DEVELOPMENT OF NONADENTATE LIGANDS FOR THE SELECTIVE SEPARATION OF LANTHANIDES AND ACTINIDES: A COMPUTATIONAL AND SYNTHETIC INVESTIGATION

By

IVAN FABE DEMPSEY HYATT

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2010
To Elisa, and my family
ACKNOWLEDGMENTS

I would first like to thank my parents and family for the support they have given me in my scholastic journey. I would not be at this level of academics without their help and most importantly their faith that I could accomplish my goals. I thank my mother, Elaine Hyatt, for motivating me to strive for the best and teaching me how to focus my mind on academics like only a teacher can. I am very thankful for my father, Andrew Hyatt, for instilling the drive to take pride in my work and how to excel through competition. I would also like to thank my extended family, especially, James and Alexander Hyatt, for always giving me something to smile about.

I could have never succeeded in academics without the support of my significant other (p < 0.0001), Elisa Livengood. She has contributed more to my success than any one person has. Her academic competitiveness has propelled us both and our mutual love for science is nearly as great as our love for each other.

Eternal appreciation is given to my high school calculus and physics teacher, Mr. Greg Hardin, who taught me the level of commitment that is needed to excel in school and to my high school chemistry teacher, Mr. Elton Caviness, who first inspired me to pursue the infinite possibilities of a career in chemistry. I thank my undergraduate adviser, Dr. Andrew Sargent, for encouraging me to go to graduate school, and teaching me how to undertake computational chemistry research. The skills he taught have been invaluable to my research.

I also thank Dr. Tammy Davidson for always giving me the opportunity to teach organic chemistry lab and Dr. Lisa McElwee-White for letting me do computational work with her. I thank Dr. Ben Smith for helping me transition to a new research group.
The last five years have been challenging but my friends are always there to help. I thank John Deaton, Rusty Coco, Mark Moseley, Benjamin Baldwin and Mike Hoose for letting me escape chemistry even if it was brief venture back to North Carolina. I also thank my fellow Scott group members, Patrick Hillesheim, Gary Guillet, Anna Sberegaeva, Nathan Strutt and Candace Zielenuik, for teaching me proper synthetic techniques and always listening to my off the wall ideas. I also have much appreciation and respect for my friends in the inorganic division, especially, Matt Jeletic, Soumya Sarkar and Shreya Mukherjee.

