g of $(C_5H_5)_2TiCl_2$ through a powder funnel and stopper the flask again. With a steady flow of nitrogen through the gas bubbler the reaction may be left for 20 min to go to completion. During this timeframe the mixture should be constantly stirred. Use this time to prepare the rotary evaporator.

Pour the contents of the reaction flask into a 250 mL RB flask and remove the solvent using the rotary evaporator. Extract the remaining residues with 100 mL of methylene chloride (CH_2Cl_2) and filter the extracts through a plug of Celite (2 cm deep) in a Büchner funnel. Again strip off the solvent using the rotary evaporator. Dark red crystals of $(C_5H_5)_2TiS_5$ should precipitate during this process.

Scrape the product out of the flask, weigh it, and recrystallize it from 20 – 30 mL (or less, depending on your yield) of hot toluene. Collect with a small Büchner funnel by vacuum filtration.

Characterization

Report the yield and melting point of your product. Record the ^1H and ^{13}C NMR spectra of the product in $CDCl_3$. Measure its UV-VIS spectrum in $CHCl_3$. Record and interpret the mass spectrum. Include an isotope analysis for the parent ion peak.

Report

Hand in your product as well as all original spectra. Provide a full interpretation of the NMR spectra, including chemical shifts, coupling constants, and relative intensities of all signals observed. What information regarding the conformation of the TiS_5 ring can be obtained from the ^1H NMR spectrum of $(C_5H_5)_2TiS_5$? Explain how the appearance of the spectrum would change if the sample were slowly heated (in a suitable solvent) to 100 °C.

The oxidation state of titanium in your product is Ti(IV), *i.e.* it has a d^0 configuration. It therefore cannot exhibit any so-called d–d transitions in its electronic spectrum. To what type of electronic transition can the colour of $(C_5H_5)_2TiS_5$ be attributed? Interpret the UV-VIS spectrum accordingly

(see the molecule modeling exercises below). Interpret the mass spectrum of your product, explaining the principles involved and discussing any unusual effects in this spectrum. At the end of your report, address the following additional questions:

1. How can $(C_5H_5)_2TiS_5$ be used to prepare S_6, S_7, and S_{10}?
2. When heated to reflux in toluene $(C_5H_5)_2TiS_5$ rearranges to its structural isomer $C_{10}H_{10}TiS_5$. What is the structure of this latter compound?
3. What is the major source of sulfur in Canada, and how is it extracted?

Molecular Modeling

1. Compare the structures of your molecular models of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2TiS_5$. How does this explain the presence of a single C_5H_5 signal in the NMR spectrum of the former, but two distinct signals of equal intensity in that of the latter?
2. In order to analyze the UV-Vis spectrum, perform a Single Point PM3 calculation on your model of $(C_5H_5)_2TiS_5$. Plot out and identify the nature of both the HOMO and LUMO. The lowest energy (longest wavelength) electronic band is usually the HOMO-LUMO transition.
3. Build a model of the isomeric structure discovered for $(C_5H_5)_2TiS_5$ after heating ("additional question #2"). Pay careful attention to the presence of single and double bonds, and the location of the hydrogen atoms. Use MM+ to optimize the geometry of this compound.

References

1. Shaver, A.; McCall, J. M. *Organometallics* **1984**, *3*, 1823.
2. Muller, E. G.; Peterson, J. L; Dahl, L. F. *J. Organomet. Chem.* **1976**, *111*, 91.
3. Bruce, M. R. M; Kenter, A.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 639.
4. Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 5620.
5. Steudel, R. *Topics Curr. Chem.* **1982**, *102*, 149.
6. Giolando, D. M.; Rauchfuss, T. B *J. Am. Chem. Soc.* **1984**, *106*, 6455.
7. Abel, E. W.; Booth, M.; Orrell, G. K. *J. Organomet. Chem.* **1978,** *160*, 75.
8. Butler, I.S.; Harrod, J.F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989.
9. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, 4th Ed.*; HarperCollins: New York, 1993.
10. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006.
11. Meissler, G. L.; Tarr, D. A. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Inc.: Upper Saddle River, 2004.
12. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry, 3rd Ed.*; Pearson Education Ltd.: Uppers Saddle River, 2008.

Pentacoordination: Preparation and Reactions of Vanadyl Acetylacetonate, $VO(acac)_2$

Introduction

Most of the complexes prepared in experiments 1 to 5 have been hexacoordinate with octahedral or at least *pseudooctahedral* inner coordination spheres. Historically, these have also been the most studied complexes. Nevertheless, there are many examples of coordination numbers ranging from 3 to 9, and a variety of structures can be found. After hexacoordinate (octahedral), the next most-studied geometries have been tetracoordinate systems, which are tetrahedral or square planar. Considerable effort has gone into elucidating the relationship between these two geometries. Some complexes can easily interconvert between the two geometries, and in fact, the halogen complexes of Ni(II) $[NiX_2\{P(CH_2C_6H_5)(C_6H_5)_2\}_2]$ can be crystallized in *both* forms.

Pentacoordinate complexes are much less common than either tetra- or hexacoordinate ones, but have received intensive study in recent years. They are more common for some metals, and often for one oxidation state, than others. There are two principal geometries, trigonal bipyramidal and square pyramidal. Figure VI-1 shows the frameworks of these shapes, and the solid-body geometry they correspond to.

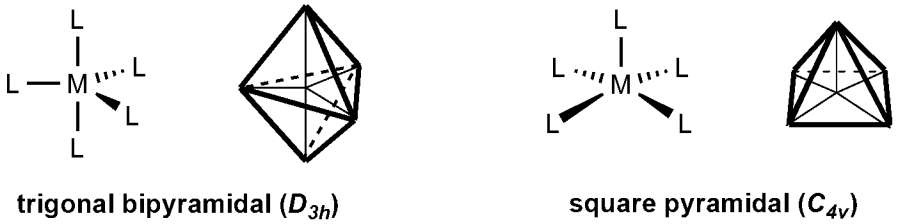


Figure VI-1 Common geomtries for pentacoordinate complexes

It is interesting and highly important that these two structures are similar enough in energy to easily interconverted. Consequently, the deformation energy is low, and many complexes exist with some intermediate shape. The interconversion process, called *Berry pseudorotation*, is used to explain the stereochemical non-rigidity (*fluxionality*) of many pentacoordinate complexes.

In this experiment a pentacoordinate complex of V(IV) using the chelating *acetylacetonate* ligand, the anion of acetylacetone, or 2,4-pentanedione, will be prepared. Consequently, the IUPAC name for this complex is *bi*-(2,4-pentanedionato)oxovanadium(IV). Although all five donors to the metal are oxygen atoms, they are of different type. The terminal V=O bond is extremely short (155 – 168 pm), and this always remains the axial ligand. In other words, vanadyl acetylacetonate is not subject to Berry pseudo-rotation. On the other hand, this complex does show a common reaction of pentacoordinate compounds, vis à vis the addition of a sixth ligand to achieve a pseudooctahedral geometry. The effect of the coordination change can be monitored by visible spectroscopy (a colour change) as well as by IR spectroscopy.

Vanadium(IV), d^1, is paramagnetic with a single unpaired electron. This oxidation state is most commonly found as the vanadyl ion, and the complex prepared in this experiment can be thought of as a derivative of the vanadyl group. Vanadyl has a very characteristic "signature" in the *electron paramagnetic resonance* (EPR) spectrum. This is due to coupling of the electron spin

with the nuclear spin of the metal atom. A copy of an EPR spectrum of vanadyl acetylacetonate, which you will interpret as part of your laboratory report, will be provided.

Instructional goals:

Properties of the following elements are highlighted: V and O.

(1) Experience with a synthetic sequence involving a redox change in a metal, which is stabilized thereafter by coordination.
(2) Use of solution IR spectroscopy to characterize a metal complex and its reaction products.
(3) Understanding the factors which govern adduct formation by a five-coordinate complex.
(4) Experience in the interpretation of EPR spectroscopic data for a paramagnetic transition metal complex.
(5) Experience in the interpretation of a mass spectrum of a covalent coordination compound.

Pre-lab exercise

1. What is the formula and structure of the acetylacetonate ion? What is the formula for the vanadyl ion?
2. Sketch the structure of the title complex and its adducts. To what point group does it belong? Ignore the rotation of the methyl groups in making this assignment.
3. Write balanced equations for the synthesis of vanadyl acetylacetonate.
4. Write balanced equations for the formation of the nitrogen base adducts with vanadyl acetylacetonate.
5. What are the naturally occurring isotopes of vanadium? How many lines do you expect in the EPR spectrum of vanadyl acetylacetonate? What should the relative intensity of these lines be?
6. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Sulfuric acid is extremely corrosive and can burn both the skin and respiratory tract. Use with care and only in a fume hood.
2. The solvents ethanol and acetonitrile are highly flammable liquids.
3. Acetylacetone emits a strong, foul odour. Use only in a fume hood.
4. Pyridine is moderately toxic, and has an extremely unpleasant odour. It is known to cause sterility in laboratory rats. Use only in the hood. Rinse wastes away (aqueous down the hood sinks, organic rinsed into the waste container with acetone) before removing glassware from the hood for washing.

