**CAPSTONE ASSIGNMENT #3**

**Energetic Cuprous Azide Complexes**

**NAME: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_**

**In order to complete this assignment, you will need to read (numerous times) the assigned article and look up specific references in the article.**

**Before you begin:**

You need to find the article. It can be found through the Electronic Journal Center (OhioLink) using the key words “Energetic Cuprous Azide Complexes” and was published in 2012.

**The assignment is broken up into three sections:**

1. Reading and Understanding the Article – Answers are (for the most part) found directly in the article or references. You simply need to find the answers and report them below. This portion of the assignment will be graded by the instructor and returned to you. Discussions related to these questions may also take place in class.
2. Beyond the Paper – These questions are similar to the Reading and Understanding questions but relate to background information. You will need to find these answers in the references or on your own (course text books *etc*.)
3. Critical Analysis/Thinking – For this part, you will have to answer questions about the article and references that require you to form your own conclusions, propose your own explanations, explain a synthetic or mechanistic process, etc. You need to answer the questions and submit them to the instructor, but this part will be graded primarily through in-class participation. Faculty will evaluate not only the correctness of your answers but also the thoughtfulness and clarity of those answers as well. **Prepare to go to the board!**

**Reading and Understanding**

1. What is dmpyz. Provide the name, formula and structure of the ligand.
2. In Figure 1, two of the azide ligands have the nitrogen bonded to the copper labeled as N2 (one is N2 the other is N2A) and N4 as the most distant from the copper. The third azide ligand is labeled in the opposite fashion. Explain this difference in labeling. Use the Cu – N bond distances in your discussion of the different labeling.
3. Figure 2 does not show the entire [Cu2(dmpyz)(N3)2]n complex. What is shown and what is missing? In the article the authors describe the bridging of the azide as -1,1,3. Identify the copper atoms and the nitrogen atoms in Figure 2 below. (You do not need to identify ALL of the Cu and N atoms. Provide it for at least two copper centers and the azide ligands attached to those centers.) What does -1,1,3 mean?

INSERT FIGURE 2 FROM paper here

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1. How does the dmpyz ligand connect the planes into a three dimensional structure as shown in Figure 3? What is the dmpyz ligand bonded to? How is it oriented in the crystal?
2. Draw the Lewis Structure of the azide ion including any resonance structures. Calculate formal charges for each resonance structure. Which structure(s) is(are) the best? What angle do you expect for the central nitrogen in azide? What angles are seen for central atoms in the azide, N(4)-N(3)-N(2), and in bonding to the copper, N(3)-N(2)-Cu(1)? Do these angles agree with the hybridization of the nitrogen in both cases?
3. Why are nitrogen rich HEDMs environmentally acceptable?
4. Are there structural or stylistic problems with this article that interfered with your understanding of the science? Give an example and explain how you interpreted what the authors had written?

**Beyond the Paper** – Many of these questions either refer to Reference 9 in the primary paper or come from this paper. Find this article.

1. What is a primary explosive? Why might a primary explosive be used as part of rocket propulsion?
2. In the last paragraph on Page 326 the authors state, “Theory postulates that for a primary explosive the structure should be capable of decomposition to products with a simple rearrangements of electrons, i.e. bonds and very limited physical movement of atoms.” Does 2,4,6-trinitro-resorcinate follow this postulate? Why or why not?
3. What property do the authors of Reference 9 relate to the sensitivity of metal azides? What relationship do they propose?
4. Most metal azides are explosive and many are quite sensitive and do not have practical uses because of this. What metal azides are not explosive? Does the property measured in this paper for these complexes agree with proposed relationship?

**Critical Analysis/Thinking**

1. Based on the Lewis structure(s) for azide ion in Question 5, why is azide unstable?
2. What do the authors of the main paper (Page 925, last paragraph, just above Figure 2) and the authors of Reference 9 (Figures 1 and 4) mean by the “non-bonded N-N distance of the azide ion”? Why might this value affect the sensitivity of the complex?
3. How does the inclusion of the dmpyz ligand change the non-bonded N-N distance as compared to CuN3 from Reference 9?
4. When the [Cu2(dmpyz)(N3)2] complex is added to the rocket propellant HMX thermal decomposition temperature decreases. The authors state that “…complex (1) can catalyze the thermal decomposition of HMX, and the catalytic ability enhances with the increase of mass.” Either support this statement or dispute it.