CHM 501
Final Exam
May 11, 2016

All references are to *J. Am. Chem. Soc.*, **2016**, *138*.

1. (15 pts) Guo, *et al*, (pages 5410 – 5416) used sulfamic acid (NH_3SO_3) as a catalyst for formation of a lead perovskite on transparent substrates for application in solar cells. Draw the lowest energy Lewis structure for sulfamic acid, show the formal charges on each atom, and predict all of the bond angles around the N and S centers. Suggest a reason that sulfamic acid is used rather than a more conventional mineral acid.

Formal Charges: N, +1; S –1; H, O, 0.
Bond angles: all bond angles ~109.5°
Sulfamic acid is zwitterionic so that there is a significant dipole in the molecule, that could influence the reactivity. Another possibility is that the molecule breaks apart into gas phase components upon reaction, which makes isolation of the product easier.

2. (15 pts) Fan and coworkers (pages 5143 – 5149) studied the exfoliation of MoS_2, which forms a two-dimensional structure with interesting properties when isolated as a single layer. In the bulk phase MoS_2 is a semiconductor. Predict which orbitals would be used to form the valence and conduction bands. Explain your reasoning.

The valence orbitals for S are 3s and 3p while for Mo the valence orbitals are 4d. Since Z^* for S is expected to be higher than for Mo, the 3s and 3p orbitals are likely to lower in energy than the 4d orbitals. Further, the 3s and 3p orbitals on S^{2-} will be filled, so any band formation is unlikely to contribute to partially filled bands. Thus, the 4d orbitals are predicted to form the valence and conduction bands. Since MoS_2 forms a two dimensional structure, the orbitals in the xy plane, $d_{x^2-y^2}$ and d_{xy}, will overlap most strongly to form bands. For the d^2 ion, the electrons will fill these bands.

3. (15 pts) Martinez, Ocampo, Park, and Fout (pages 4290 – 4293) investigated the use of the carbene ligand, ^{DIPP}CCC, shown below, in nickel chemistry. They synthesized $Ni(^{DIPP}CCC)Cl$, which is orange. They then oxidized this compound with $PhICl_2$ (Ph = phenyl) to give a purple product with stoichiometry $Ni(^{DIPP}CCC)Cl_3$. Predict the geometry of the two Ni complexes. Are the colors consistent with the geometries you have drawn? Why or why not? Are either (or both) stable by the EAN rule? Why or why not? What is the oxidation state of I in the oxidant?

^{DIPP}CCC

Ni(^{DIPP}CCC)Cl must be 4-coordinate square planar, since the chelation of the ligand occupies three planar sites. This is consistent with the color for a Ni^{2+}, d^8 compound. Ni(^{DIPP}CCC)Cl$_3$ will be 6-coordinate (*mer* conformation). The metal is Ni^{4+}, d^6, in a low-symmetry mixed ligand-strength environment, which accounts for a deeper color.

EAN for Ni(^{DIPP}CCC)Cl: Ni^{2+}, 8 e$^-$ + ^{DIPP}CCC, 6 e$^-$ + Cl$^-$, 2 e$^-$ = 16 e$^-$; probably stable.
EAN for Ni(^{DIPP}CCC)Cl$_3$: Ni^{4+}, 6 e$^-$ + ^{DIPP}CCC, 6 e$^-$ + 3 Cl$^-$, 6 e$^-$ = 18 e$^-$; stable.
The oxidant is PhICl$_2$, which I in the +3 oxidation state.

4. (15 pts) Zhang, *et al*, (pages 4334 – 4337) proposed that under the right conditions a B-H- - -π hydrogen bond could be formed. In the classical sense borohydride bonds do not form hydrogen bonds. Explain why.

Hydrogen bonds are defined to have H-atoms with a partial positive charge attracted to an atom more electronegative than H. Borohydrides have H as a partial negative charge, so do not fit the definition of a hydrogen bond.