Procedure

Preparation of $[VO(acac)_2]$

Add 6 mL of distilled water, 4.5 mL of concentrated sulfuric acid and 12.5 mL of 95% ethanol to a 250 mL RB flask containing 2.5 g of pure vanadium(V) oxide. Heat the mixture, with stirring, using a heating mantle set to approximately 60 V. Be sure to equip the RB flask with an appropriate condenser. As the reaction proceeds the initial slurry of vanadium(V) oxide darkens, becomes light green and finally turns dark blue. The reduction of vanadium(V) is completed in 30 minutes. Add 10 mL of water and gravity filter the solution; collect the filtrate in a 750 mL Erlenmeyer flask. Add 6.5 mL of acetylacetone (2,4-pentanedione) and stir the solution for 10 minutes. Neutralize the solution by slowly adding, with continuous stirring, a solution of 10 g of sodium carbonate dissolved in 60 mL of water. Collect the precipitated product by filtration in a Büchner funnel and air dry.

Recrystallize the product by dissolving in a minimal amount of hot chloroform in a small Erlenmeyer flask. Hot filter the solution by gravity through fluted filter-paper, and cool to room temperature. Add 10 mL of diethyl ether to complete the precipitation. Filter and allow the product to dry in air.

Spectroscopic study of adduct formation in $[VO(acac)_2]$

Note: If necessary the spectroscopic study may be left after the recrystallization of $[VO(acac)_2]$. At least one full period will be required for the spectroscopic study.

Measure IR spectra of $[VO(acac)_2]$ as solutions in (1) CH_2Cl_2, (2) CH_3CN and (3) pyridine using the 0.2 mm NaCl solution cells. Remember that these solvents are very volatile, so do not leave the cells in the path of the IR light for any longer than is necessary to record the spectrum, and do all solvent handling in a fume hood. *Pyridine is toxic and is known to cause sterility.*

Prepare 0.025 M solutions (concentrations known to at least 2 significant figures are required to calculate ε values) of $[VO(acac)_2]$ in the following solvents: (1) CH_2Cl_2, (2) CH_3CN and (3) pyridine. Obtain the visible spectra of these solutions in the range 350 – 800 nm.

Characterization

Record the yield and melting point of the recrystallized $VO(acac)_2$. Record the mass spectrum of $VO(acac)_2$.

Report

Hand in your product as well as all original spectra. Discuss the IR and visible spectra with respect to the identification of the parent complex and its adducts. Obtain a copy of the EPR spectrum of vanadyl acetylacetonate from your instructor. Interpret the spectrum completely. This means accounting for the number and the intensity of the lines, calculating the size of the hyperfine coupling constant and the value of the g-factor. Provide a detailed interpretation of the mass spectrum. Your discussion should address at least the following points:

1. What is the expected position of the ν(V=O) band in the IR spectrum?

2. What effect does adduct formation have on the frequency of this band? What difference might one expect between pyridine and acetonitrile?
3. What is the origin of the g-factor in EPR spectroscopy?
4. Briefly describe what is thought to be the origin of the visible spectrum, *i.e.* to what transitions are the three observed bands attributed?
5. What is the main difference between the electronic spectra of $[VO(acac)_2]$ measured in different solvents? Why do the solvents have such a marked effect on the spectrum? With what chemical property of the solvents can this difference be correlated?

References

1. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006.
2. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989, 221. (A simple introduction to ESR spectroscopy.)
3. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987, Vol 1, p. 47; Vol. 2, p. 365; Vol 3, p. 504.
4. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry, 6th Ed.*; Wiley: New York, 1999.
5. Lever, A. B. P. *Inorganic Electronic Spectroscopy, 2nd Ed.*; Elsevier: Amsterdam, 1984, p. 389.
6. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.

Metal-Metal Multiple Bonds: Dimolybdenum Tetraacetate and Cesium Di-μ-chloro-hexachloro-μ-hydrido-dimolybdate

Introduction

In the past two decades, the synthesis and study of metal-metal bonded compounds has been one of the most intensely investigated aspects of inorganic chemistry. Ever since the discovery that the $Re_2Cl_8^{2-}$ anion possesses a strong metal-metal interaction, which was attributable to a quadruple bond, hundreds of research papers and several books have been written on the topic of metal-metal multiple bonding.

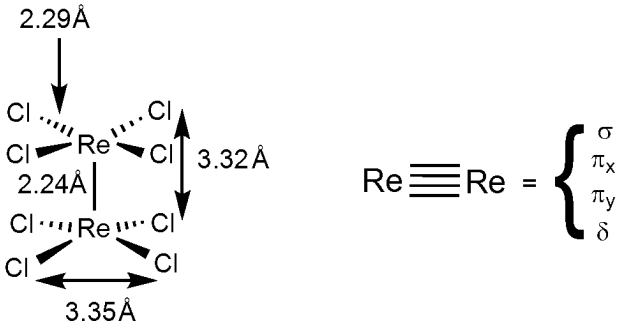


Figure VII-1 The quadruple bond in $[Re_2Cl_8]^{2-}$ as evidenced by eclipsed conformation and the short Re Re distance

Metal-metal quadruple bonds are unique in that they possess one σ, two π and one δ bond. δ bonds are an entirely new type from those found for the main-group elements, and were therefore of great interest. In fact, multiple bonds between metals have proven to be very useful, and complexes of this general type have found applications as catalysts for a variety of organic transformations. The δ bonds themselves have not assumed a great practical significance, however. In this experiment two classic complexes with metal-metal bonds of different formal bond order, $Mo_2(O_2CCH_3)_4$ and $Cs_3[Mo_2Cl_8H]$ will be prepared. The latter is made from the former, and is just one example of dozens of complexes which can be prepared from $Mo_2(O_2CCH_3)_4$.

Instructional goals:

Properties of the following elements are highlighted: Mo, O, H, Cl, and Cs

(1) Experience with a synthetic procedure under an inert atmosphere.
(2) The preparation and subsequent reaction of a metal-metal quadruple bond.
(3) Use of Raman spectroscopy and its unique advantages over IR spectroscopy.
(4) Experience in the interpretation of a mass spectrum of a complex inorganic molecule.

Pre-lab exercise

1. What are the structures of $Mo_2(O_2CCH_3)_4$ and $[Mo_2Cl_8H]^{3-}$? To what point groups do they belong? What is the function of the cesium in $Cs_3[Mo_2Cl_8H]$?
2. Write balanced equations for all of the reactions involved in the synthesis of $Mo_2(O_2CCH_3)_4$.
3. Write balanced equations for all the reactions involved in the synthesis of $Cs_3[Mo_2Cl_8H]$.
4. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. $Mo(CO)_6$ is a volatile solid and is highly toxic. CO gas is toxic and is released during this experiment. Perform all operations in a fume hood.
2. Glacial acetic acid can cause severe burns. Use gloves and handle accordingly.
3. Concentrated HCl is corrosive and releases vapours of the acid. Handle only in a fume hood.
4. Ether is a highly flammable liquid and should be handled accordingly.

Procedure

Note: This experiment must be started the night before the lab period. The time required to set up and start the experiment is approximately 30 minutes.

Also Note: $Mo(CO)_6$, like all metal carbonyls, is highly toxic. All operations involving this compound should be done IN THE FUME HOOD. The entire procedure for this laboratory should be done in the fume hood. Move a balance to the hood temporarily to weigh the $Mo(CO)_6$

Preparation of $Mo_2(O_2CCH_3)_4$

Place 3 g of $Mo(CO)_6$ and a teflon coated magnetic stir bar into a 2-necked 250 mL RB flask equipped with a ground glass joint and a side arm. Flush the flask and its contents with nitrogen for five minutes, and while maintaining the nitrogen stream add 100 mL of glacial acetic acid and 10 mL of acetic anhydride to it. [CAUTION: Glacial acetic acid can cause severe burns – handle it with caution! If you do spill any on your skin, immediately wash the area with copious amounts of cold water.]

Fit the flask with a reflux condenser to which a mineral oil bubbler is attached. Place the apparatus in an electric heating mantle (controlled with a Variac set to approximately 70 V) on a magnetic stir plate (Figure VII-2). Heat the reaction mixture to reflux overnight while stirring and maintaining the inert atmosphere in the system.

Allow the reaction mixture to cool to room temperature and filter in a Büchner filter in a fume hood. If little product is obtained cool the reaction mixture with an ice bath and filter again. Wash the bright yellow solid, $Mo_2(O_2CCH_3)_4$, with 3 – 10 mL portions of ethanol followed by 3 – 10 mL portions of ether.

