

**SYLLABUS**  
**CHEMISTRY 402/502**  
**Spring, 2009**

**Advanced Inorganic Chemistry**

**Instructor:** Robert D. Pike  
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**Office Hours:**  
Tuesday 9:00-10:30 AM  
Thursday 1:30-3:00 PM  
(and by appointment)

**Course Description:** This course is intended for chemistry majors and is designed to help prepare the student for graduate school or employment in the physical sciences. The course is intended to expand the student's knowledge base in inorganic chemistry by providing new ways of understanding molecular orbitals, bonding, and reactivity. The mathematics of symmetry is applied to chemical issues, such as bonding, spectroscopy and crystallography. Organometallic and bioinorganic chemistry are introduced and a number of physical and analytical instrumental techniques are discussed.

**Text:** G. L. Miessler and D. A. Tarr, Inorganic Chemistry, 3<sup>rd</sup> ed.; Prentice Hall: Upper Saddle River, NJ, 2004.

**Supplementary Texts on Reserve in Chemistry Reading Room:**

F. A. Cotton, Chemical Applications of Group Theory, 3<sup>rd</sup> ed.; Wiley: New York, 1990.  
A. F. Hill, Organotransition Metal Chemistry; Wiley-Interscience: New York, 2002.  
E. A. V. Ebsworth, D. W. H. Rankin, and S. Cradock, Structural Methods in Inorganic Chemistry, 2<sup>nd</sup> ed.; CRC Press: Boca Raton, FL, 1991.

**Lectures:** Monday, Wednesday, Friday, 10:00–10:50 AM, Integrated Science Center 2018.

**Examinations:** (20, 20, 15%) February 18\*/19, March 26/27\*, April 23/24\*.

Each exam is given in a self-scheduled two hour block. On the starred date there will be no lecture, so this time can be used as part of the exam time. The lowest of the three exam grades for each student will be counted as 15%, while the other two exam grades will count 20% each.

**Final Examination:** (30%) May 7, 2:00 PM

**Problem Sets:** (15%)

These are very important to your success in the course for two reasons: (a) They count as 15% of the grade and (b) They will prepare you for the sort of material that will appear on the exams. Late submission of problem sets will not be permitted. Collaboration is allowed on the problem sets, but it is important develop independent skills for use in the exams.

**X-ray Crystallography Practicum:** (Chem 502: required, Chem 402: extra credit – replaces one problem set)

The student is expected to grow crystals, solve a crystal structure (with the instructor's help) and report on the details and novelty of the structure using the Cambridge Crystallographic Database. The compound(s) chosen can be inorganic or organic and can originate from the student's own research or be an off-the-shelf solid.

**Course Outline** (Chapter reading assignments in Miessler & Tarr indicated in parenthesis):

I. Introduction and Review of Basic Bonding Principles (2,3)

- A. Octet rules
- B. Resonance
- C. Valence shell electron pair repulsion
- D. Effective nuclear charge and electronegativity

II. Group Theory (4 and handouts)

- A. Introduction
- B. Basic definitions and theorems regarding mathematical groups
- C. Assignment of symmetry
  - 1. Symmetry elements
  - 2. Symmetry operations
  - 3. Point groups
    - a. point groups derived from a single symmetry element
    - b. point groups derived from two or three elements
    - c. special point groups
- D. Some elementary applications of symmetry
  - 1. Chirality
  - 2. Dipole moment
  - 3. Chemical equivalence
- E. Matrix representations of groups
  - 1. Transformation matrices
  - 2. Character tables
  - 3. Reducible and irreducible representations
  - 4. Reduction of representations
- F. A further application of group theory – vibrational spectroscopy
  - 1. Vibrational modes of H<sub>2</sub>O
  - 2. Vibrational modes of (CO<sub>3</sub>)<sup>2-</sup>
  - 3. Vibrational modes of [Mo(CO)<sub>4</sub>(P(OPh)<sub>3</sub>)<sub>2</sub>] isomers and [Cr(CO)<sub>6</sub>]