5. (15 pts) Lu and coworkers (pages 3970 – 3973) reported the properties of Y$_5$Si$_3$. Determine the formal oxidation state of each atom in the formula unit and the distribution of integer oxidation states. They found that this compound is metallic, with a high room temperature conductivity that increases as the temperature is reduced. Is this consistent with your oxidation state assignments? Why or why not? A metallic state requires a partially filled band. How is that achieved in this compound?

Y$_5$Si$_3$ has Si in the –4 oxidation state and Y formally in the +2.4 oxidation state. Y can be +2 or +3, so to achieve a formal state of +2.4 requires a distribution of 3 Y^{2+} and 2 Y^{3+}. The mixed oxidation state is stoichiometric so that the bands formed by the d orbitals will not be filled, which is consistent with the oxidation states.

6. (15 pts) Yang, *et al*, (pages 4046 – 4052) determined the structure of a number of lithium aurides. LiAu was found in a simple body centered cubic lattice. Which ion will determine the packing and which will fill the holes? Why? Sketch the unit cell.

The large ion determines the packing, in this case Au^- and the small Li^+ ions will fill the holes.

Sketch (black = Au, white = Li):

7. (15 pts) Iyo, *et al*, (pages 3410 – 3415) structurally characterized several superconductors with formula $CaAFe_4As_4$, where A = K, Rb, or Cs. The compound has a layered structure with the Fe and As atoms forming one layer and the Ca and A atoms occupying a second layer. The iron ion is 4-coordinate with approximately T_d local symmetry. What color do you expect this compound to be? Explain your reasoning. Suggest a reason that the coordination around the iron is not exactly tetrahedral.

> The oxidation state of the iron must be formally +2.25, i.e. the distribution of oxidation states is Fe^{2+}, Fe^{2+}, Fe^{2+}, and Fe^{3+}. The T_d coordination and the mixed oxidation state suggests a low energy, allowed transition so the compound is expected to be dark blue to black. In T_d coordination the electron configuration for Fe^{2+}, d^6, is $e^3t_2^3$, which is Jahn-Teller active so the structure distorts away from perfect T_d geometry. Fe^{3+}, d^5, is $e^2t_2^3$, which is not Jahn-Teller active but the +3 site is likely not static so all of the iron sites are distorted.

8. (15 pts) Walroth, *et al*, (pages 1922 – 1931) synthesized and characterized $[Cu(CF_3)_4]^-$. The UV-vis spectrum of this ion has a doublet peak centered at about 37,000 cm^{-1} with a molar absorptivity of ~22,000 $M^{-1}cm^{-1}$. Assign the transition. Based on this information, predict the point group for the molecule.

> 37,000 cm^{-1} is in the UV range of the spectrum and the molar absorptivity suggests a charge transfer transition. This means that the d-d transitions for the d^7 Cu^{3+} are weak and likely buried under the CT transition. If the complex were tetrahedral the lowest energy d-d transition would likely be observable. Since there is no evidence of such, the complex must be square planar belonging to the D_{4h} point group

9. (15 pts) Fataftah, *et al*, (pages 1344 – 1348) studied the complex $[Cr(C_3S_5)_3]^{3-}$. The ligand, $C_3S_5^-$, is cyclic (with a five membered ring) and chelates through two sulfur atoms. Draw the Lewis structure for the ligand and give the point group.

C_{2v}

10. (15 pts) Sharenko and Toney (pages 463 – 470) wrote a Perspective on lead halide perovskites. The perovskite structure, ABX, has a cubic unit cell with the A ions on the corners, the B ion in the center, and the X ion on the faces. Determine the stoichiometry of the perovskite structure. Explain how you arrived at your conclusion.

There are 8 A ions in the corners that contribute 1/8 each to the unit cell for a total of 1 A ion. There are 6 X ions on the faces that contribute ½ each to the unit cell for a total of 3 X ions. Finally, the single B ion in the center contributes entirely to the unit cell. Thus, the stoichiometry is ABX_3.