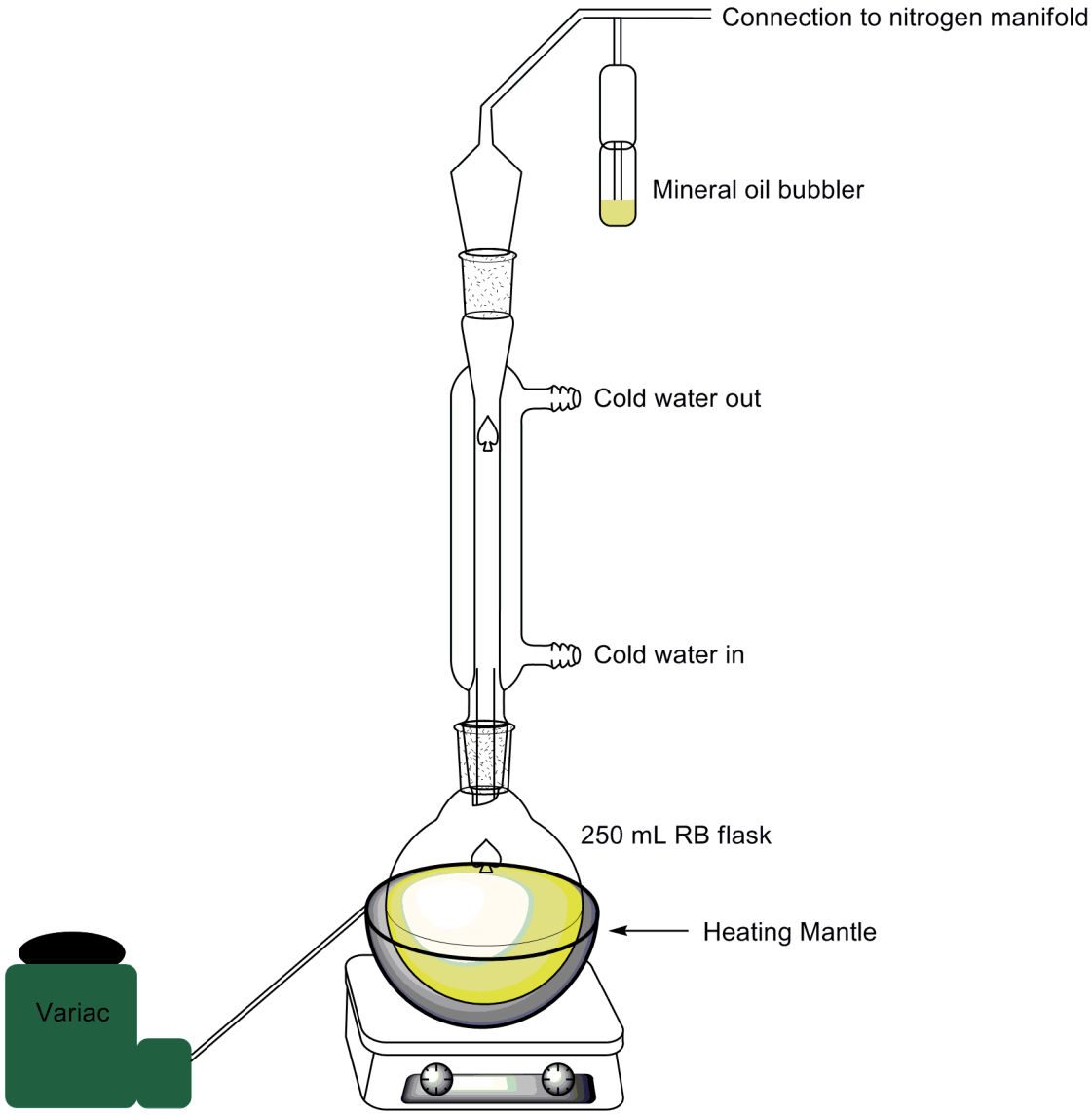


Figure VII-2 Apparatus for preparation of $Mo_2(O_2CCH_3)_4$

The product can be handled in air for brief periods of time, but is best stored in a nitrogen-filled Schlenk tube. The Schlenk tube is first attached to the double-manifold vacuum line, and all of the air is pumped out. Nitrogen gas is then admitted to refill the tube. Repeat at least twice. The empty tube can then be tared, filled with the molybdenum acetate, and purged once again. Whenever the seal is broken, the purge cycle must be performed.

Preparation of $Cs_3[Mo_2Cl_8H]$

Note: All operations involving this compound should be done IN THE FUME HOOD

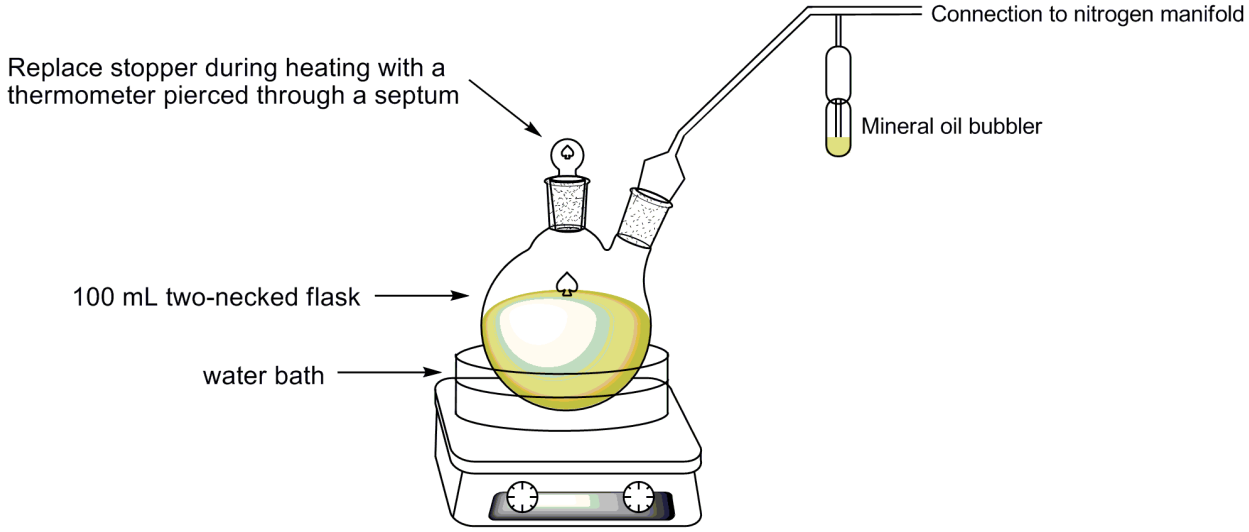


Figure VII-3 Aparatus for the synthesis of $Cs_3[Mo_2Cl_8H]$

Place 0.5 g of $Mo_2(O_2CCH_3)_4$ and a teflon coated magnetic stir bar in a 100 mL, two-necked RB flask equipped with a ground glass joint and a side arm. Flush the flask and its contents with nitrogen for five minutes. Slowly add 50 mL of 12 M HCl while maintaining the nitrogen stream. Allow the reaction mixture to stir at 60 °C for one hour (a thermometer inserted through a rubber septum can be placed into the flask through one joint, while nitrogen continues to be introduced to the flask through the other joint). Add 0.75 g of CsCl to the warm solution. Remove the thermometer and replace with a stopper. Cool the solution slowly to room temperature. Collect the yellow product, $Cs_3[Mo_2Cl_8H]$, using a Büchner funnel and wash with 3 – 10 mL portions of ethanol followed by 3 – 10 mL portions of ether.

Characterization

Report the yield of both products, and measure their melting points. Record the IR spectra of both complexes. Record Raman spectra of your samples in sealed melting point capillaries. Record the mass spectrum of $Mo_2(O_2CCH_3)_4$. Compare the data with literature values.

Report

Hand in your product**s** as well as all original spectra. Interpret the IR and Raman spectra. Assign the mass spectrum of $Mo_2(O_2CCH_3)_4$. Your discussion should also address at least the following points:

1. Using the metal d-orbitals, pictorially illustrate the components of a metal-metal quadruple bond in an $M_2X_8^{n-}$ species (*e.g.* M = Re, Mo.)

2. Construct a simple molecular orbital energy level diagram for $Mo_2(O_2CCH_3)_4$. Be sure to show the proper orbital occupancies and include the relevant antibonding orbitals in the figure.
3. What does the Raman spectrum of $Mo_2(O_2CCH_3)_4$ show which the IR spectrum does not? Why?
4. Why was acetic anhydride added to the reaction mixture in part 1 of the procedure?
5. What other types of bidentate ligands could replace the carboxylate groups in $Mo_2(O_2CCH_3)_4$ to yield structurally analogous metal-metal bonded complexes?

References

1. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry, 6th Ed.*; Wiley: New York, 1999.
2. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006.
3. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989.
4. Cotton, F. A.; Harris, C. B. *Inorg. Chem*. **1965**, *4*, 330.
5. Norman, J. G.; Ryan, O. B. *J. Comput. Chem.* **1980**, *1*, 59.
6. Brignole, A. B.; Cotton, F. A. *Inorg. Synth*. **1972**, *13*, 87.
7. Norman, J. G., Jr.; Kolari, H. J.; Gray, H. B.; Trogler, W. C. *Inorg. Chem.* **1977**, *16*, 987.
8. Trogler, W. C. *J. Chem. Educ*. **1980**, *57*, 424.
9. Shriver, D. F.; Cooper, C. B. *Adv. Infrared Raman Spectroscopy* **1980**, *6*, 127. (On the vibrational spectra of these compounds.)
10 Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, 4th Ed.*; HarperCollins: New York, 1993.
11. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987, Vol 3, p. 1304.
12. Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1976**, *15*, 522.
13. Miller, S. S.; Haim, A. *J. Am. Chem. Soc.* **1983**, *105*, 5624.
14. Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 4150.
15. Nguyen, T.; Sutton, A. D.; Brynda, M.; Fettinger, J. C.; Long, G. J.; Power, P. P. *Science* **2005**, *310*, 844. (The first quintuple bond)

Cyclopentadiene Complexes: The Preparation and Characterization of Ferrocene

Introduction

In 1950, the known transition metal organometallic compounds included several metal carbonyls (*i.e.* M–CO compounds) and a variety of very unstable alkyl complexes analogous to Grignard and organozinc compounds (*i.e.* M–CH_2–(–CH_2–)$_n$–CH_3 compounds). The latter were much less stable than their main-group analogues. When ferrocene was independently discovered by both Kealy and Pauson, and Miller and co-workers, its structure was unknown, but its properties were strikingly different. It was stable in air and resisted decomposition if heated *in vacuo* above 500 °C; it could even be sublimed in the open atmosphere.