III. Symmetry-based Molecular Orbital Theory (5,10)

- A. Introduction to LCAO-MO
- B. Second row diatomic molecules
  - 1. Homonuclear diatomics, N<sub>2</sub>
  - 2. Heteronuclear diatomics, CO
- C. Molecules of type: AB<sub>n</sub>

1.  $(\text{CO}_3)^{2-}$

2.  $[\text{FeF}_6]^{3-}$

D. Crystal field theory and ligand field theory

1. Crystal field theory review

2. Ligand field theory – angular overlap

3. Contributions to  $\Delta_o$  from the metal

4. Contributions to  $\Delta_o$  from the ligands

5. Spectrochemical series

6. Other coordination geometries and crystal field stabilization energy

E. Jahn-Teller effect

IV. Organometallic Chemistry - Bonding (13)

A. Introduction - The eighteen electron rule

B. A survey of organometallic ligands and their complexes

1.  $\pi$ -Acid ligands

a. carbonyl

b. phosphine and phosphite

c. nitrosyl

d. cyanide and isocyanide

e. dinitrogen and dioxygen

f. dihydrogen

g. alkylidene and alkylidyne

2.  $\pi$ -Olefin ligands

a. ethylene and acetylene

b. butadiene and benzene

c. allyl and cyclopentadienyl

3.  $\sigma$ -Donor ligands

a. alkyl

b. hydride

c. halide

d. bridging donors and agostics

V. Physical Methods in Inorganic Chemistry (handouts)

A. NMR spectrometry

1. Nuclei for inorganic NMR

2. NMR analysis of non-rigid compounds

a. fluxionality vs. tautomerism

b. NMR line-broadening

c. ring whizzing

d. polyene rotation

e. ligand exchange

B. X-ray techniques

1. Generation and diffraction of X-rays

2. The unit cell and Miller indices

3. Space group symmetry

- a. crystal systems and Bravais lattices
  - b. new symmetry operations: the glide plane and screw axis
  - c. space groups and systematic absences
- 4. Powder diffraction
- 5. Single crystal diffraction
- 6. X-ray fluorescence and X-ray photoelectron spectroscopies
- C. Electrochemical techniques
  - 1. Cyclic voltammetry
  - 2. Spectroelectrochemistry
  - 3. Electron paramagnetic resonance spectrometry

## VI. Organometallic Chemistry - Reactivity (14)

- A. Reactions of organometallic complexes
  - 1. Ligand dissociation and substitution
  - 2. Oxidative addition and reductive elimination
  - 3. Migratory insertion and deinsertion
  - 4. Hydride elimination and abstraction
  - 5. Nucleophilic and electrophilic attack at coordinated ligands
- B. Homogeneous catalytic cycles
  - 1. Acetic acid syntheses
  - 2. Hydroformylation
  - 3. Hydrogenation
  - 4. Olefin metathesis and cyclooligomerization
  - 5. Ziegler-Natta polymerization
- C. A Heterogeneous process – Fischer-Tropsch

## VII. Coordination Chemistry (6,11,12)

- A. Introduction – how does this differ from organometallic chemistry?
  - 1. Comparison of organometallic and coordination complexes
  - 2. Hard-soft acid-base theory
- B. Electronic spectra
  - 1. Intra-d-subshell transitions
  - 2. Charge-transfer phenomena
- C. Reactions and mechanisms
  - 1. Inert and labile compounds
  - 2. Electron transfer reactions

## VIII. Bioinorganic Chemistry (16)

- A. Introduction - metals in the human body
- B. Iron-containing proteins
  - 1. Electron transfer proteins (cytochrome C)
  - 2. Respiratory proteins (hemoglobin and myoglobin)
  - 3. Iron enzymes (cytochrome P<sub>450</sub>)
  - 4. Iron-sulfur clusters (ferredoxins and nitrogenase)
  - 5. Iron storage and transport proteins (transferrin, ferritin, and siderophores)

C. Copper-containing proteins

1. Respiratory proteins (hemocyanin)
2. Electron transfer proteins (copper blue proteins)
3. Copper (and zinc) enzymes (superoxide dismutase)