Chem 103 Midterm 1

Prof. Chris Chang
October 3rd, 2013

Name ____
SID ____
Signature ____

Problem 1:	______________	(16 pts)
Problem 2:	______________	(36 pts)
Problem 3:	______________	(60 pts)
Problem 4:	______________	(72 pts)
Problem 5:	______________	(24 pts)
Problem 6:	______________	(20 pts)
Problem 7:	______________	(22 pts)
Total:	______________	(250 pts)

This exam has 14 pages. There is a periodic table on the final page for your reference.

1) **Metals in Biology.** (16 points)

Match each of the following roles/substances in the left column with a relevant metal from the list. You may use each metal once and only once:

Co V Fe K W Cd Bi Zn

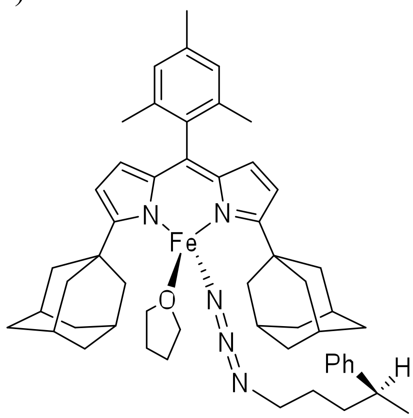
N_2 fixation	____
Hydrogen production/consumption	____
Toxic heavy metal	____
Vitamin B12	____
Halogenation	____
Gene expression	____
Neuronal charge carrier	____
Antacid medication	____

2) Electron Counting. (36 points)

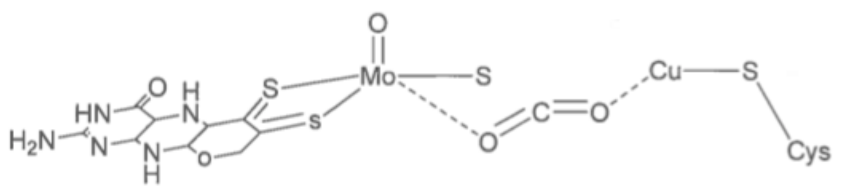
For the following complexes, determine:

i. formal oxidation state of each metal center.
ii. d-electron counts for each metal center.
iii. total electron count of the complex.

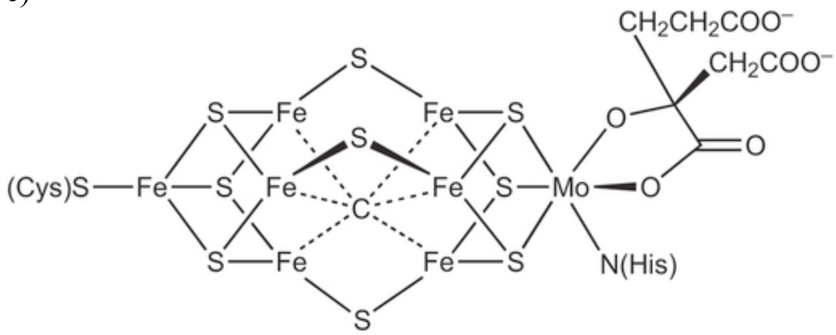
a)



b)



c)



CH2CH2COO−
CH2COO−
S
S—Fe
Fe—S
O
S
=O
(Cys)S—Fe—S
Fe
C
Fe
S—Mo
O
S—Fe
Fe—S
N(His)
S

3) **Valence Bond Theory and Molecular Orbital Theory**. (60 points)

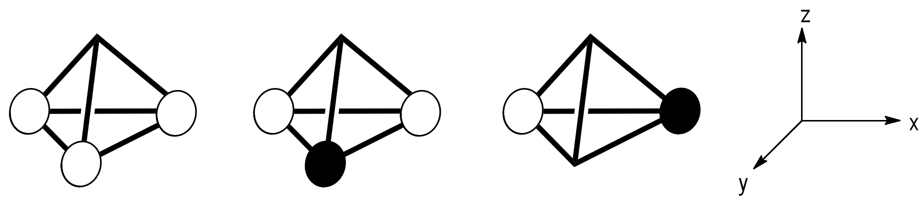
Hydrogen is a candidate fuel for carbon-neutral energy cycles, and current research is geared toward new ways to store it under ambient conditions. A promising material is the simple Lewis Acid/Base complex ammonia borane, H_3NBH_3.

a) Draw Lewis structures for NH_3 and BH_3. Designate which is a Lewis Acid and which is a Lewis Base.

