**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?

Lanthanides
La: Refinery catalyst, camera lenses, lighter flints

Ce: Catalytic converters, glass polishing, lighter flints

Pr: Magnets, lighter flints, greenish-yellow glass and ceramics

Nd: Magnets, lasers, violet glass and ceramics

Pm: Radioactive; luminous pain, pacemaker batteries

Sm: magnets, cancer therapy, nuclear reactor control rods, organic reagent of Barbier reaction

Eu: Red phosphors for lighting and color displays

Gd: Refractive glass, MRI contrasting agent, nuclear reactor shielding

Tb: Green phosphorus for lighting, magnetorestrictive alloys

Dy: Stabilizing agent in magenets, lasers

Ho: laser, magnets

Er: lasers, fiber optics, nuclear reactor control rods

Tm: Portable x-ray source, light filaments, lasers

Yb: Lasers, chemical reducing agent, stainless steel additive, cancer therapy

Lu: PET scan detectors, refractive glass, refinery catalyst

Actinides (half-lifes given for most stable isotopes)

Ac: Used in medicine to product Bi-213. Radio-immunotherapy. Battery. 21 year half-life

Th: Coats W filaments in TV sets. Used to make U-233 for nuclear fuel.

Pa: no uses outside research. Half-life is 32,760 years

U: Nuclear weapons and fuel. Depleted uranium is U-238 used for its high density.

Np: Spacecraft and terrestrial generators. Neutron detection equipment

Pu: Nuclear weapons and fuel. Batteries on spacecraft. 88 year half-life.

Am: Smoke detectors. 7370 year half-life

Cm: Power sources for space and medicine.

Bk: Accumulates in the skeletal system. Formed in cyclotron.

Cf: Neutron source for on-the-spot detection of gold or silver. Moisture gauges.

Es: Discovered in the debris of the first hydrogen bomb test.

Fm: Research

Md: Research

No: Research

Lr: Research

1. 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?

From La to Lu, the ionic radii vary by 103.2 to 86.1 pm

From Ac to Es, the ionic radii vary by 112 to 83.5 pm

Two s-electrons and one d-electron are removed to give just the f-electrons remaining in the electron configuration

1. Draw/examine pictures of the structures of BTP and TPAm; 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.



The donor atoms are circled in the structures.

Denticity of both compounds is terdentate, aka tridentate

There are three ligands for every lanthanide of actinide to complete the 9-coordinate complex

The ligands could be found commercially from outside the US, but the importance of synthesizing them is to create derivatives and also to link three of them to the triphenoxymethane scaffold

1. Discuss the advantages and disadvantages of using BTP as a complexing agent, and compare to TPAm, *e.g.* availability, stability of these ligands.

The advantage to BTP is that the ligands preferentially extract the actinides over the lanthanides due to the “softer” donating groups. The disadvantage is that BTP is not stable to radiation so it would decomposed if used in the intended application of nuclear waste extraction. It is also not stable to hydrolysis thus would not work in the nitric acid solution of a dissolved nuclear fuel rod. TPAm is not as good at selectively extracting the actinides over the lanthanides as BTP but is thought to be more stable to radiation. TPAm can also be diversified to be added onto the scaffold of triphenoxymethane more easily.

1. 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 assigned 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.



The point group of a tricapped trigonal prism is D3h. The actual complex is very close to this idealized symmetry with a small twist distortion.

 

1. 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.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **D3h** | **E** | **2C3** | **3C'2** | **σh** | **2S3** | **3σv** | **linear, rotations** | **quadratic** | **cubic** |
| **A1'** | 1 | 1 | 1 | 1 | 1 | 1 |  | x2+y2, z2 | x(x2-3y2) |
| **A2'** | 1 | 1 | -1 | 1 | 1 | -1 | Rz |  | y(y2-3x2) |
| **E'** | 2 | -1 | 0 | 2 | -1 | 0 | (x, y) | (x2-y2, xy) | {xz2, yz2}, {x(x2+y2), y(x2+y2)} |
| **A1''** | 1 | 1 | 1 | -1 | -1 | -1 |  |  |  |
| **A2''** | 1 | 1 | -1 | -1 | -1 | 1 | z |  | z3, z(x2+y2) |
| **E''** | 2 | -1 | 0 | -2 | 1 | 0 | (Rx, Ry) | (xz, yz) | {xyz, z(x2-3y2)} |

s = A1' p = E' + A2" d = A1' + E' + E"

f = A1' + A2' + E' + A2" + E"

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **D3h** | **E** | **2C3** | **3C'2** | **σh** | **2S3** | **3σv** |
| **SALCs** | 9 | 0 | 1 | 3 | 0 | 3 |

SALCs = 2A1'+A2'+2E'+A2"+E"

All of the atomic orbitals have an appropriate symmetry to overlap with one or more of the ligands SALCs, so none will come over as nonbonding in an MO diagram.