In closing, I wish to express gratitude to my adviser, Dr. Mike Scott. I will always remember his unique way of teaching and try to use what I have learned from him in my own career. I am most thankful that he accepted me into the group at a time of great need. I appreciate the independence and trust he gave me in exploring my own computational research and for contributing to my knowledge of chemistry as a whole.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>10</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>13</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>15</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>1 INTRODUCTION</td>
<td>16</td>
</tr>
<tr>
<td>1.1 The Current Status of Nuclear Power</td>
<td>16</td>
</tr>
<tr>
<td>1.2 Nuclear Waste Reprocessing</td>
<td>16</td>
</tr>
<tr>
<td>1.2.1 Plutonium Uranium Recovery by Extraction Method</td>
<td>18</td>
</tr>
<tr>
<td>1.2.2 Transuranium Extraction Method</td>
<td>19</td>
</tr>
<tr>
<td>1.2.3 Diamide Extraction Method</td>
<td>20</td>
</tr>
<tr>
<td>1.2.4 Selective Actinide Extraction Method</td>
<td>21</td>
</tr>
<tr>
<td>1.3 Separation of Lanthanides and Actinides</td>
<td>22</td>
</tr>
<tr>
<td>1.4 Benefits of Preorganization on a Molecular Platform</td>
<td>23</td>
</tr>
<tr>
<td>1.5 Experimental Research Objectives</td>
<td>26</td>
</tr>
<tr>
<td>1.6 Computation Research Objectives</td>
<td>27</td>
</tr>
<tr>
<td>1.6.1 Semi-Empirical Calculations</td>
<td>28</td>
</tr>
<tr>
<td>1.6.2 Density Functional Theory Calculations</td>
<td>29</td>
</tr>
<tr>
<td>2 STRUCTURAL ANALYSIS OF NONADENTATE LANTHANIDE COMPLEXES USING SEMI-EMPIRICAL METHODS</td>
<td>31</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>31</td>
</tr>
<tr>
<td>2.2 Computed Structures</td>
<td>32</td>
</tr>
<tr>
<td>2.3 Structural Evaluation</td>
<td>36</td>
</tr>
<tr>
<td>2.4 Lanthanide Contraction</td>
<td>38</td>
</tr>
<tr>
<td>2.4 Conclusions</td>
<td>40</td>
</tr>
<tr>
<td>2.5 Computational Details</td>
<td>41</td>
</tr>
<tr>
<td>3 SYNTHESIS OF BENZIMIDAZOLE-PRIDYL FUNCTIONALIZED NONADENTATE LIGANDS</td>
<td>42</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>42</td>
</tr>
<tr>
<td>3.2 Synthetic Difficulties of Ether Linkage Ligands</td>
<td>42</td>
</tr>
<tr>
<td>3.3 Synthesis of Amide Linkage Ligands</td>
<td>45</td>
</tr>
<tr>
<td>3.3.1 Carboxylic Acid Functionalization of the Ligand Arm</td>
<td>46</td>
</tr>
</tbody>
</table>
3.3.2 Incorporation of the Amide Linkage as a Donor Group for Metal Binding ................................................................. 48
3.4 Synthesis of Triazole Linkage Ligands .................................................. 49
3.5 Conclusions .................................................................................... 50
3.6 Experimental Section ...................................................................... 52
  methyl 2-(6-(diethylcarbamoyl)pyridin-2-yl)-1-ethyl-1H-benzo[d]imidazole-5-carboxylate (3-21): ................................................................. 52
  2-(6-(diethylcarbamoyl)pyridin-2-yl)-1-ethyl-1H-benzo[d]imidazole-5-carboxylic acid (3-20): ................................................................. 53
  methyl 6-(ethyl(4-(methoxymethyl)-2-nitrophenyl)carbamoyl)picolinate (3-23): ................................................................. 54
  6-(1-ethyl-5-(methoxymethyl)-1H-benzo[d]imidazol-2-yl)picolinic acid (3-25): 54
  2-(6-bromopyridin-2-yl)-1-methyl-1H-benzo[d]imidazole (3-30): ............... 55
  1-methyl-2-(6-((trimethylsilyl)ethynyl)pyridin-2-yl)-1H-benzo[d]imidazole (3-31a): ................................................................. 56
  2-(6-ethynylpyridin-2-yl)-1-methyl-1H-benzo[d]imidazole (3-31b): .................. 56
  Tris(2-ethylacetoxy-3-methyl-5-tert-pentylphenyl)methane (3-14c): ............. 57
  Tris[2-(2-hydroxylethoxy)-3-methyl-5-tert-pentylphenyl]methane (3-15c): ....... 57
  Tris[2-(2-toluenesulfonylethoxy)-3-methyl-5-tert-pentylphenyl]methane (3-16c): ................................................................. 58
  Tris(2-(2-azidoethoxy)-3,5-di-tert-pentylphenyl)methane (3-32): ............... 59
  tris[2-(2-(4-(6-(1-methyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)-1H-1,2,3-triazol-1-yl)ethoxy)-3,5-di-tert-pentylphenyl)methane (3-33): .......... 59
General Procedure for the Synthesis of 3-22 and 3-26 .................................. 60

4 METAL COMPLEXATION EXPERIMENTS OF LANTHANIDES USING BANZIMIDAZOLE-PRIDYL FUNCTIONALIZED NONADENTATE LIGANDS ...... 62

4.1 Introduction ..................................................................................... 62
4.2 Extraction Results ......................................................................... 62
4.3 Crystal Structure ............................................................................ 64
4.4 Conclusions ................................................................................... 67
4.5 Experimental Section ..................................................................... 69
  4.5.1 Extraction Experiment ................................................................. 69
  4.5.2 Crystal Structure of Yb(3-26)3+: .................................................. 69
  4.5.2 Crystal Structure of Yb(3-33)3+: .................................................. 70

5 ELECTRONIC STRUCTURE OF EUROPIUM, AMERICIUM, AND CURIUM COMPLEXES USING DENSITY FUNCTIONAL THEORY .............................................. 73