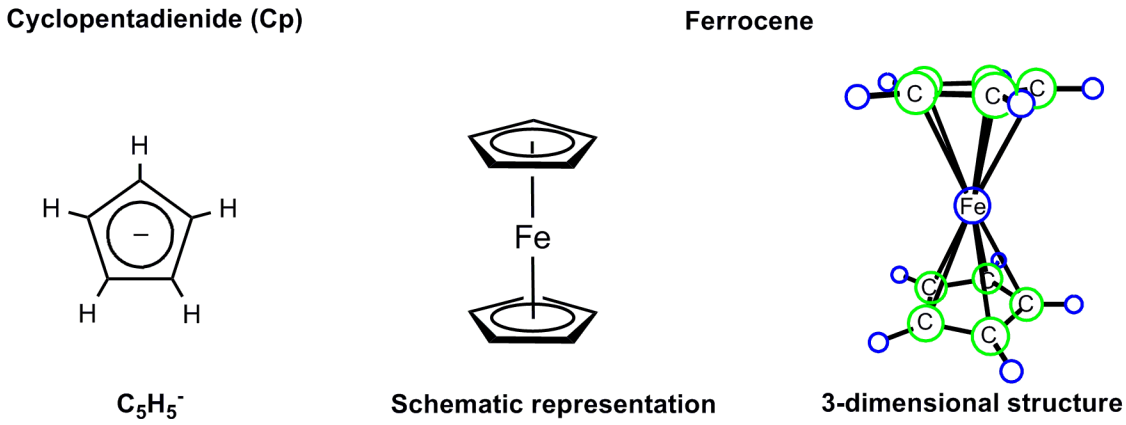


Figure VIII-1 Structures of the cyclopentadienide ion and ferrocene

These properties are explained by the physical and electronic structure of ferrocene. The physical structure is that of a metal atom "sandwiched" between two planar aromatic C_5H_5 rings. The electronic structure necessitates a molecular orbital description, but requires the involvement of metal *d* orbitals which overlap with the *p* orbitals of the aromatic ring. The cyclopentadiene anion is a 6π-electron aromatic ring which obeys the Hückel 4N + 2 rule, and since the molecule is overall neutral, this implies that the formal oxidation state of the iron atom is +2.

In this laboratory ferrocene will be prepared and purified by sublimation in air. The infrared, UV-visible and NMR spectral data on this compound will be obtained. Are the data consistent with the proposed structure?

Instructional goals:

Properties of the following elements are highlighted: Fe, C and H

(1) Experience with the synthesis of a transition-metal organometallic compound.
(2) Use of sublimation to purify a volatile organometallic compound.
(3) Learn to distinguish the electronic absorption spectra of organometallic complexes from traditional coordination complexes.
(4) Experience with NMR for the characterization of diamagnetic organometallic compounds.

Pre-lab exercise

1. Write balanced equations for the synthesis of ferrocene from the indicated starting materials.
2. What is the role of the KOH in this experiment?
3. What range of IR frequencies need to be recorded in this experiment?
4. What is a good starting concentration to use in the UV-visible spectral measurement of ferrocene?
5. What is sublimation, and how can it be used to purify a compound? What properties must the compound possess to make it suitable for this type of purification?
6. Map out the timing of this project. Several steps, *e.g.* the cracking of dicyclopentadiene and the sublimation of ferrocene must be performed outside of regular lab hours, but require minimal supervision. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Cyclopentadiene emits a strong, foul odour. Use only in a fume hood.
2. Dimethylsulfoxide (DMSO) is a mildly toxic, flammable solvent which readily penetrates the skin. Although it has relatively low toxicity, any chemicals dissolved in it also penetrate the skin. Use gloves an handle accordingly. Note that nitrile gloves can dissolve in DMSO; hence, great effort should be taken to minimize contact with the solvent.
3. Ethanol and 1,2-dimethoxyethane are highly flammable liquids and should be handled accordingly.

Procedure

Preparation of cyclopentadiene, C_5H_6 (cracking of dicyclopentadiene)

This procedure must be started several hours before the laboratory begins, using the preassembled apparatus for the cracking of dicyclopentadiene. Charge the distillation flask with 25 mL of dicyclopentadiene. Warm the recirculating heating bath to 60 °C. While running warm water through the column of the still, and cold water through the collection condenser, slowly distill C_5H_6 from the dimer, collecting only the low boiling point fraction (below 44 °C; the b.p. of C_5H_6 is 42.5 °C, whilst that of $C_{10}H_{12}$ is 142 °C). Since slow dimerization occurs at ambient temperature, the freshly distilled C_5H_6 must be used within 2 to 3 hours, or stored at –78 °C until used.

Preparation of [Fe(η^5-C_5H_5)$_2$], ferrocene

Using the blender provided, grind up 60 g of KOH pellets. Store the ground material in a capped jar since finely ground KOH is deliquescent.

In a fume hood with nitrogen outlets, assemble the apparatus depicted in Figure VIII-2. Charge the 500 mL flask with an egg-shaped stir bar, 120 mL of 1,2-dimethoxyethane and the powdered KOH. Stopped one side-arm and connect the other via a bubbler to the nitrogen outlet. While the mixture is slowly stirring the flask should be flushed with a strong stream of nitrogen gas. After stirring and flushing for 15 minutes, add 11.0 mL of cyclopentadiene. Continue flushing for an additional 5 minutes. Attach the 100 mL dropping funnel (with the stopcock open) to the central neck of the flask. After allowing the funnel to be thoroughly flushed, close the stopcock and charge it with a solution of 13.0 g of $FeCl_2 \cdot 4H_2O$ in 50 mL of dimethylsulfoxide (the iron chloride should be ground to a fine powder with a mortar and pestle before attempting to prepare this solution).

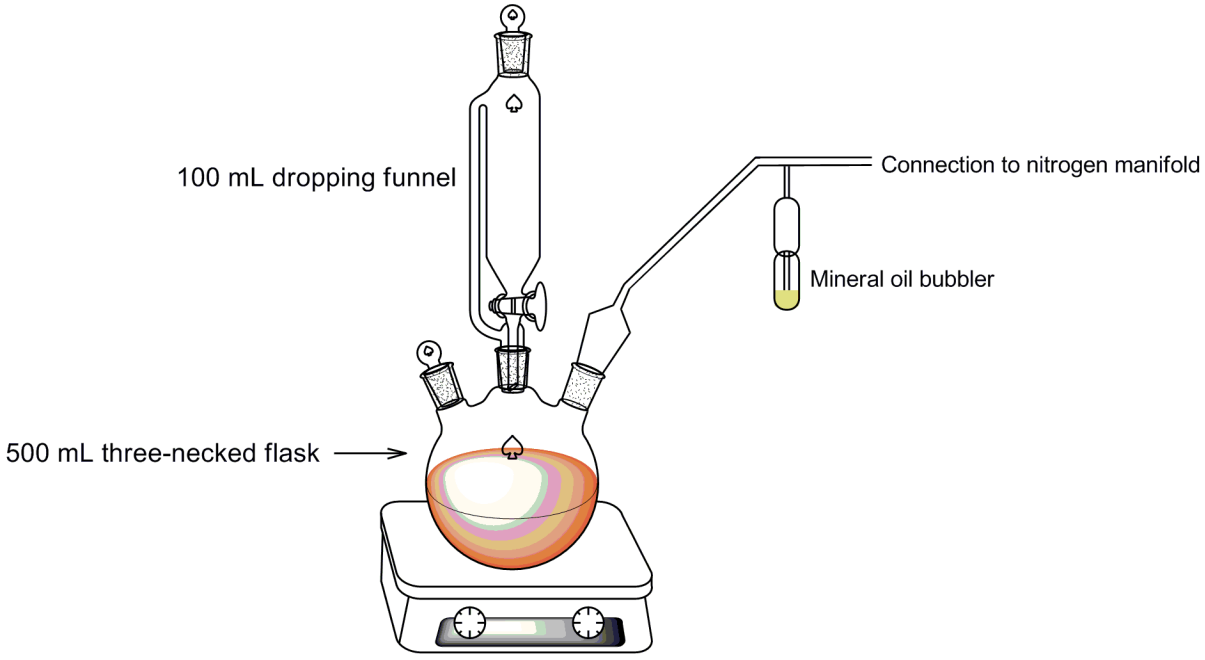


Figure VIII-2 Aparatus for the synthesis of ferrocene

Stir the cyclopentadiene mixture vigorously while adding the iron chloride solution at a rate so that addition is complete after 45 minutes. Close the stopcock at this point and continue stirring for a further 30 minutes.

Stop the nitrogen flow and add the mixture to a slurry of 180 mL of 6 M HCl and 200 g of crushed ice. Use the resulting liquid to rinse out the flask if necessary. Stir the slurry for approximately 15 minutes, and then gently warm the mixture to melt any remaining ice. Collect the precipitate in a Büchner funnel and wash it with 4 – 25 mL portions of distilled water. Spread the moist solid out on a large watch glass to air dry overnight.

Purification of ferrocene

An extremely pure product can be obtained by sublimation. Place the material to be sublimed in the inverted cover of a Petri dish so that none of the material is within 2 mm of the wall of the cover. The layer should not be more than 5 mm deep. Invert the Petri dish and carefully place it inside the cover (Figure VIII-3).

Place the apparatus on a hot plate and gradually warm it until the top surface of the apparatus is almost too hot to touch. After 4 to 10 hours, the ferrocene should be completely sublimed onto the upper glass surface. It should be separated from the small amount of residue on the bottom of the dish by a gap of several mm. If any of the ferrocene crystals are touching the residue, the temperature of the hot plate should be increased, and more time allowed for complete sublimation.

