**Zr/Hf Polyoxocation Chemistry**

In fall 2022, May Nyman from Oregon State was awarded the F. Albert Cotton Award in Synthetic Inorganic Chemistry for her outstanding accomplishments in synthesis and development of polyoxometalates and metal oxohydroxoclusters, including their structures, speciation, reaction mechanisms, and function. In this assignment you will examine her recent paper “Differentiating Zr/HfIV Aqueous Polyoxocation Chemistry with Peroxide Ligation” *Inorg. Chem.* 2021, **60**, 1631-1640 which is related to that work. You will apply a variety of inorganic concepts to understand what is so exciting about what she and her collaborators are doing.

1. Who is supporting this research financially (hint: this is usually found in the Acknowlegements)? Based on the introduction to the paper, why might this organization be interested in the research that Professor May and coworkers are doing?
2. In the second sentence of the paper, the authors say “Not surprisingly, hafnium(IV) behaves similarly [to Zr(IV)] in synthesis, structure, and function of MOFs”

Let’s pick this statement apart:

1. Write the electron configurations of hafnium (IV) and zirconium (IV). Comment briefly on the electrons you removed to form the ions.
2. Given where hafnium and zirconium are on the periodic table what would you expect about the relative sizes of the +4 cations? Would you expect the size difference between Ti(IV) and Zr(IV) be more or less similar than the size difference between Zr(IV) and Hf(IV)? Explain your reasoning.
3. What is a MOF? Why are people interested in MOFs?
4. Why are the authors particularly interested in trying to develop chemistry that allows them to distinguish between Zr(IV) and Hf(IV) and control the ratios of these ions in materials?
5. Authors of scientific papers frequently give abbreviations to simplify their writing. These authors refer to “Zr4-perchlorate” in the introduction section. What is the chemical formula for this compound?
6. In the introduction the authors talk about isolating two Zr (IV) compounds including peroxide as a ligand with the formulas [Zr25O10(OH)50(O2)5(H2O)40](ClO4)20•xH2O and [Zr4(OH)4(µ-O2)2(µ4-O)(H2O)12](ClO4)6•xH2O. Prove that both of these complicated compounds are neutral!
7. In the 2nd compound above, draw the possible coordination environment of both the (µ-O2) and the (µ4-O) ligands.
8. Identify the point group symmetry of each of the Hf cluster structures shown in figures 1a, b, and c! (you can ignore the water molecules in red to simplify!)
9. What is the benefit of using peroxide as a ligand in these Zr/Hf systems?
10. The authors describe the synthesis of the Hf4-perchlorate as “Briefly, hafnium

oxyhydroxide is precipitated from an aqueous HfOCl2 solution by adding base (NH4OH). The solid precipitate is isolated and redissolved in perchloric acid, and crystals are obtained by evaporation.” Do you have any criticisms of this description based on your knowledge of acid- base chemistry?

1. The authors provide “bond valence sums” (BVS) based on the crystallographic data for compounds 1a, b, and c. Do a little research to find out how a BVS is calculated and how it is used in chemistry.

1. In Figure 2, the Raman spectrum shows the peroxide stretches for the Hf and Zr complexes, respectively. In your own words, state what these figures say about the differences in the Hf and Zr systems in solution.
2. At the bottom of page 1633, the authors give a formula for calculating hydroxide-peroxide occupancy in the Hf structures. Explain why they are using this equation.
3. Based on ESI mass spectrometry, the authors propose that “in methanol, Hf4Per1 and Hf4Per2 remain largely intact but exchange hydroxyl ligands for methoxyl ligands.” Draw a picture of the core structure of Hf4Per1 in methanol (you can leave out the terminal (non-bridging) ligands!).
4. SAXS (small angle X-ray scattering) is a technique that is somewhat similar to the more commonly used powder X-ray diffraction. What is the advantage of using SAXS in this particular study (Hint: what is the state of matter that is being measured)?
5. Near the bottom of page 1635, the authors say that “However, as the water evaporates and Hf species become more concentrated, the solution becomes considerably more acidic, owing to the tendency of HfIV-bound H2O to deprotonate.” Write a reaction showing this process. Why does this process make the solution more acidic? This type of process is favored for many metal ions. Why is it particularly important for HfIV?
6. What were some of the unexpected results from the attempts to make mixed Zr/Hf clusters?