5.1 Introduction ..................................................................................... 73
5.2 Geometry Optimizations .................................................................. 74
5.3 Electronic Structure Analysis .......................................................... 77
  5.3.1 Mulliken and Natural Charge Analysis .......................................... 77
  5.3.2 Molecular Orbital Analysis .......................................................... 78
5.4 Conclusions ................................................................................... 88
5.5 Computational Details .................................................................... 90
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Average Metal Bond Lengths (Å) and Twist Angles (°) of Amide Structures</td>
<td>36</td>
</tr>
<tr>
<td>2-2</td>
<td>Average Metal Bond Lengths (Å) and Twist Angles (°) of Triazole Structures</td>
<td>37</td>
</tr>
<tr>
<td>4-1</td>
<td>Extraction Efficiency</td>
<td>63</td>
</tr>
<tr>
<td>4-2</td>
<td>Comparison of bond lengths (Å) and twist angles (°) between the crystal</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>structure, SE calculation, and crystal SE calculation of Yb(3-26)</td>
<td></td>
</tr>
<tr>
<td>4-3</td>
<td>Comparison of bond lengths (Å) and twist angles (°) between the crystal</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>structure, SE calculation, and crystal SE calculation of Yb(3-33)</td>
<td></td>
</tr>
<tr>
<td>4-4</td>
<td>X-ray data for crystal structures Yb complexed by 3-22 and 3-33 using triflate</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>counter ions grown from the diffusion of ether into methanol</td>
<td></td>
</tr>
<tr>
<td>5-1</td>
<td>Calculated M-N bond distances for structure 5-1</td>
<td>75</td>
</tr>
<tr>
<td>5-2</td>
<td>Calculated M-N bond distances for structure 5-2</td>
<td>76</td>
</tr>
<tr>
<td>5-3</td>
<td>Calculated M-N bond distances for structure 5-3</td>
<td>76</td>
</tr>
<tr>
<td>5-4</td>
<td>Comparison of Mulliken Charges for ML$_3^{3+}$</td>
<td>77</td>
</tr>
<tr>
<td>5-5</td>
<td>Orbital compositions (%) of bonding interactions</td>
<td>89</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>The nuclear fuel cycle. Filled boxes represent the currently used open fuel cycle and unfilled boxes represent the proposed closed fuel cycle.</td>
<td>17</td>
</tr>
<tr>
<td>1-3</td>
<td>Structure of tributylphosphate (TBP), an extractant used in the PUREX process.</td>
<td>19</td>
</tr>
<tr>
<td>1-4</td>
<td>Structure of N,N-diisobutylcarbamoyl-methyl-octylphenyl-phosphineoxide (CMPO), an extractant used in the TRUEX process.</td>
<td>20</td>
</tr>
<tr>
<td>1-5</td>
<td>Structure of DMDOHEMA and DMDBTDMA, extractants used in the DIAMEX process.</td>
<td>20</td>
</tr>
<tr>
<td>1-6</td>
<td>Structure of Cyanex 301 and BTP, extractants used in the TRUEX process.</td>
<td>22</td>
</tr>
<tr>
<td>1-7</td>
<td>Tricapped trigonal prismatic (TTP) geometry.</td>
<td>23</td>
</tr>
<tr>
<td>1-8</td>
<td>A simple calixarene. Functionalities can be added to bolster metal extraction.</td>
<td>24</td>
</tr>
<tr>
<td>1-9</td>
<td>CMPO moieties attached to a calixarene platform.</td>
<td>24</td>
</tr>
<tr>
<td>1-10</td>
<td>Triphenoxymethane molecular platform.</td>
<td>26</td>
</tr>
<tr>
<td>1-11</td>
<td>DGA attached to triphenoxymethane.</td>
<td>26</td>
</tr>
<tr>
<td>1-12</td>
<td>Common moiety used in all synthesized ligands. The groups R, R’ and R” refer to the various linkages, donor groups and solubility modifiers.</td>
<td>27</td>
</tr>
<tr>
<td>2-1</td>
<td>Semi-empirical calculation structures.</td>
<td>33</td>
</tr>
<tr>
<td>2-2</td>
<td>Semi-empirical geometry optimization of structure 2-7.</td>
<td>34</td>
</tr>
<tr>
<td>2-3</td>
<td>Semi-empirical geometry optimization of structure 2-8.</td>