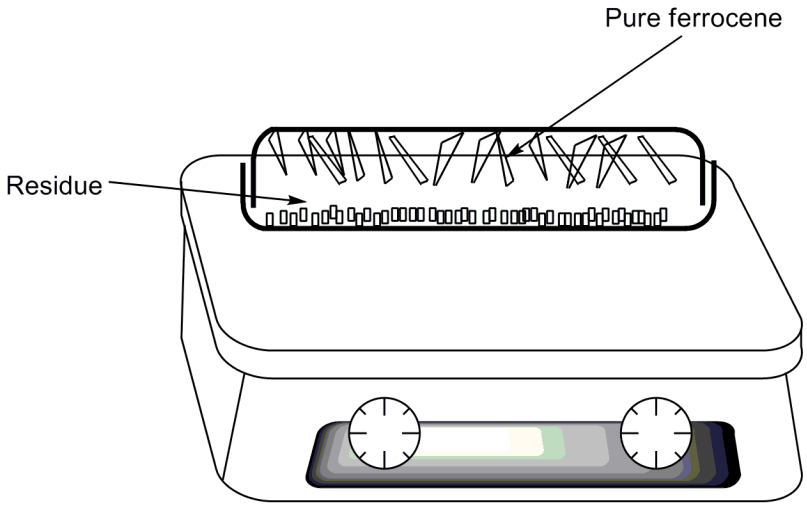


Figure VIII-3 Aparatus for the sublimation of ferrocene

Characterization

Record the melting point of the sublimed material. If all of the material did not fit in the sublimation apparatus, a crude yield can be reported, and from the amount sublimed an estimate obtained of the true yield. Measure the IR spectrum. Record the UV-visible spectrum in 95% ethanol (make up a quantitative solution of known concentration in a small volumetric flask) in the range 300 to 600 nm. Record the ^{1}H and ^{13}C NMR spectra of ferrocene in $CDCl_3$.

Report

Hand in your product as well as all original spectra. Discuss the spectral data as supporting or contradicting the proposed "sandwich" structure of ferrocene. What other structures are possible? Interpret the UV-visible spectrum in terms of the likely chromophore in this complex, and with

reference to the ligand field splitting and *d*-electron populations. Your discussion should address at least the following points:

1. What is the structure of dicyclopentadiene? Draw the mechanism for the Diels-Alder reaction of cyclopentadiene with itself.
2. X-ray diffraction data indicate that the ferrocene molecule is centrosymmetric, but that ruthenocene is not. What can be said about the structures of these two compounds (in the solid state) as a consequence of these observations? What is the gas-phase structure of ferrocene? Assign the point groups of the structures you mention.
3. Describe two other methods for the preparation of ferrocene.
4. Use a molecular orbital energy level diagram to interpret the electronic absorption spectra.

References

1. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry, 6th Ed.*; Wiley: New York, 1999, p. 684.
2. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
3. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006.
4. Lukehart, C. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, 1985, p. 85.
5. Bard, A. J. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980, p. 215.
6. Harris, D. C. *Quantitative Chemical Analysis*; W. H. Freeman: San Francisco, 1982, p. 452.
7. Headridge, J. B. *Electrochemical Techniques for Inorganic Chemistry*; Academic Press: New York, 1969, p.42.
8. Bochmann, M. *Organometallics 1: Complexes with Transition Metal–Carbon σ-Bonds*; Oxford University Press: Oxford, 1994.
9. Bochmann, M. *Organometallics 2: Complexes with Transition Metal–Carbon π-Bonds*; Oxford University Press: Oxford, 1994.
10. Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall Inc.: Upper Saddle River, 1997.
11. Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.

Aromaticity in Cyclopentadiene Complexes: The Preparation and Characterization of Acetylferrocene

Introduction

Ferrocene has a vast organic chemistry because it is sufficiently stable to survive the reaction conditions required for electrophilic aromatic substitution. The rate of the Friedel-Crafts acylation reaction on ferrocene is 3×10^6 faster than with benzene, indicating that ferrocene is significantly activated toward electrophilic aromatic substitution. It is possible that the metal is directly involved in the reaction, and a mechanism has been proposed in which initial attack of the electrophile occurs at the metal, with subsequent re-arrangement as follows:

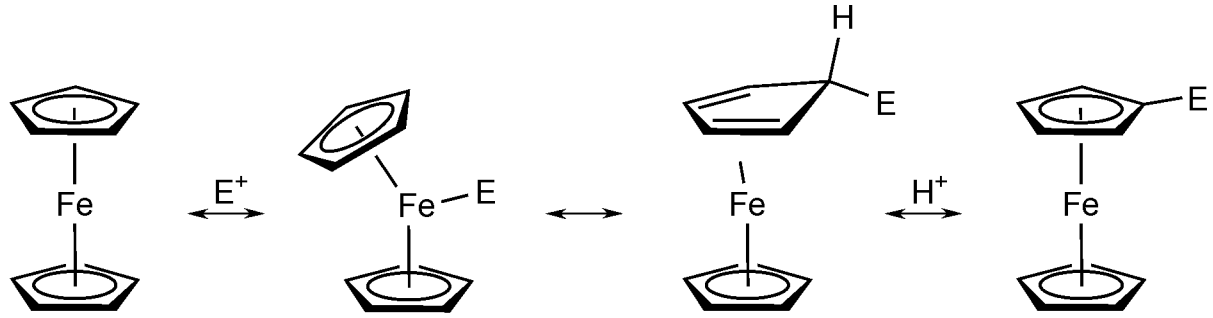


Figure IX-1 Proposed mechanism for electrophilic aromatic substitution of ferrocene

In this experiment, a Friedel-Crafts acylation of ferrocene will be performed. The most common catalyst for acylation of an aromatic ring is aluminum trichloride. However, because of the activation of the ferrocene ring, this leads to a large amount of disubstitution:

$$\{\eta^5\text{-}C_5H_5\}_2Fe \quad + \quad 2\ CH_3C(O)Cl \quad \xrightarrow{AlCl_3} \quad \{\eta^5\text{-}C_5H_4(C(O)CH_3\}_2Fe$$

Using a milder acylation catalyst, phosphoric acid, in the presence of acetic anhydride (*i.e.* a source of the acyl group and one mole of acetic acid after protonation by the acid) affords a higher yield of primarily the mono-substituted product, acetylferrocene:

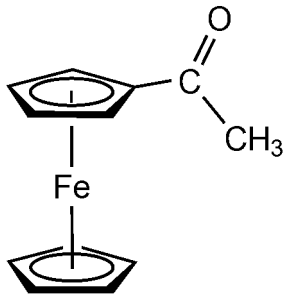


Figure IX-2 Structure of acetylferrocene

Instructional goals:

Properties of the following elements are highlighted: Fe, O, C and H

(1) Experience with performing reactions on a transition metal organometallic compound.
(2) Use of thin-layer and column chromatography to purify an organometallic compound.
(3) Use of IR, UV-vis, and especially NMR spectroscopy, to characterize an organometallic compound.

Pre-lab exercise

1. Write balanced equations for the synthesis of acetylferrocene from the indicated starting materials.
2. What kind of signals do you expect in the ^{1}H and ^{13}C NMR spectra?
3. What range of IR frequencies need to be recorded in this experiment?
4. What is a good starting concentration to use in the UV-visible spectral measurement of acetylferrocene?
5. What is the basic principle behind silica gel chromatography? In what order of polarity must the solvents be used in chromatography on a silica column? Read the background information on chromatography in section B.
6. Map out the timing of this project. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Phosphoric acid is corrosive and can burn both the skin and respiratory tract. Use with care and only in a fume hood.
2. Ligroin and ethyl acetate are highly flammable liquids and should be handled accordingly.

Procedure

Preparation of $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C(O)CH_3)]$, acetylferrocene

Add 1 mL of concentrated (85%) phosphoric acid dropwise, with constant stirring, to a mixture of 1.5 g of ferrocene and 5 mL of acetic anhydride in a small Erlenmeyer flask. (If the acid is in a small graduated cylinder, a disposable pipette may be used to dispense it). Use sublimed ferrocene, as prepared in experiment 8, or consult the instructor. After the addition is complete, attach a drying tube to the flask as shown in Figure IX-3a.

Heat the reaction mixture on a steam bath for 10 minutes. Pour the mixture onto approximately 20 g of ice in a tall beaker. When the ice has melted, neutralize the mixture by slowly adding solid sodium bicarbonate until CO_2 is no longer evolved. Be sure to stir the mixture so as to dissolve the $NaHCO_3$ when it is being added. Cool the mixture in an ice bath for 30 minutes to ensure complete precipitation of the ferrocenes. Suction-filter the solid using a Büchner funnel and wash it with water until the filtrate is only pale orange. Air-dry the solid on the funnel for 15 minutes. This

solid largely contains unreacted ferrocene and acetylferrocene, along with smaller amounts of other impurities.

Thin layer chromatography of the product mixture

Using t.l.c. determine which solvent mixture will allow you to separate $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4C(O)CH_3)$ from the product mixture. Use the commercial t.l.c. plates with the plastic backing. Cut these into thin (1.5 cm) strips just long enough to fit into the 1 oz. jars provided in the kit. Use the solvents ligroin (petroleum ether, 60 – 70 °C boiling fraction) and ethyl acetate. Run at least four trials, including the two pure solvents and some judicious choice of mixtures. Make the solvent mixtures using a graduated cylinder, and *use small quantities*!

