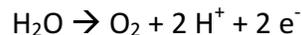
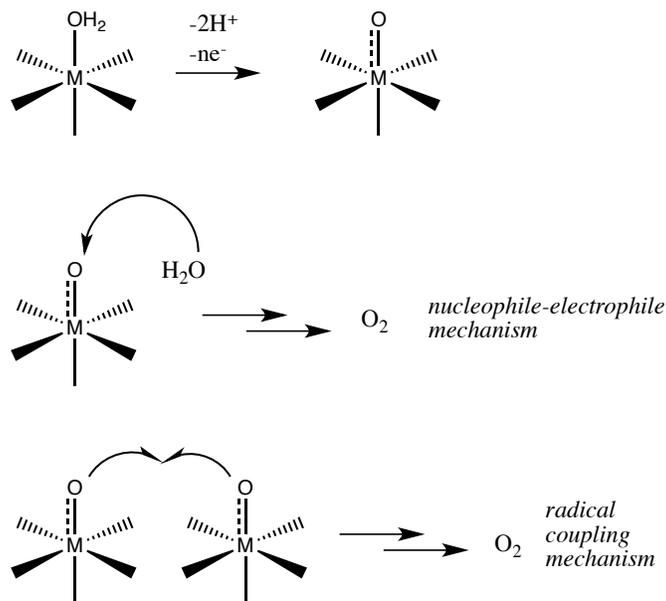


Inorganic Cumulative Exam
February 4, 2016
Written by: Neal Mankad

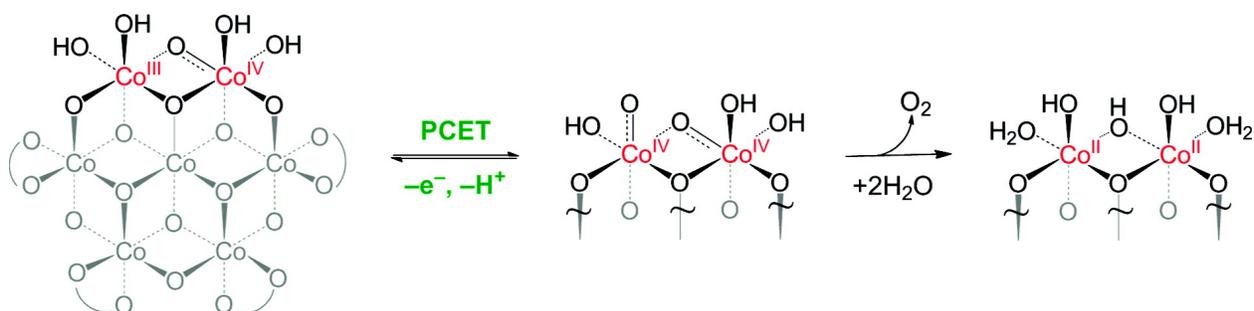
1. A frontier area in inorganic chemistry is the search for materials that catalyze the oxygen evolution reaction (OER), one of the half reactions required to achieve solar water splitting:



From a mechanistic standpoint, an interesting aspect of OER catalysis is the metal-mediated formation of the O-O bond in O_2 . Two classes of O-O bond forming mechanisms are generally considered. Both of them depend on H_2O coordinating to active metal sites, getting oxidizing to terminal oxo ligands, and then proceeding to O_2 . The operative mechanism in an individual OER systems depends on the metal-oxo species in question and the resulting electron structure of the metal-oxo multiple bond:



One of the most exciting OER catalysts to be reported recently is an amorphous cobalt phosphate material developed by Nocera, shown below, and originally reported in *Science* in 2008. Here, O-O bond formation is thought to involve one or more cobalt-oxo intermediates formed along the material's surface. Spectroscopic studies have indicated that O-O bond formation is rate-limiting, and that this step involves the cobalt(IV) oxidation state, as shown below.



Use qualitative d-orbital splitting diagrams to justify your answers to the following:

- Assuming that O-O bond formation involves 6-coordinate cobalt(IV)-oxo intermediates as shown in the figure, would the Nocera system favor the radical coupling mechanism (involving two adjacent Co sites) or the nucleophile-electrophile mechanism (involving external attack on a Co site by H₂O) to form O₂? Explain.
- Name a metal and its oxidation state to replace cobalt(IV) that would favor the other mechanism. Explain.
- Name a non-octahedral coordination geometry and oxidation state for cobalt that would favor the other mechanism. Explain.

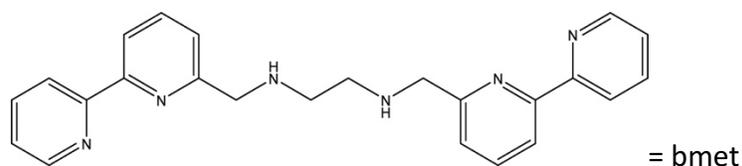
2. The OER reaction is catalyzed in biology as part of photosynthesis in green plants. The catalytic active site here is the oxygen evolving complex (OEC) found in photosystem II (PSII). The OEC is a multimetallic cluster featuring transition metal and alkaline earth metal sites. Name the transition metal(s) and alkaline earth metal(s) involved. Specify their stoichiometry in the OEC (i.e., M_nM'_m).

