Chemistry 510
Special Topics in Inorganic Chemistry

Professor J. Kovacs
Wed & Fri 9:00–10:20 am
Bagley 331A

Concepts:

1. Evidence of M^{+n} importance to life
   - $[M^{+n}]$ in ocean vs body
   - Number of Metalloenzyme structures in Protein data bank
   - Number of Gordon conferences devoted to the topic
   - Workshops
2. Key Roles of M^{+n} in Biology
   - Why transition-metals?
3. Metal ion properties important for catalytic activity
   - Labile M-L bonds
   - Ligand Field and Covalent bonds
   - Spin-state and Magnetic properties
   - Metal ion Lewis acidity
   - Redox potentials
4. Selecting the right M^{+n} for a given function
   - Chelate effect/macrocyclic effect
   - M^{+n} radius
5. How Nature tunes M^{+n} properties
   - H-bonding
   - Entatic State
   - Protein constraints
6. How M^{+n} can be spectroscopically probed
   - Overview
7. Biological O_2 Chemistry
   - Overview
   - Kinetics
   - Spin-Forbidden
   - Thermodynamics
   - Proton-coupled electron transfer (PCET)
8. Thermodynamics and kinetics of electron transfer
   - Redox potentials
   - Marcus theory
   - Role of protons in making e- transfer energetically feasible
9. The electron transport chain
   - Why are Fe_4S_4 clusters and Blue Cu so good at electron transfer?
   - Mossbauer
   - EPR

10. Controlled Dioxygen Activation
    - Mechanism overview
    - Assessing extent of activation using rRaman
    - Superoxo intermediates in P450 and IPNS
11. H-atom Transfer and PCET in Biological Oxidation Rxns
    - Are Fe-$O_2^{\bullet -}$ potent enough to cleave C-H bonds?
    - Deuterium isotope effects
    - Hydroperoxo intermediates (homolytic and heterolytic cleavage)
    - Binuclear peroxo intermediates
    - High-valent Fe(IV)=O and Fe(V)=O intermediates
    - The oxo wall
    - Electronic structure of high-valent oxos
    - Thermodynamic cycle of HAT
    - Asynchronous PCET
12. Electronic structure Fe(IV)=O compounds
    - Spin-state dependent reactivity
    - Incipient formation of Fe-oxyl
13. Nitrogenase
14. Photosynthetic water oxidation