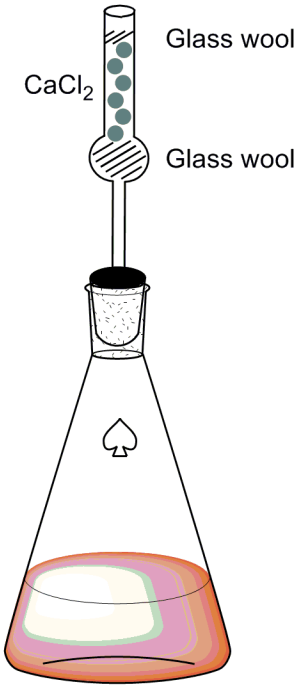


Figure IX-3a Aparatus for the synthesis of acetylferrocene

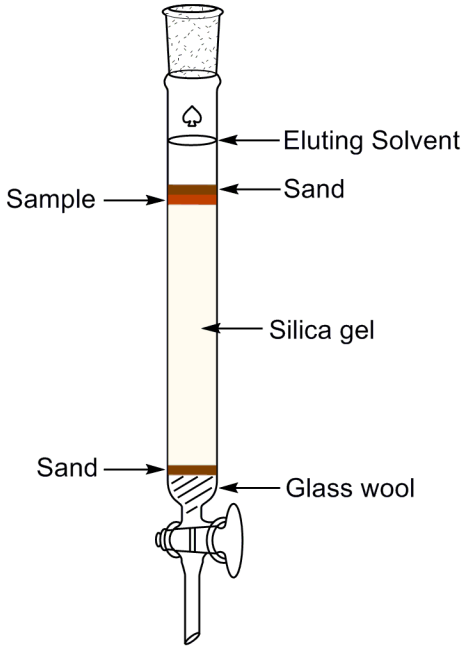


Figure IX-3b Chromatrography column for purification of acetylferrocene

Fill the bottles only to a depth of 5 mm with solvent. Using a small quantity of crude product make a concentrated toluene solution. Using a **capillary** spot the plates with this solution about 10 mm from the bottom. The spots should not be larger than 4 mm in diameter. If sufficient material is not transferred, spot repeatedly. *However, these commercial t.l.c. plates are very thin, and are easily overloaded. If the solution of crude material is reasonably concentrated, one spot will usually be sufficient.*

Mark the developed t.l.c. plates and paste them into your lab notebook. When you have finished the t.l.c. investigation, check the plates under a UV light to see if there are any colourless spots which were missed.

Use your t.l.c. results to choose the order of elution for the column chromatography. You may use one solvent which gives good separation, or a sequence of solvents in which the first washes the

initial component off the column, and then a different solvent is used to remove the remaining components.

Column chromatography of the bulk product

Prepare a chromatography column as depicted in Figure IX-3b. Use the 20 mm i.d. column provided, stuffing the bottom with a little glass wool and then using sand to make a filter at the bottom. Make a slurry of silica gel (80 – 200 mesh) in the solvent you are initially going to use to elute the column. Pour the slurry through a funnel into the column to a height of about 300 mm, slowly drawing off the solvent so that the column is uniform in gel to the full 300 mm. Gentle tapping of the column with a cork ring often helps to dislodge any air bubbles which form.

This column should have sufficient capacity for a total of approximately 1 g of crude product. Do not overload the column. Dissolve the crude product in a minimal amount of the same solvent, and add silica gel to create a slurry. Carefully pour this slurry onto the top of the column so as to form a uniform disc of product gel. Carefully add sand to make a 10 mm buffer layer.

Start eluting by adding solvent slowly and carefully above the sand with a disposable pipette. Only when this solvent does not take up any colour can you start adding more solvent to completely fill the column. Withdraw solvent at a constant rate of 1 drop per second, without interruption. Cover the part of the column containing the silica with aluminum foil to shield the ferrocenes from most of the light. They are slowly decomposed by light.

Collect the eluted fractions of ferrocene and acetylferrocene in *pre-weighed* round bottom flasks. These flasks should also be shielded from excessive exposure to light. Leading and middle fractions not containing product can be combined in an Erlenmeyer flask for later disposal. Use the rotary evaporator to remove the solvent, and weigh the flasks to obtain the amount of product (check each fraction for purity using NMR spectroscopy). Use these values to estimate an overall yield for the reaction.

Note: The spent silica gel is potentially hazardous, and must be disposed of safely. IN A FUME HOOD eject the gel into a beaker, using a little compressed air through a hose attached to the tip of the column, if required. Set the wet gel at the back of the hood until the solvent has evaporated. Finally, transfer it into the waste silica container.

Characterization

Record the melting points of both products. Measure the IR spectra of both materials. Record their UV-visible spectra in 95% ethanol (make up a quantitative solution of known concentration in a small volumetric flask) in the range 300 to 600 nm. Record the ^{1}H and ^{13}C NMR spectra of both ferrocene and acetylferrocene.

Report

Hand in your product as well as all original spectra. Give a full interpretation of the NMR spectra of acetylferrocene and the bearing they have on the structure. Your discussion should address at least the following points:

1. Was ferrocene or acetylferrocene eluted first? Why?
2. What might be the tar that remained at the top of the chromatography column?
3. The rates at which ferrocene derivatives elute from a silica gel column depend upon any pretreatment of the silica gel. Would acetylferrocene move down a column made of silica gel that had been heated at 150 °C under vacuum for 8 hours faster or slower than it would on a column using silica gel that had been sitting open in the laboratory for a few days? Explain.
4. Use a molecular orbital energy level diagram to interpret the changes in the electronic absorption spectra which occur on substituting a hydrogen atom with an acetyl group.

References

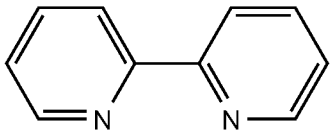
1. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, *6th Ed.*; Wiley: New York, 1999.
2. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
3. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006.
4. Charles Lukehart, *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, 1985, p. 85, p. 304.
5. Bard, A. *J. Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980, p. 215.
6. Harris, D. C. *Quantitative Chemical Analysis*; W. H. Freeman: San Francisco, 1982, p. 452.
7. Headridge, J. B. *Electrochemical Techniques for Inorganic Chemistry*; Academic Press: New York, 1969, p.42.
8. Bochmann, M. *Organometallics 1: Complexes with Transition Metal–Carbon σ-Bonds*; Oxford University Press: Oxford, 1994.
9. Bochmann, M. *Organometallics 2: Complexes with Transition Metal–Carbon π-Bonds*; Oxford University Press: Oxford, 1994.
10. Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall Inc.: Upper Saddle River, 1997.
11. Yamaguichi, Y.; Ding, W.; Sanderson, C. T.; Borden, M. L.; Morgan, M. J.; Kutal, C. *Coord. Chem. Rev.* **2007**, *251*, 515-524.

Metal Carbonyls: Preparation and Reactions of Tetracarbonyl(2,2'-bipyridyl)tungsten(0)

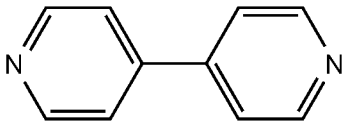
Introduction

The chemistry of low-valent metal coordination compounds has been dominated by a few ligands, *e.g.* carbonyls, tri(organo)phosphines, and unsaturated organic moieties (alkenes, alkynes). Each of these ligands has the ability to participate in synergic bonding, in which the ligand *donates* σ electrons to the metal, but *accepts* π electrons from the metal. Since a low-oxidation state metal (for example, as in this experiment, zero-valent tungsten) has an excess of electron density, it requires *back-bonding* to a π-acceptor ligand which can delocalize that charge away from the metal centre. A ligand is normally an electron donor, hence a Lewis base, towards a metal atom or ion. In backbonding, however, the ligand also acts as a Lewis acid. Ligands of this type are often called π-acids.

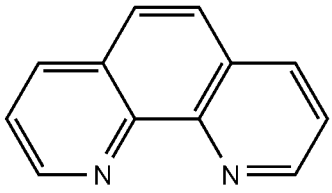
Certain polycyclic aromatic amines can also behave as π-acid ligands. Aliphatic amines, *e.g.* NH_3 or Et_3N, can only act as σ-donor ligands, and form complexes with electron-poor metals, *i.e.* those in positive oxidation states. Many of the classic coordination compounds encountered earlier in this sequence of experiments were ammine complexes. However, aromatic amines can use their π *antibonding* orbitals as metal *d*-electron acceptors. These orbitals, known as π-acceptor orbitals, like those of the common R_3P ligands, are higher in energy than the metal orbitals, but unlike the phosphines, are low enough in energy to strongly affect the electronic spectra of the complexes. The intense colours of many low-valent aromatic amine complexes are due to so-called *inverted electron transfer* or *metal-to-ligand charge transfer* (MLCT) absorption bands. That is, during excitation by a photon, electrons are moved from metal-centred orbitals into ligand-centred orbitals. Thus, some "charge" is "transferred".



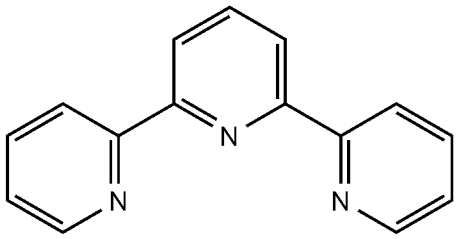
2,2'-bipyridine



4,4'-bipyridine



1,10-phenanthroline



2,2':6',2"-terpyridine

Figure X-1 Common nitrogen-containing polycyclic aromatic ligands

Some examples of π-acid amine ligands which form low-valent metal complexes are 2,2'-bipyridine (bipy), 4,4'-bipyridine, 2,2':6',2'' terpyridine (terpy), and 1,10-phenanthroline (phen). These are all conjugated aromatic heterocycles composed of linked pyridine rings. Note: they are known to be highly toxic; handle with caution! It is a particular ability of these ligands to stabilize a wide range of oxidation states, and complexes of these ligands have an extensive redox chemistry. This is because such ligands are both strong σ donors and strong π acceptors.

