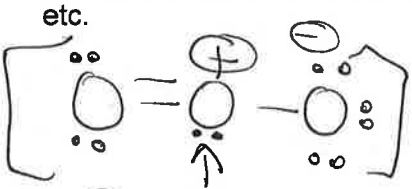
Chem 130
Fall 2015

KEY

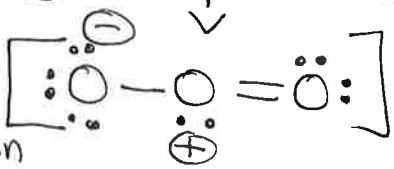
Sample Exam Questions (from recent previous exams)

1. (14 pt) We have talked a lot about different models of covalent bonding in this class. Using the relatively simple example ozone, O_3 (all connected in a row), go through as many different bonding models as you can apply (**be sure to name each model as you go**), stating briefly how each model improves on the one before it and what you can infer from the structure based on that model like relative bond lengths, angles, etc.

Lewis dot



Resonance (need to explain why both bonds are same length)

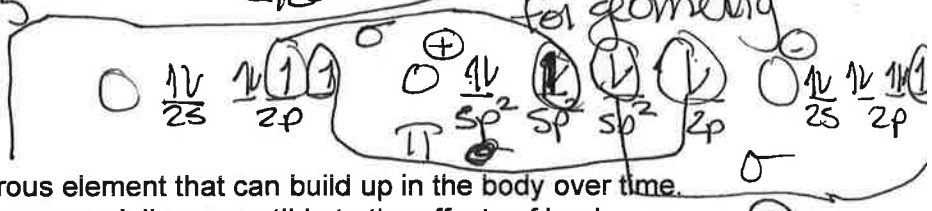


B.O. = 3/2 = 1.5

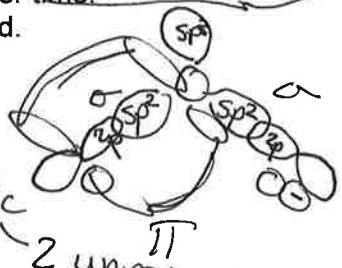
VSEPR - shows geometry at the central atom so can predict shape

bent <120°

Valence bond - puts electrons in orbitals
Hybridization - orbitals point in correct direct for geometry



1. (18 pt) Lead (Pb) is a dangerous element that can build up in the body over time. Children under the age of six are especially susceptible to the effects of lead. Exposure can cause mental and/or physical impairment.



a. Write the electron configuration for Pb. Would it be paramagnetic or diamagnetic? (4 pt)

$[Xe]\,6s^2\,4f^{14}\,5d^{10}\,6p^2$ paramagnetic (6p: ↑ ↑ _) 2 unpaired e⁻

b. What oxidation state or states would you expect for Pb? Explain briefly using your electron configuration to justify where you would add or remove electrons. (4 pt)

+2, +4

$Pb^{2+}\,[Xe]\,6s^2\,4f^{14}\,5d^{10}$ (lose 6p)

$Pb^{4+}\,[Xe]\,4f^{14}\,5d^{10}$ (lose all highest Q.L. electron)

c. **Briefly** explain if Pb in the oxidation state(s) you picked might be expected to be soluble in ion form in blood at the neutral pH of blood. (4 pt)

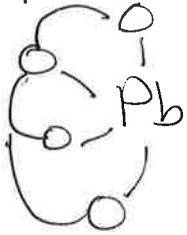
pKa = 7.7
Pb^{2+} yes soluble

$Pb^{2+}(aq)$	7.2	$Pb(OH)_2(s)$

Pb^{4+} is not on chart but should be lower (probably not soluble)

d. If we were designing a ligand to treat Pb poisoning, what characteristics should that ligand have and why? Draw a sketch of it (6 pt)

Chelating - wrap around it



KEY

4. (19 pt total) The latest issue of *Nature Communications* (Nov 22, 2011) contains an article by researchers from the Materials Science Dept. at Stanford University describing a highly efficient new type of battery derived from a metal-organic framework built from coordination complexes of metal ions. The formula for the initial complex $KCuFe(CN)_6$ is actually pretty similar to something you made in Laboratory 4! The overall structure of one unit cell of the compound is shown in color below, with an enlarged structure showing how more clearly how the individual ions interact at the right. In this structure, the Fe ions are green, the Cu ions are blue and the K ions occupy the large pink spheres (note: the color version is available one the course website). The cyanide ions are located between each pair of Fe and Cu ions.