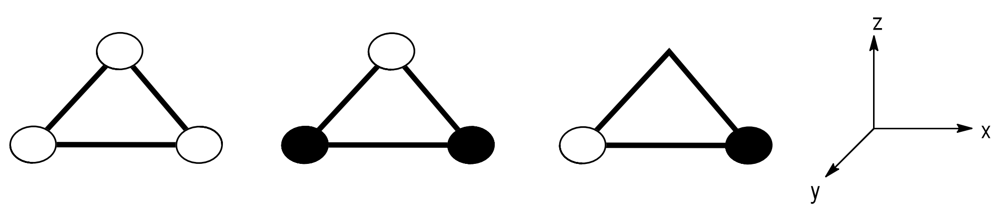
b) Make Valence Bond Theory (VBT) diagrams for NH_3 and BH_3.

c) Combining NH_3 and BH_3, make a Lewis structure and VBT diagram of H_3NBH_3.

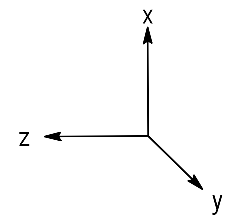
d) Using the SALCs and coordinate axes given below, make a molecular orbital (MO) diagram for NH_3 (remember you have seen this before).



e) Using the SALCs and coordinate axes given below, make a molecular orbital (MO) diagram for BH_3.



f) Using fragments from parts d) and e) and knowledge of Lewis Acid/Lewis Base complexes, make a MO diagram of H_3NBH_3 (use the coordinate axes given).

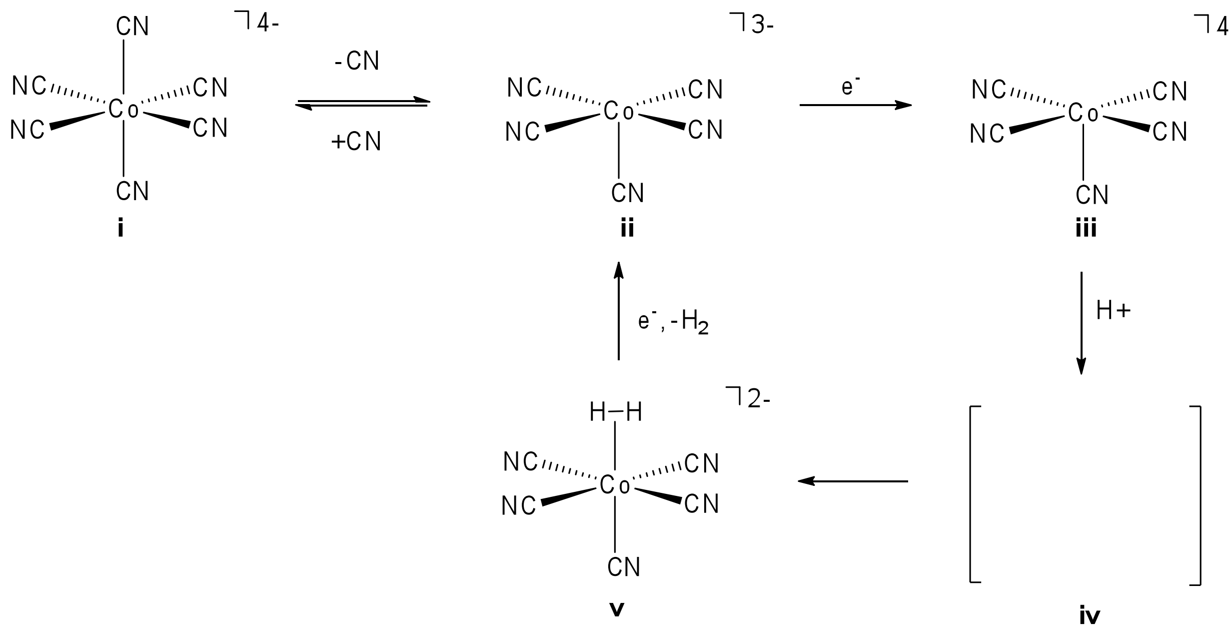


g) **Bonus:** For H_3NBH_3, predict the product of release of 3 H_2 molecules. Include the chemical structure of this product.

4) Crystal Field Theory (72 points)

Generation of H_2 from non-carbon sources such as H^+ (from H_2O) is important for sustainable energy sources. One candidate platform is based on classic cyanide-metal complexes of the type $[(CN)_5ML]^{n-}$.

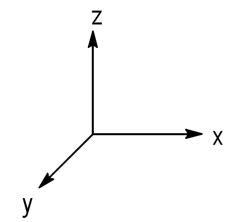
a) For the following cycle, fill in the missing intermediate (**iv**).



