The Effects of Pressure and Ligand Type on Valence Electron Bonding in Lanthanide Compounds

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ABSTRACT

One of the most promising realms of study within the field of chemistry has to do with the heaviest elements, specifically the lanthanides and actinides, elements 57-71 and 89-103 respectively. These elements have a number of unique properties that have not been studied sufficiently to fully understand. Thus, the aim of this research is to synthesize lanthanide compounds, specifically ones that will form solid crystals, so that we can more fully determine their structure and corresponding properties. Once we find compounds that will crystalize in a satisfactory manner, we can put them under extreme pressure in diamond anvil cells and then use x-ray crystallography to determine how the electrons within the metal are engaged in bonding when under high pressure. The goal is to better understand how both pressure and the type of ligand affect the degree to which the 4f and 5f valence electrons in these compounds are involved in bonding. The current task is to synthesize a lanthanide benzene dithiolate with a crown ether on the ring, since this structure has a relatively high likelihood of being able to crystalize. If we can successfully synthesize the compound, then we will be able to move on to the analysis of its properties and deepen our understanding of the lanthanides and actinides.

LANTHANIDES	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDES	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

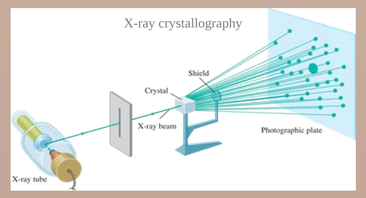
BACKGROUND

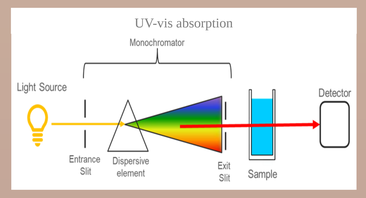
Characteristics of the lanthanides and actinides

- High molar masses
- Can form a variety of oxidation numbers
- Are quite radioactive
- Many can form various unique structures in compounds

Techniques for determining the structure of compounds

- X-ray crystallography: shoots X-rays at a sample and uses the diffraction pattern of those X-rays to determine the arrangement of the atoms in the compound.
- UV-vis absorption spectroscopy: measures the intensity of the light that is passed through a sample and can allow scientists to determine the different types of bonds present.





METHODS

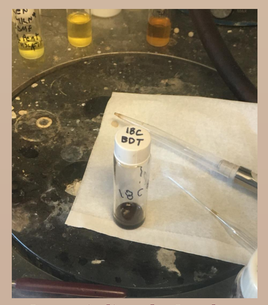
Our main task up to this point has been to generate a lanthanide compound that will crystallize so that we can study its structure using x-ray crystallography and high pressure diamond anvil cells.

We have been working on synthesizing a lanthanide benzene dithiolate with a crown ether on the ring through the following steps:

1. Add 10 mg of the lanthanide-iodine compound (NdI3 or EuI3) to 0.200 mL of the benzene dithiolate complex (shortened to bdt).
2. Dissolve the resulting solution in a solvent (either THF or pyridine).
3. Filter out the solid.
4. Place the remaining solution into a pentane vapor diffusion to evaporate off the excess liquid.

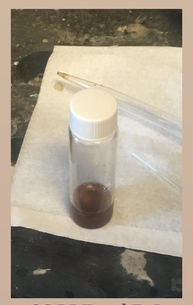
We have been trying our procedure with multiple different lanthanides (specifically neodymium and europium) and multiple different solvents (THF and pyridine) with the goal of trying to try to find the combination that will crystallize most effectively.

We have been working in an air-evacuated glove box because some of the chemicasl are very reactive with air or other substances found in an uncontrolled system.

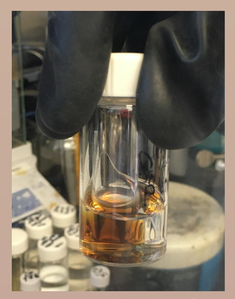


Our main ligand, 18 carbon benzene dithiolate complex

Europium tri-iodide, one of the lanthanides we are using



18C BDT and EuI3 mixed together and dissolved in pyridine



18C BDT, EuI3, and pyridine solution in pentane vapor diffusion

Labels show the lanthanide type, volume of the ligand, and vapor diffusion solvent

Inside of the glove-box we are using, our vapor diffusion solution in center

RESULTS

Since we have not had enough time to complete our experiment yet, we do not have any definitive results.

The first step we need to complete is crystallizing the lanthanide benzene dithiolate compound, since that will allow us to further analyze the structure and bonding of such compounds.

Most of our research until this point has in determining the right chemicals and concentrations to use in order to generate a lanthanide bdt compound that will crystallize.

We have determined that both europium and neodymium appear to work with the bdt and pyridine solutions to form a homogenous solution. We have been trying to identify the different solids and solutions that we get at each point in the reaction in order to verify that we are synthesizing the correct compound.

NEXT STEPS AND FUTURE WORK

Assuming we are able to successfully crystallize the compound and place the crystal under high pressure in the diamond anvil cell, we expect to see patterns of diffraction from the X-ray diffraction that will help us determine the exact structure of the compound.

Furthermore, we hope that these results will help us identify how the 4f and 5f electrons in the lanthanides and actinides are involved in bonding, since that is not currently known.

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