**Selective Complexation and Separation of Lanthanides and Actinides – Discuss!**

***Read this article before class:***

Guillet, G.L.; Hyatt, I.F.D.; Hillesheim, P.C.; Abboud, K.A.; Scott, M.J. *“*1,2,4-Triazine-picolinamide functionalized, nonadentate chelates for the segregation of lanthanides(III) and actinides(III) in biphasic systems.” *New J. Chem.*, **2013**, *37*, 119-131, doi: 10.1039/c2nj40586e

**Questions**

***Background***

1. Briefly discuss the importance of lanthanides and actinides in our everyday lives. Where would we encounter them in the home, in medicine, and in industry?
2. The most common oxidation state of lanthanides (Ln) and actinides (An) is +3. Explore the ionic radii of Ln(III) and An(III) as a function of atomic number. How much do they vary in each period? What valence electrons are removed when a neutral atom is ionized to +3?
3. Draw/examine pictures of the structures of BTP (fig. 5) and TPAm (scheme 2); identify the donor/ligating atoms on each. What is the denticity of BTP and TPAm, and what are the stoichiometries of metal complexes of each? Are the ligands commercially available or do they need to be synthesized? Explain.
4. Discuss the advantages and disadvantages of using BTP as a complexing agent, and compare to TPAm, *e.g.* availability, stability of these ligands.
5. The metal-TPAm complex can be considered ideally as a tricapped trigonal prismatic shape. Draw a picture of the tricapped trigonal prismatic metal-ligand complex (ML9 in which L = individual ligating atoms), and assign the ideal point group symmetry. Refer to Figure 2 in the article, and compare the apparent point group symmetry to the idealized ML9 symmetry. Ignore connecting atoms present in TPAm; consider only the ligating atoms.
6. Using symmetry analysis, determine the {*s,p,d*} orbital splitting in the ML9 complex; *f*-orbitals reduce to A1' + A2' + E' + A2'' + E''. Starting with the reducible representation for the SALCs of the ligating atoms, determine the irreducible representations, and decide which of the valence Ln or Ac orbitals could overlap to form sigma bonds with the ligating atoms.

***Analytical Techniques***

1. What major analytical technique was used to track synthesis of TPAm? Why was this a particularly useful technique for this part of the research?
2. What major analytical technique(s) was used to identify the metal-ligand complexes? (*i.e.* why not just NMR?) Explain.
3. What major analytical technique was used in the kinetic study (fig.4)? Did it exploit a property of the metal ion or a property of the ligand? Explain.

***Chemistry***

1. State the purpose(s) of this research.
2. What thermodynamic advantage is gained in complex formation by using a nonadentate ligand versus three terdentate (tridentate) ligands? Compare/contrast BTP and TPAm – metal complexes in light of this question.
3. Compare/contrast the HSAB preferences of Ln(III) and An(III), referring back to the information discussed in question #4. How do the HSAB properties of BTP and TPAm match with those of Ln(III) and An(III)? How does this help to understand the purpose and strategy of this research?
4. Compare/contrast selective complexation trends found in the extraction studies with BTP and TPAm for the chosen Lns and Ans. Explain in terms of HSAB matching of metal ions and ligands. Does TPAm achieve the goals desired by the researchers?

***Molecular Modeling***

1. What were the simplifications applied to the ligands in the molecular modeling, and why were they chosen?
2. Discuss the M-L orbital interactions found in the molecular modeling. In general, did the calculations indicate significant M-L orbital overlap, or did they indicate that electrostatic interactions between metal ion and ligands were more important? Did all of the Ln(III) and An(III) ions behave the same? Explain.
3. Design your own nonadentate ligand that you would think would work well to selectively separate Ln(III) from An(III). Explain your reasoning.

***Future Research***

1. What other comparisons of metal-ligand complexes would you propose to further determine if TPAm is an improvement over what is already used to separate lanthanides and actinides?