Advanced Inorganic Reaction Mechanisms

This is the second time I am offering this course. The first edition was in the winter term of 2014. Based on this initial offering, some topics have been added and some removed. The general feeling of the class was that there should be more emphasis on Catalysis at the expense of Bioinorganic Chemistry. Some of you will have been introduced to catalysis (Z-Natta, for example) and some bioinorganic chemistry (metals in biology, proteins) in Advanced Inorganic Chemistry II, CH 512. We will lightly touch on these topics to get everyone up to speed and proceed to the meat and potatoes of this course: mechanisms.

This is an advanced course and students are expected to do a lot of work on their own. Lectures may not cover all the contents listed below, but it is to the student’s advantage to know most of these topics. The course’s worth is evident mostly after you have completed your studies here at Portland State. Catalysis and bioinorganic chemistry are the hottest topics in the chemistry industry and in drug development. Questions and discussion during the lectures are strongly encouraged. If you have difficulties, the professor is more than willing to work with you. In general, it is a very exciting course, full of surprises with every lecture.

This course, after the preamble on transition metal complexes, stresses mainly bioinorganic chemistry and catalysis. For example, interactions of Pt(II) with DNA might give us a peek at the mechanism of cisplatin antimetastatic behavior. Inclusion of Ru(II) interactions will allow us to extrapolate to the putative new breed antimetastatic inhibitors based on ruthenium.

Inorganic catalysts are being developed for a variety of new processes, especially in C-H bond activations, where abundant hydrocarbons can be functionalized into value-added products.

Some of the topics will be handled as student projects for presentation. It will be impossible to cover all these topics in 20 lectures. The most important aspect of this course is to avail to the student this wide world of inorganic catalysis and metals in the physiological environment. It is a very wide field.

Though text books exist for the first part of the course; they are all very expensive, and not worth spending large sums of money for 10 lectures. The later part of the course will be derived from recent published research works. The professor’s lecture notes, plus the overhead scribbles will be uploaded onto D2L as pdf files. The book by Spessard and Miesler is very (very) good; but it gave me a sticker shock when I saw it on Amazon. For Bioinorganic Chemistry, there are not that many books available on this very important topic. The few that are available cost an arm and a leg. However, we will source most of our materials from recent publications. The Bertini et al book is excellent as a base for all bioinorganic chemistry stuff. Also a very good book to have on your shelf way after you have completed this course because you might need to continue referring to it in your career. I have my own dog-eared copy on my
shelf. It handles topics such as metals in proteins, transport and storage of metal ions in biology, metals in medicine, transferrin, ferritin, metallothioneins, oxygen metabolism, etc etc... in short, everything you ever wanted to know about bioinorganic chemistry.
CHEMISTRY 410/510: ADVANCED TOPICS IN INORGANIC CHEMISTRY

Course Title:  *Advanced Inorganic Reaction Mechanisms* [Inorganic Chemistry Graduate Course: offered under the official PSU title of ‘Special Topics in Inorganic Chemistry’]

Prerequisites: Undergraduates: Chem. 440 (otherwise check with the professor)

Graduate students: None

Instructor: Reuben H. Simoyi (SB2 372, phone 5-3895, rsimoyi@pdx.edu)

Office Hours: Tuesday, Thursday; 1:45 – 3:45 PM (Final office hours to be set after first week of classes).

Timetable: Two 100-minute lectures per week on Tues & Thurs 1000 – 1150. Final timetable will be set after first week of classes. These times may end up being retained, or they may be altered, depending on students’ schedules.

Venue: SB1 304

Text: Recommended Text: None that are reasonably priced


Exam Format:

Two take-home exams: one after 8 lectures and the second after 15 lectures (35 % each) and a class presentation (30 %) There will be no final exam in this course. [Pizza and munchies available during presentations.. not yet sure who will pay for this...but we will have pizza]. Each presentation will be video-taped and uploaded onto D2L.

Chemistry 410/510 Schedule and Syllabus (Advanced Inorganic Reaction Mechanisms):

Spring, 2016

Topics to be covered.

Redox Reactions and the Taube Experiment
Inner and outer sphere mechanisms for electron transfer

Organometallic chemistry, mechanisms of organometallic reactions (some aspects covered in Inorg. II)
Radical chain mechanisms in inorganic and organometallic chemistry

Inorganic metal ions and Fenton-type reactions
Haber-Weiss reaction and toxicity in biological systems.

Marcus theory and self-exchange rates, long range electron transfer.

Transition metal ion – DNA interactions. Specifically Pt(II) and Ru(II). Interactions with biological thiols and proteins.

Detailed mechanism of cisplatin’s antimetastatic effect. Also analogs carboplatin, oxaliplatin, iroplatin. Use of monoclonal antibodies in cancer treatments (relatively new technique)

Comparison between platinum and ruthenium based antimetastatic drugs. NAMI-A, RAPTA, KP1019, RM-175 (Ruthenium diamines).

Other antimetastatic drugs: Ifosfamide, Lupon (testosterone blocker), Mesenex, Methotrexate, Taxol, Adriamycin, etc etc. We will not cover all these; most likely some will be assigned as
assignments or presentation topics.

**Catalysis.**
Homogeneous Catalysts: Basic Principles. Examples of the most Important Catalytic Reactions: Heterogeneous Catalysts, Hybrid Catalysts, Solid/Liquid Systems, Liquid/Liquid Biphasic Systems

Characteristics of central metal atom & influence of attached ligands on catalytic activity
Important reaction types: oxidative addition, reductive elimination, migratory insertion, beta hydride elimination. Tollman catalytic cycles. Introduction into Grubbs and Wilkinson Catalysts. Hoechst-Wacker process, Gerhard Ertl’s work for which he won the Nobel Prize.

Catalysts for C-H bond activation. The possibility of direct introduction of a new functionality (or a new C–C bond) via direct C–H bond transformation is a highly attractive strategy in covalent synthesis. The range of substrates is virtually unlimited, including hydrocarbons, complex organic compounds of small molecular weight, and synthetic and biological polymers. C-H activation using transition metal catalysts; Ruthenium and rhodium catalysts.

Hydrogenases and H-H bond activation

Transition metal catalysts; high oxidation state low valence imine ligand-type catalysts, heterocyclic (carbene ligands..... covered in Inorg. II)

Insertion mechanisms, olefin insertion into M-H bonds, nucleophilic attack on metal-bound ligands.
CO – Olefin copolymerization catalysts