***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?

UV/Vis was used because the complexation of the ligand to the metal can be tracked by the isosbestic point. The extraction experiments were also tested with UV/Vis against a blank to evalulate the extraction efficiency of each ligand (See the last paragraph of the General Considerations section).

1. What major analytical technique(s) was used to identify the metal-ligand complexes? (*i.e.* why not NMR?) Explain.

NMR is good at characterizing the ligand because it has protons and carbons, but not so great at the metal complex for a variety of reasons including solubility, paramagnetism, and limited chemical shifts of hydrogens upon complexation. The main technique for characterization is single crystal X-ray crystallography.

1. What major analytical technique was used in extraction studies? Did it exploit a property of the metal ion or a property of the ligand? Explain.

UV/Vis was used in the extraction studies. The experiment relied upon the Arsenazo(III) dye complexing with the metal ion in control and extraction samples, which changed the max of the dye.

***Chemistry***

1. State the purpose(s) of this research.

To devise a method for improved separation of lanthanides and actinides from nuclear waste with more stable ligands.

1. 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.

The complexation is very entropically favored as one nonadentate ligand displaces nine water molecules as opposed to three tridentate ligands. Therefore, formation of the nonadentate TPAm-metal complexes should be entropically favored over the formation of the tridentate (BTP)3-metal complexes.

1. 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 Ac(III)? How does this help to understand the purpose and strategy of this research?

Ln(III) are harder metals and bond more ionically than An(III) which is softer and bonds more covalently. Since nitrogen is less electronegative than oxygen, ligands that contain only nitrogen donors are softer than those that contain oxygen. More covalent bonding means the actindes will be favored over the lanthanides when they are pulled into the organic phase during the extraction process. This is the key to selective extraction. BTP is a softer donor ligand thus will bind more preferentially to actinides than lanthanides as opposed to the hard oxygen donor in the TPAm ligand. Even though TPAm is harder, it was thought that it would be a better at pulling out more metals (both An and Ln) from the solution although selectivity might suffer.

1. 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?

A BTP vs. TPAm comparison was shown computationally but not experimentally. Different conditions of testing for extraction efficiency make it difficult to compare values with other publications (solvents, acid concentration, method used, etc.). Theoretically, BTP outperformed TPAm in the amount of covalent bonding interactions of the frontier orbitals; an indicator that TPAm is not reaching the same efficiency as BTP. See above explanation

The main issue encountered with TPAm was due to the solubility which was shown to be tunable by making a more aliaphatic triphenoxymethane scaffold (increased efficiency for complexes using ligand 10 and 11). In that regard, the study showed from experiment that the triphenoxymethane scaffold can help, but computationally showed that the TPAm ligand moiety was likely not as good as BTP.

***Molecular Modeling***

1. What were the simplifications applied to the ligands in the molecular modeling, and why were they chosen?

For full electron structure (population analysis) the triphenoxymethane scaffold was removed from the geometry optimizations and single-point energy calculations. This was done to make the calculations faster (in actuality it made then feasible since even without the scaffold and with multiple processors and lots of memory they took up to 2 weeks to complete). Computation time in molecular modeling increases steeply as the number of atoms increases. The triphenoxymethane scaffold could be ignored when focusing on the metal-ligating atoms orbital interactions.

1. 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 the electrostatic interactions between metal ion and ligands were more important? Did all of the Ln(III) and An(III) ions behave the same? Explain.

The calculations suggested that the M-L overlap was more ionic with Ln(III) complexes (frontier orbitals did not show overlap of M-L and the M orbitals were energetically buried, a.k.a. very different in energy, thus ionic) and more covalent with the softer donating ligands complexing with An(III). This agrees with experimentally observed preferences of Lns for harder ligating atoms (e.g. oxygen), and Ans for softer ligating atoms (e.g. nitrogen in aromatic ring).