a. Propose reasonable charges on the Fe and Cu based on the formula above and your knowledge of the periodic table. Explain briefly. (2 pt)

$CN^- \times 6 = -6$ total charge $= 0$
$K = +1$ so Cu^{2+}, Fe^{3+} to get $+5$

b. How many Fe ions are there in a unit cell? Show your work clearly. (2 pt)

8 corners $\times (1/8)$ + 6 faces $(1/2) = 4$

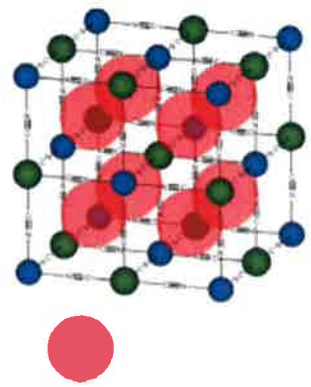
c. This unit cell is considerably bigger than the ones we've looked at previously, but it is not so hard to understand! In this case, the structure can be described as one set of cations forming the lattice and the other cations filling some of the holes, and then the whole thing being connected (between those holes) by the cyanide ligands. If the Cu ions are viewed as forming the lattice (and the cyanides are ignored), what kind of holes are the green Fe ions occupying? (2 pt)

octahedral

d. What kind of holes are the pink K ions occupying? (2 pt)

tetrahedral

e. What is the coordination number of the Fe ions on the edges of the cube (the cyanides are the closest things to the Fe!)? (2 pt) 6



f. What kind of ligand (classify using one or more of the 4 types we discussed in class) is cyanide? (2 pt)

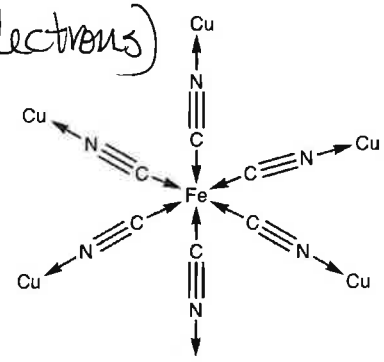
bridging

g. This battery works by having K^+ ions move back and forth between two different compounds (like the Li^+ ion battery we talked about in class). If extra K^+ migrate into the structure (without changing the overall charge), is the compound oxidized or reduced? (2 pt)

reduced (need extra electrons)

h. If a battery is made using the $KCuFe(CN)_6$ as one of the electrodes, based on your answer to f. above, which electrode is it, the anode or the cathode? (2 pt)

cathode



i. One of the reasons that this battery is so effective is that it can be charged and recharged multiple times without it losing power. Discuss this observation in terms of what must be true about the reactions involved. (3 pt)

you must be able to reverse the reactions easily without producing byproducts

2. Explain the all parts of the following statement as clearly and as concisely as you can using material learned in this course. **Use diagrams, calculations, chemical equations, etc. to support your answers whenever possible. You are significantly more likely to get full credit when these are included!** (8 pt each)

   $Ni(H_2O)_6^{2+}$ is green and $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$ is purple. However, the corresponding octahedral Pt^{2+} complexes of the same ligands are colorless or yellow (Note: $NH_2CH_2CH_2NH_2$ = en). ← don't worry about ½ well - didn't get to that.

   H_2O is lower on the spectrochemical series than en, so its Δ_o will be smaller. This is consistent w/ the data because green complex absorbs ~~purple~~ reddish and the ~~purple~~ violet complex absorbs yellow. Since yellow is ~~less~~ more energetic than red, it is higher energy

