**Terminal Uranium (VI) Nitrides: Exploring Photoredox**

In fall 2020, Marinella Mazzanti from the Swiss Federal Institute of Technology was awarded the F. Albert Cotton Award in Synthetic Inorganic Chemistry for her outstanding accomplishments in uranium and lanthanide chemistry, including the stabilization of unusual oxidation states and multimetallic cluster synthesis and small-molecule activation. In this assignment you will learn about the latter when you examine her recent paper “Photochemical Synthesis of a Stable Terminal Uranium(VI) Nitride” *J. Am. Chem. Soc.* 2020, **142**, 19047−19051. You will apply a variety of inorganic concepts to understand what is so exciting about her work.

1. The authors are from Ecole Polytechnique Fédérale de Lausanne in Lausanne, Switzerland. What kind of organization is this? Who supported this research?
2. Why do the authors want to make a terminal U(VI) nitride? Based on the introduction to the paper, why might the organizations in 1 be interested in funding such a study?
3. Why were people unable to isolate such a compound in the past (be specific!)?
4. The authors use the term “terminal” to describe the nitride synthesized in this paper. Explain what they mean by “terminal” in this context.
5. The authors describe their compound as the *second* example of a U(VI) nitride. Draw the chemical structure of the first example (Hint: it is described in the introduction but the formula is not given in the paper!).
6. Draw valid closed shell Lewis dot structures of each of the ligands in [NBu4][U(OSi(OtBu)3)4(N)] and [NBu4][U(OSi(OtBu)3)4(N3)]. Rationalize that the U can be characterized as U(VI) in [NBu4][U(OSi(OtBu)3)4(N) by assigning charges to the ligands and counterions. Similarly justify that the U in starting material [NBu4][U(OSi(OtBu)3)4(N3)] is U(IV).
7. What is meant by the term “sterically demanding”? Which ligands are “sterically demanding” in this paper? Why did the authors choose to use “sterically demanding” ligands for the uranium in their synthesis?
8. In the Materials and Methods section of the Supplementary Material, the authors say they used “depleted” uranium. What does that mean and why you think they used it?
9. Identify five additional words in the paper that are not familiar with in this context and find the definition for at least two of them. Be prepared to share these with the class.
10. Why did the authors use 13CO in addition to just normal CO for their experiments?
11. The wavelength for maximum irradiation was 253.7 nm. What is the energy of this light in kJ/mol? How does that energy compare to the bond strength of the NN bond that has to be cleaved in the azide (you’ll have to look this up somewhere!)?
12. In the Materials and Methods section in the Supplementary Material, the authors describe the reaction of U(OSi(OtBu)3)4 with 1 eq of KN3 at room temperature as resulting in an “intractable mixture” as shown in figure S1 in the supplementary data. Why do you think the NMR shows this, and why did the authors include this information in the paper?
13. What are some of the challenges that you’d have to deal with if you wanted to carry out the experiments of this paper in our lab?
14. On the second page of the article, the authors state that the N-N bonds are nearly identical to one another. They then go on to say in the next paragraph that “[t]hese values do not necessarily suggest a low activation of the azide...” and provide a counter example. Why might a reasonable person suspect a low activation of the azide in this case?
15. The stability that the **[K(18c6)]+** cation confers on the azide complex is an important aspect of this work, yet the authors do not show a figure showing this interaction in the paper. Draw a chemical diagram, showing all the atoms, of this interaction.
16. The authors compare the νas(N3) of [K(18c6)]-**2** (2096 cm−1) to [NBu4]-**2** (2057 cm−1) in order to explain the azide’s activation in the former. What would you expect to be true of νas(N3) when the azide is more activated? How does that compare to what the authors state in the paper?
17. The U(IV) nitride is said to have an “inverse trans influence.” What is “trans influence” and why do the authors say this complex has an “inverse” one?