3. The other half reaction required for water splitting is the hydrogen evolution reaction (HER):

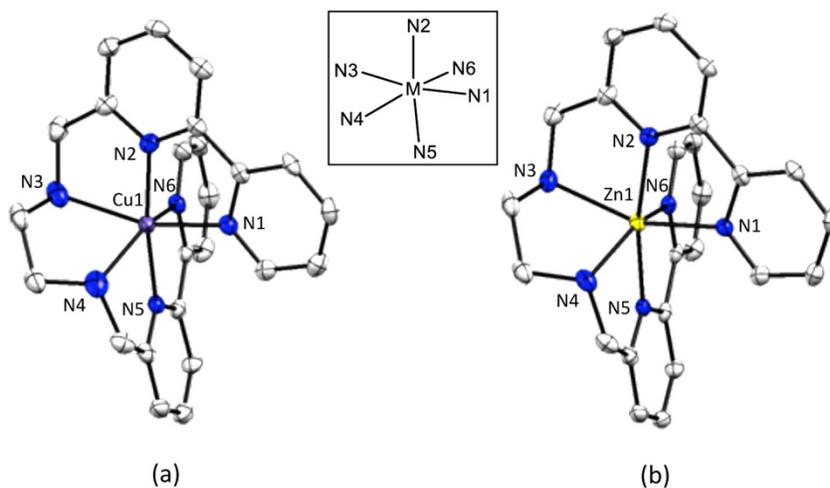


Again, synthetic catalyst development takes inspiration from biology, where the HER is catalyzed by hydrogenase enzymes found in certain microorganisms that metabolize H₂. Three such hydrogenase featuring different catalytic active sites have been identified, each involving a different combination of transition metal sites. Name the transition metal(s) involved in any one class of biological HER active site. Specify the stoichiometry of these metals (i.e., M_nM'_m).

4. Last week in the journal *Inorganic Chemistry*, Duboc reported Cu(II) and Zn(II) complexes of the bmet ligand (upon its double deprotonation):



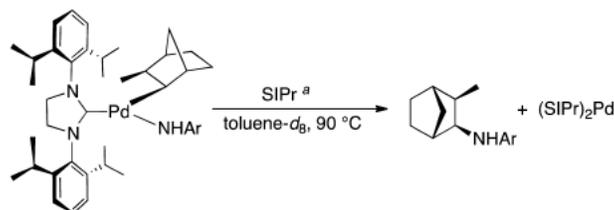
Analysis of these complexes by single-crystal X-ray diffraction revealed the solid-state structures shown below:



The Cu(II) complex shown on the left exhibited crystallographic disorder involving elongation of the Cu-N3, Cu-N4, and Cu-N6 bonds. This behavior was not observed with the (otherwise isostructural) Zn(II) complex shown on the right.

- Give a possible explanation for this distinction between the 6-coordinate complexes of Cu(II) and Zn(II), including qualitative d-orbital splitting diagrams in your answer.
- Suggest a complementary experimental technique, other than X-ray diffraction, that could support your hypothesis.
- If the authors were to synthesize the corresponding Ni(II) complex, would you expect this species to behave like Cu(II) or like Zn(II) in this respect? How about Co(II)?

5. Among a series of careful studies on the mechanism of C-N reductive elimination, Hartwig reported the following reaction series in *J. Am. Chem. Soc.* in 2012 (SIPr = the carbene ligand shown bound to Pd on the left):



For each of the following, predict which gives the faster rate of reductive elimination and provide an explanation:

- Ar = 4-MeOC₆H₄ vs. Ar = 4-F₃CC₆H₄
- Ar = 2,6-Me₂C₆H₃ vs. Ar = 2,4-Me₂C₆H₃

6. Complexes of the type LNi(CO)₃ exhibit two infrared absorptions associated with CO stretching vibrations.

- Explain why two CO stretching vibrations are observed by IR for the three CO ligands. Use a simple group theory analysis to support your explanation.

Character table for C_{3v} point group

	E	2C ₃ (z)	3σ _v	linear, rotations	quadratic
A ₁	1	1	1	z	x ² +y ² , z ²
A ₂	1	1	-1	R _z	
E	2	-1	0	(x, y) (R _x , R _y)	(x ² -y ² , xy) (xz, yz)

- The energies of these two vibrations are sensitive to the identity of L. The energy of one of these CO vibrations is given below as a function of L. For comparison, ν_{CO} = 2143 cm⁻¹ for free CO in the gas phase. The different L ligands represented in the table are P(OEt)₃, PMe₃, PPh₃, PPh₂Me, PPhMe₂, and PF₃. Place each L in its appropriate place in the table.

CO stretching frequencies for Ni(CO)₃L complexes where L is a PR₃ donor.

L (fill in the blanks)	ν _{CO} (cm ⁻¹)
	2064
	2065
	2067
	2069
	2077
	2111