**Under pressure: Structure and bonding in actinide complexes (Arnold)**

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*To prepare for discussion, write out answers to these questions and bring them to class. Please note that the answers to the first four questions cannot be found in the paper; these questions draw on your previous knowledge of oxidation states, electron configuration, bonding and VSEPR, and will be helpful in preparing you to read and understand the content of the paper. You may wish to look to other sources e.g. previous lecture notes or textbooks such as Cotton’s Advanced Inorganic Chemistry (6th Edition) to aid you in answering these questions.*

Contrasting behaviour under pressure reveals the reasons for pyramidalization in tris(amido) uranium(III) and tris(arylthiolate) uranium(III) molecules, Amy N. Price, Victoria Berryman, Tatsumi Ochiai, Jacob J. Shephard, Simon Parsons, Nikolas Kaltsoyannis & Polly L. Arnold, *Nat. Commun.*, **2022**, 3931. <https://doi.org/10.1038/s41467-022-31550-7>

**Introduction to bonding in actinide complexes**

The two molecules studied in this paper are U[N(SiMe­3)2]3 (UN3) and U(S-C6H2-But-2,4,6)3 (US3). In each case, the uranium is attached to three bulky, anionic ligands.

1. What is the oxidation state of uranium in the two molecules? Show your work.

2. Write the (shorthand) electron configuration for the uranium ion.

3. Metal-ligand bonding in lanthanide and actinide complexes is primarily ionic. Explain why. (Hint: use the words “valence orbitals” and “radial extent” somewhere in your answer.)

**Shapes of actinide complexes**

4. What shapes can 3-coordinate complexes have? Give an example of each possibility. (Think back to VSEPR here. *Include approximate bond angles*).

We might expect a 3-coordinate UX3 actinide complex, like the ones in this paper, to be *trigonal planar*, as it is sterically most favored to distribute three groups farthest from each other. However, UX3 complexes, and most tricoordinate f-element complexes are *trigonal pyramidal*. The reason for this has been a topic of discussion for some time. The f-orbitals do not have strong spatial overlap with the ligand orbitals and are not expected to play a strong role in determining the structure.

One way to describe just how pyramidal the molecules are (the “pyramidalization” or how much they stray from planarity) is the out-of-plane (oop) distance as shown in Figure 1a.

5. In your own words, describe what the oop distance is.

**Four models that could be used to explain the geometry of UX3 complexes**

The authors describe four models that chemists might invoke to explain the non-planarity of these 3-coordinate actinide molecules. Each model represents the application of a chemistry concept that you might be familiar with; however, you might not be familiar with how they’re applied here.

**Fig 1b: Polarizable ion model.** The first model is one that is most likely new to you. Pyramidalization of the UX3 molecule generates a molecular dipole which lowers the energy of the molecule relative to the nonpolar planar configuration due to *induction stabilization*. In other words, if the metal ion is polarized, there can be dipole-dipole interactions (attractions) between the ligands and the (now polarized) metal ion. Although this concept may be new, you can apply your knowledge of polarizability to the problem.

6. (a) Uranium is a large polarizable metal ion. Let’s consider the individual U-X bonds. Which of the two molecules in the paper has more polar U-X bonds? Explain.

(b) The computed dipole moments of the two molecules are given in the second paragraph of the “Computational studies” section. What are the dipole moments, and are their magnitudes consistent with your answer to a? Explain.

**Fig 1c:** **Ligand dispersion forces.** Both molecules in the paper have large, “greasy” ligands.

7. Explain how ligand dispersion forces could impact the planar versus pyramidal geometry.

**Figure 1d: Metal-ligand agostic interactions.** A close distance between a metal center and the hydrogen of a ligand C-H bond is called an agostic interaction. Depending on the geometry of the ligand, this could favor either a planar or a pyramidal structure to maximize the number and strength of these interactions.

The red dashed lines in Figure 3b signify the agostic interactions in the high-pressure structure of UN3. Note: The three silylamide ligands are identical by symmetry, so there are actually six of these agostic interactions, although only two are shown. The text notes (and you can see in the figure) that they are “above” the pyramid.

8. In your own words, how would you expect these agostic interactions to affect how pyramidal the UN­3 molecule is.

**Fig 1e: M(d)-X(p) 𝜋 overlap.** Computational arguments have been made (see reference 12 in the paper to learn more) that𝜋-bonding between metal d-orbitals and ligand p-orbitals would favor a planar geometry in UX3 molecules (much like the argument for the importance of B(p)-F(p) **𝜋**-bonding in planar BF3). Given the large uranium ion and the relatively long U-ligand bonds in these molecules, **𝜋**-bonding would probably not play a significant role in influencing the structures of these molecules.

**Understanding the effects of pressure on the structure of two three-coordinate uranium complexes**

The crystal structures of the two molecules are determined at ambient (regular atmospheric) pressure and high pressure.

9. From Figure 2, record the oop distances (with uncertainties) for the molecules at ambient pressure and high pressure. How do they change at increased pressure?

|  |  |  |  |
| --- | --- | --- | --- |
|  | oop distance (ambient pressure), Å | oop distance (high pressure), Å | More pyramidal or more planar at high pressure? |
| U[N(SiMe­3)2]3 |  |  |  |
| U(S-C6H2-But-2,4,6)3 |  |  |  |

Another important concept here is molecular volume. *Computationally*, the authors determine the volume of both the pyramidal and planar forms of the molecules. *Experimentally*, using the crystal structures, they determine the volumes of the molecules at ambient and high pressure. The details of how molecular volume is determined are beyond the scope of this discussion, so we will focus on the results.

10. Compare the calculated volumes of pyramidal versus planar UN3. (Note: The authors also call the planar version of the molecule the “transition state structure.”)

11. Compare the calculated volumes of pyramidal versus planar US3. (Note: The authors use the term “theoretical structures” here.)

12. Intuitively, what would you predict would happen to molecular volume as the pressure is increased. Explain.

13. How do the experimental molecular volumes of the two molecules actually change when pressure is increased?

14. What do the authors conclude are the most important factors contributing to pyramidal versus planar structures in these complexes? What are your thoughts?