3. Give answers to the following:

   a. The name of the compound MgH_2 magnesium hydride

   b. A +2 cation with the electron configuration $[Ar]3d^7$ Co^{2+}

   c. The designation (label) for an orbital with the quantum numbers n=6 and l=2 6d

   d. The **formula** for the **octahedral** complex formed between Fe^{2+} and the bidentate ligand oxalate (for full credit give the formula rather than the abbreviation for oxalate) $Fe(ox)_3^{4-}$ $Fe(C_2O_4)_3^{4-}$

   e. The period 4 element with the highest ionization energy Kr

   f. A species that will oxidize Cr^{2+} but not Cr^{3+} E_{ox} Cr^{2+} = +0.41V ($-E^\circ_{red}$ Cr^{3+})
   E_{ox} Cr^{3+} = 1.33V ($-E^\circ_{red}$ $Cr_2O_7^{2-}$)
   ∴ Fe^{3+} (E°_{red} = 0.770)

   g. The name of the geometry with 1 lone pair and 4 bonded atoms see saw

   h. The **name** and **formula** of a weak acid acetic acid $HC_2H_3O_2$ (or others)

   i. The closest packing structure with an "ababab" arrangement of layers
   hexagonal closest packing

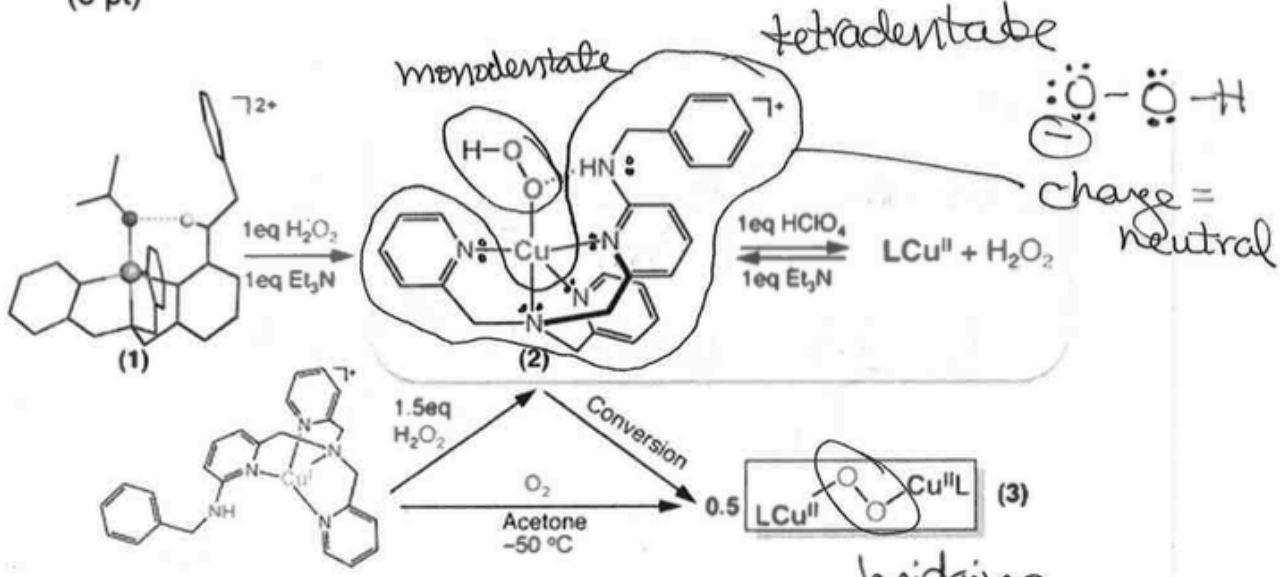
1. (14 pt) In a recent issue of Inorganic Chemistry (*Inorg. Chem.*, **2012**, *51* (23), pp 12603–12605, **DOI:** 10.1021/ic302071e), Ken Karlin and his research group at John's Hopkins report the following complicated reaction scheme. His group is attempting to mimic the chemical behavior of copper enzymes that process molecular oxygen species and lead to a number of different important intermediates. He isolates structure (2) at -90°C!

   a. Examine structure (2) below. What is the coordination number of the Cu? (2 pt) 5

   b. Clearly identify each of the ligands in structure (2) by circling them and classifying the type of ligand (monodentate, etc) (3 pt)

   c. What is the charge on each of the ligands in structure (2) and what is the charge on the Cu? (4 pt) (Hint: if you are not used to looking at carbon stick figures, just assume that the sticks and hexagons have no formal charges (but the N's might). Also you can ignore the dotted line connecting the NH and O (not a bond)!) overall charge = +1 = Cu charge + (-1) + 0
   Cu charge = +2

   d. For structure (3), what kind of ligand is the O_2? Based on the structure drawn in (3), what is the likely charge on the O_2? How would you name it? (5 pt)



bridging ligand

O_2^{2-} = peroxide