In the first part of this experiment bipy will be utilized to replace two carbonyl groups of $W(CO)_6$, a colourless, volatile organometallic solid, to form the coloured $[W(CO)_4bipy]$ complex. It will be characterized by IR spectroscopy; the C≡O stretching bands are highly diagnostic of the structure and donor strength of the other attached ligands.

In the second part of this experiment $[W(CO)_4bipy]$ is further reacted with triphenylphosphine to displace a third CO ligand. The volatility of CO helps both reactions to proceed to completion. Careful attention should be paid to getting the correct stoichiometry, otherwise undesired further substitution may occur.

Instructional goals:

Properties of the following elements are highlighted: W, N, C, and P

(1) Experience with the synthesis of an air-sensitive organometallic complex under an inert atmosphere.
(2) Learning to use ν(CO) bands in the IR to determine structure of metal carbonyl derivatives.
(3) Observation of MLCT bands in the electronic spectrum, and the effect of ligand substitution on those bands.
(4) Experience with heteronuclear NMR in the characterization of a coordination complex.
(5) Experience in the interpretation of a mass spectrum of an organometallic complex.

Pre-lab exercise

1. Write balanced equations for the preparation of $[W(CO)_4bipy]$ and $[W(CO)_3(bipy)PPh_3]$.
2. Sketch the structures of $[W(CO)_6]$ and $[W(CO)_4(bipy)]$. To what point groups do they belong?
3. What precautions must be taken in making solutions of these two compounds for spectral work (IR, electronic and NMR)?
4. Write out the possible isomeric structures of $[W(CO)_3(bipy)PPh_3]$. Assign the point group of each isomer. Do you think the spectroscopic measurements will enable you to distinguish between them? Which ones, and how?
5. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. $W(CO)_6$ is a volatile solid and is highly toxic. CO gas is toxic and is released during this experiment. Perform all operations in a fume hood.
2. Xylenes and hexanes are highly flammable liquids and should be handled accordingly.
3. 2,2'-bipyridine is highly toxic and should only be used in a fume hood. Wear gloves when handling.
4. Dichloromethane is a suspected carcinogen, and is toxic by inhalation. It is not flammable.

Procedure

Note: $W(CO)_6$, like all metal carbonyls, is highly toxic. All operations involving this compound should be done IN A FUME HOOD. In fact, the entire procedure for this laboratory should be conducted in a fume hood. Temporarily move a balance to the hood to weigh $W(CO)_6$. During the course of the reaction carbon monoxide is released; this gas vents safely in a properly functioning fume hood, but is dangerous in the open laboratory.

Preparation of tetracarbonyl(2,2'-bipyridyl)tungsten.

Charge a 250 mL RB flask with 1.7 g of tungsten hexacarbonyl, 1.0 g of bipy, a teflon coated stir bar, and 80 mL of dry xylenes. The xylenes are stored in special bottles under nitrogen, and the solvent is removed using a 50 mL syringe and a long (12") needle while the bottle is under a constant backflow of nitrogen gas. (Ask for help if this is new to you!) Set up a reflux apparatus (**IN A FUME HOOD**) as depicted in Figure X-2. While under N_2 heat the solution to reflux for two hours with stirring. CAUTION: Overheating will cause the carbonyl to sublime out of the flask and greatly reduce the yield. A suggested setting for the Variac is 60 V, but there is no substitute for careful monitoring of the reaction as it proceeds. Remove the heating mantle, stop the stirring, and allow the solution to cool, whereupon the product should crystallize as red needles. Filter the mixture using a Büchner funnel, and wash the solid product with 50 mL of petroleum ether (30 – 40 °C fraction). The complex is stable in air **when dry**.

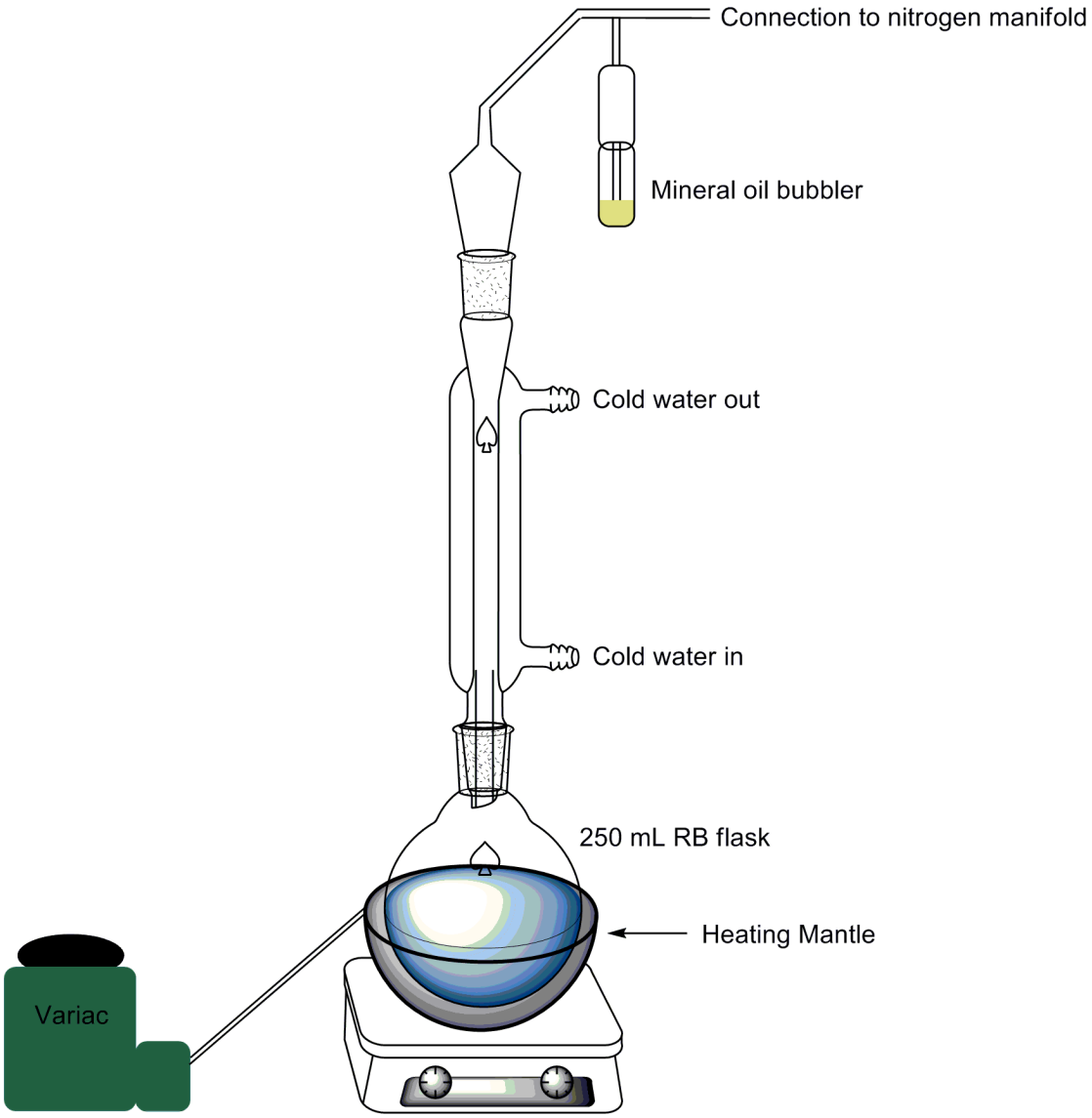


Figure X-2 Apparatus for preparation of Tungsten Complexes

Preparation of tricarbonyl(2,2'-bipyridyl)(triphenylphosphine)tungsten.

Charge a 250 mL RB flask with 0.5 g of $[W(CO)_4bipy]$, 0.4g of triphenylphosphine, a teflon-coated stir bar, and 50 mL of dry xylenes. Reflux the mixture under nitrogen for one hour with stirring. Cool the solution, filter the product and wash it with three portions of hexanes.

Dissolve the product in 20 mL of chloroform and filter the solution through a medium-porosity fritted glass funnel (30 mL size) into a clean filtration flask. Gradually add 40 mL of hexane to the filtrate while swirling. Collect the purified product and wash it with hexane as before. This material is referred to as "reprecipitated"; it is a fast method of purifying, but may still have some occluded impurities.

Characterization

Measure the melting point of both products. Calculate the percent yields and obtain their IR spectra. Measure the electronic absorption spectra of both products from 200 to 800 nm. It does not matter if some of the intense bands in the UV range go off-scale. The intensity of the visible bands should be in the range 0.3 to 0.7 absorbance units. Prepare these solutions to sufficient accuracy to obtain molar absorptivities to 2 significant figures.

Measure the ^{1}H NMR and ^{13}C NMR spectra of both products in $CDCl_3$. Also measure the ^{31}P spectrum of $[W(CO)_3(bipy)PPh_3]$. Record the mass spectrum of $[W(CO)_4(bipy)]$.

Note: it is not necessary to wait until both products are prepared to start the characterization. It often takes several tries to get a measurement on a new compound right!