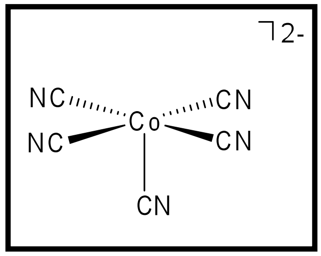
b) Give the oxidation state, d-electron count, and total electron count for (**i**) – (**v**) above.

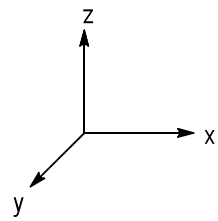
i	Oxidation State: ____ d-electron count: ____ Total electron count: ____		**iv**	Oxidation State: ____ d-electron count: ____ Total electron count: ____
ii	Oxidation State: ____ d-electron count: ____ Total electron count: ____		**v**	Oxidation State: ____ d-electron count: ____ Total electron count: ____
iii	Oxidation State: ____ d-electron count: ____ Total electron count: ____			

c) Give the crystal field splitting for (**i**) – (**v**), showing how the field will change relative to each intermediate. Use the coordinate axes given.

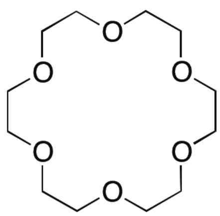
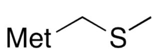
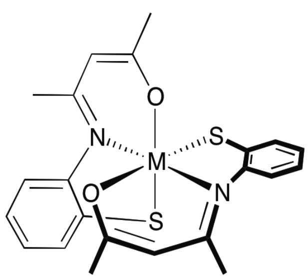


d) Using the crystal field for the fragment shown below and the MO diagram for H_2, draw a MO diagram for complex (**v**). Use the coordinate axes given.





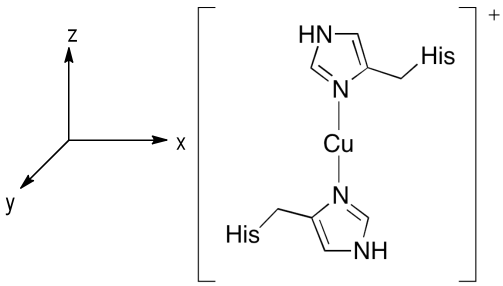
5) **Ligands**. (24 points) Decide the properties for each ligand in the table below.

Ligand	**Hard, soft, or intermediate**	**σ-donor, π-donor, or π-acceptor**	**Prefers Fe^{2+} or Ca^{2+}**
			
			
			
Cl^{-}			

6) Crystal Field Theory (20 points)

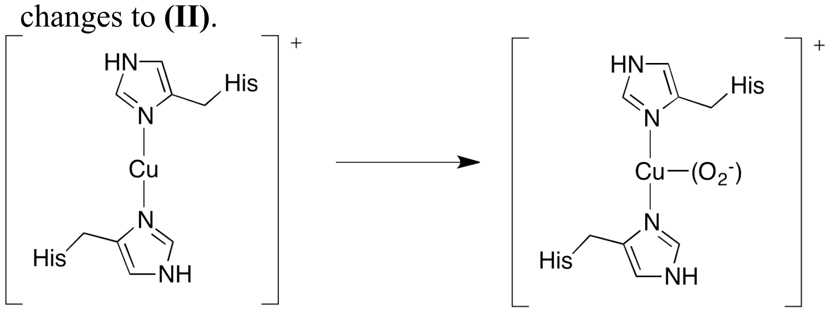
The linear complex $[Cu(His)_2]^+$ is a potential therapeutic for restoring normal copper levels in the body.

a) Using the orientation given below, (i) Draw a crystal field diagram for $[Cu(His)_2]^+$ and (ii) determine the d-count and oxidation state for the metal center.



(I)

b) Under certain circumstances under long-term storage, an O_2 adduct of this compound can form, making the bound O_2 a superoxide (O_2^-). Draw a crystal field, showing how **(I)** changes to **(II)**.

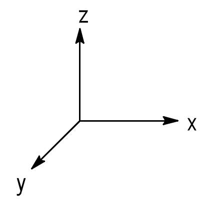


(I) **(II)**

7) Molecular Orbital Theory (22 points)

Phosphorous is a limiting element on the planet required for DNA/RNA as well as other phosphate-containing metabolites and materials (e.g. bone).

a) Draw a MO diagram for the P_2 fragment. Use the coordinate axes given.



b) The P_2 fragment is reactive and can form higher adducts, such as P_3^-. Using part (a) and an appropriate phosphorous source, make a MO diagram for P_3^-.

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)