Report

Hand in your product as well as all original spectra. Your discussion should address at least the following points:

1. The $\nu(C{\equiv}O)$ in $W(CO)_6$ is 1986 cm^{-1}. Compare this with the average frequency of your two products. What do the results indicate about the π-acceptor ability of bipy relative to triphenylphosphine?
2. Construct an MO diagram to explain the origin of the electronic absorption spectra. Consider primarily the band in the visible region, which is an MLCT band. What effect does substitution of CO by PPh_3 have on the λ_{max} of this MLCT band? Explain the origin of this effect on the MO diagram. Correlate your answer with the conclusion to question 1.
3. Summarize the evidence from the IR and NMR spectra regarding the stereochemistry of $[W(CO)_3(bipy)PPh_3]$.
4. Based on the experimental evidence for stereochemistry, devise a simple mechanism to explain the course of the reaction of PPh_3 with $[W(CO)_4bipy]$.
5. Discuss the mass spectrum of the product.

References

1. Atkins, P. W.; Overton, T.; Rourke, J.; Weller, M.; Armstrong, F. *Inorganic Chemistry, 4th Ed.*; W. H. Freeman: New York, 2006. (An introduction to metal carbonyl complexes, bonding, symmetry applied to IR bands, etc.)
2. Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987, Vol 2, p. 89.
3. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989, p. 162, p. 665. (An introduction to IR spectroscopy, and the use of group-theoretical symmetry arguments to assign structures.)
4. Lukehart, C. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, 1985, p. 53.
5. Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, 1985, p. 103.

6. Bochmann, M. *Organometallics 1: Complexes with Transition Metal–Carbon σ-Bonds*; Oxford University Press: Oxford, 1994.
7. Bochmann, M. *Organometallics 2: Complexes with Transition Metal–Carbon π-Bonds*; Oxford University Press: Oxford, 1994.
8. Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall Inc.: Upper Saddle River, 1997.

Olefin Complexes: Preparation and Reaction of Bis(1,5-cyclooctadiene)dichloropalladium(II)

Introduction

Most of the platinum metals (*i.e.* Ru, Os, Rh, Ir, Pd and Pt) are often commercially purchased as the halide salts. Direct conversion of this salt to a soluble organometallic species can be quite straightforward, or exceedingly difficult, depending upon the ligands to be used. Consequently, one tends to initially prepare a convenient organometallic compound and promote the required ligand substitutions in a subsequent step. The title compound is such a precursor.

In this complex, an olefin, *i.e.* an alkene, is used as a ligand for Pd. Alkenes are neutral organic molecules which can coordinate to certain transition metal ions to form stable bonds, in which the double bond acts both as a Lewis donor through the π orbital and as a Lewis acid through the π^* orbital. The latter interaction is known as "back-bonding". The purpose of the neutral ligands is to displace bridging halide ions in solid $PdCl_2$ to form a molecular halide complex, *i.e.* L_nPdCl_2. With a suitable choice of ligand, L_n, the resulting complex will be stable, relatively non-polar, and soluble in organic solvents.

This experiment describes the synthesis and characterization of the precursor using mass spectrometry, IR and NMR spectroscopy. A derivative of this complex is also similarly investigated.

Instructional goals:

Properties of the following elements are highlighted: Pd, C, O, and Cl

(1) Experience in the synthesis of an organometallic compound of a platinum-group metal.
(2) Use of syringe transfer techniques in handling air-sensitive reagents.
(3) Experience with IR spectroscopy as applied to problems in stereochemistry.
(4) Experience in the use of heteronuclear NMR spectroscopy for structure elucidation of organometallic compounds.
(5) Experience in the interpretation of a mass spectrum of an organometallic compound.

Pre-lab exercise

1. Sketch the structure of $[(COD)PdCl_2]$. To what point group does it belong? Which isomer is it, and how can you be sure?
2. Sketch a possible structure for *cis*-[(COD)Pd(Cl)(OMe)]. What is its geometry and to what point group does it belong?
3. Write balanced equations for the preparation of both products.
4. What range of IR frequencies do you need to record in this laboratory? Why?
5. Map out the timing of the afternoon's work. Use free gaps of time to do other operations. Be realistic in the time allotted for each operation!

SAFETY NOTES

1. Palladium is highly toxic. Wear gloves when handling.
2. COD emits a strong, foul odour. Use only in a fume hood.
3. Ethanol, methanol, and especially ether, are highly flammable liquids and should be handled accordingly.
4. Concentrated HCl is corrosive and releases vapours of the acid. Handle only in a fume hood.

Procedure

Note: All solutions and filter papers used in this experiment must be deposited in the Palladium waste container in the fume hood. Palladium is expensive, and can be recovered from the waste. Do not mix this waste with that of other heavy metals!

Preparation of *cis*-[(COD)$PdCl_2$]

IN A FUME HOOD, dissolve 0.20 g of palladium(II) chloride in 0.5 mL of concentrated hydrochloric acid in an Erlenmeyer flask by gently warming the mixture on a hot plate. When the solid has dissolved, cool the solution and dilute with 15 mL of 95% ethanol. Filter through a small Büchner funnel into a clean filtration flask and wash any residue with 20 mL of ethanol.

Combine all of the filtrates in a 50 mL beaker and add 0.3 mL of 1,5-cyclooctadiene (COD) by syringe. Stir the mixture for 10 minutes. The COD is kept in a "Sure-seal" bottle; refer to "General laboratory Procedures" in this manual for proper use of such bottles. Collect the yellow solid in a Büchner funnel and wash it with 3 – 3 mL portions of diethyl ether.

Note: COD has a revolting odour. Wear disposable polyethylene gloves and do not remove the cyclooctadiene or any glassware or solutions that have been in contact with it, from the fume hood. If you bring the odour out into the lab, you are bound to be strangled by your lab mates]

Preparation of *cis*-[(COD)Pd(Cl)(OMe)]

Prepare a stock solution of sodium methoxide in methanol by performing a 1:25 dilution of 25% NaOMe in MeOH. Withdraw the concentrated NaOMe under nitrogen using a dry syringe with a long needle. Make sure that the needle itself is filled with nitrogen before inserting it into the flask! The needle must be cleaned out thoroughly with water immediately after use to prevent permanent blockage by sodium carbonate.

This dilution should give you a 0.15 M solution. Add 5.2 mL of this solution to 0.200 g of the previously prepared [(COD)$PdCl_2$] in a 25 mL RB flask. With stirring, the yellow colour should quickly disappear as a white precipitate forms. Continue to stir the mixture for 30 min, filter through a clean, dry, pre-weighed 30 mL sintered glass funnel (fine porosity) and allow the sample to air dry.

Characterization

Measure the melting point of both products. Calculate the percent yields and obtain their IR spectra. Also run the spectrum of COD itself as a thin film (smear) between two NaCl plates. Load the plates in a fume hood, and clean them off in the same place.

Record the ^{1}H and ^{13}C NMR spectra of both products in $CDCl_3$ solution. They are only slightly soluble, thus, it may be necessary to run the spectrum for quite some time to record enough scans to achieve acceptable signal:noise. If necessary, arrange for a long run during a morning or overnight slot. Prepare the solutions in small shell vials, using only sufficient $CDCl_3$ to run a 5 mm NMR experiment (~0.75 mL). Filter the solution into the NMR tube through a disposable pipette containing a small wad of glass wool firmly pushed into the narrowed part of the pipette. This should be sufficient to remove insoluble matter from the NMR sample. After recording the spectra, recover the samples in the NMR tubes.

Record the mass spectrum of *cis*-[(COD)Pd(Cl)$_2$].

Report

Hand in your product as well as all original spectra. Interpret the IR, mass spectrum and NMR spectra, and correlate them to proposed structures for the two products. Your discussion should address at least the following points:

1. What are the isotopes of Pd? Are any NMR active? Do you expect to see the effect of these isotopes in the NMR spectra? In the mass spectrum?
2. What can you say about the purity of the products you have prepared?
3. What effect does coordination have on the IR bands of double bonds?
4. What are the expected positions of the Pd–Cl bands in the IR spectra? What do you expect to see for *cis*-[(COD)PdCl$_2$] based on symmetry considerations? Use this information to assign this region of the IR spectrum. What changes occur in this region of the spectrum upon forming *cis*-[(COD)Pd(Cl)(OMe)]?
5. Why is this organometallic compound of Pd so stable (*i.e.* it can be handled in air)? Discuss various factors which come into play in discriminating the stability to oxygen, water and heat for organometallic compounds.
6. Propose a simple mechanism for the formation of *cis*-[(COD)Pd(Cl)(OMe)].
7. Discuss the bonding in *cis*-[(COD)PdCl$_2$]. Construct an MO diagram, and use this diagram to explain the synergic bonding between the metal and the olefin.

References

1. Quinn, H. W.; Tsai, J. H. *Adv. Inorg. Chem. Radiochem*. **1969**, *12*, 217.
2. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1997.
3. Butler, I. S.; Harrod, J. F. *Inorganic Chemistry*; Benjamin/Cummings: Redwood City, 1989, p. 162, p. 180. (An introduction to IR spectroscopy, and the use of group-theoretical symmetry arguments to assign structures.)
4. Lukehart, C. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, 1985, p. 140.

5. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, 4th Ed.*; HarperCollins: New York, 1993.
6. Bochmann, M. *Organometallics 1: Complexes with Transition Metal–Carbon σ-Bonds*; Oxford University Press: Oxford, 1994.
7. Bochmann, M. *Organometallics 2: Complexes with Transition Metal–Carbon π-Bonds*; Oxford University Press: Oxford, 1994.
8. Spessard, G. O.; Miessler, G. L. *Organometallic Chemistry*; Prentice-Hall Inc.: Upper Saddle River, 1997.
9. Ayres, G. H.; Tuffly, B. L. *Anal. Chem*. **1952**, *24*, 949.
10. Schults, R. G. *J. Organomet. Chem.* **1966**, *6*, 435.
11. Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.