<td>35</td>
</tr>
<tr>
<td>2-4</td>
<td>The graph shows the metal to donor atom bond lengths for structure 2-4.</td>
<td>39</td>
</tr>
<tr>
<td>2-5</td>
<td>The graph shows the metal to donor atom bond lengths for structure 2-7.</td>
<td>39</td>
</tr>
<tr>
<td>3-1</td>
<td>Tripodal helicate ligand developed by Piguet et al.</td>
<td>43</td>
</tr>
<tr>
<td>3-2</td>
<td>Synthesis of ligand arm 3-10, which contains the chloride functionality needed to attach triphenoxymethane via Williamson ether synthesis.</td>
<td>43</td>
</tr>
<tr>
<td>3-3</td>
<td>Synthesis of two carbon linker triphenoxymethane.</td>
<td>45</td>
</tr>
<tr>
<td>3-4</td>
<td>Synthesis of the three carbon linker amine triphenoxymethane, 3-18</td>
<td>46</td>
</tr>
</tbody>
</table>
3-5 Synthesis of carboxylic acid functionalized ligand arm, 3-20 ................................................. 46
3-6 Synthesis of the nonadentate ligand, 3-22 .................................................................................. 47
3-7 Synthesis of the carboxylic acid functionalized benzimidazole-pridyl ligand arm, 3-25 .................. 48
3-8 Synthesis of the nonadentate ligand, 3-26 .................................................................................. 48
3-9 Synthesis of the alkyne ligand arm, 3-31 .................................................................................. 49
3-10 Synthesis of the nonadentate triazole ligand, 3-33 ................................................................. 50
4-1 Crystal structure of Yb complexed by ligand 3-26 with ellipsoids at 50% probability ......................... 65
4-2 Crystal structure of Yb complexed by ligand 3-33 with ellipsoids at 50% probability ......................... 66
5-1 Simplified ligands computed by DFT. Each ligand was computed with Eu, Am, and Cm as the metal .......................................................................................... 75
5-2 Representation of benzimidazole centered HOMO of Cm(5-3)\(^3^+) ........................................ 79
5-3 Representation of ligand to metal donation in the HOMO-9 of Am(5-1)\(^3^+) ........... 80
5-4 The HOMO-1 of Am(5-1)\(^3^+\). The black lines signify anti-bonding interactions .. 81
5-5 The HOMO-12 of Am(5-1)\(^3^+) does not display any overlap of orbitals since the overlap population was computed as zero. ................................................................. 82
5-6 MO for Eu(5-1)\(^3^+\), Am(5-1)\(^3^+\), and Cm(5-1)\(^3^+\). Metal energy levels shifted by approximately 18 eV and ligand orbitals by -8 eV................................................................. 83
5-7 Degenerate orbitals HOMO-43 and HOMO-44 of Cm(5-1)\(^3^+) at -17.803 eV ...... 84
5-8 MO for Eu(5-2)\(^3^+\), Am(5-2)\(^3^+\), and Cm(5-2)\(^3^+\). Metal energy levels shifted by approximately 18 eV and ligand orbitals by -8 eV................................................................. 85
5-9 Representation of ligand to metal donation in the HOMO-36 of Cm(5-2)\(^3^+) ...... 86
5-10 MO for Am(5-3)\(^3^+\), and Cm(5-3)\(^3^+\). Metal energy levels shifted by approximately 18 eV and ligand orbitals by -8 eV................................................................. 87
A-1 NMR of 3-21 .......................................................................................................................... 95
A-2 NMR of 3-20 .......................................................................................................................... 96
A-3 NMR of 3-23 .......................................................................................................................... 96
<table>
<thead>
<tr>
<th></th>
<th>NMR of 3-25</th>
<th>NMR of 3-30</th>
<th>NMR of 3-31b</th>
<th>NMR of 3-14c</th>
<th>NMR of 3-15c</th>
<th>NMR of 3-33</th>
<th>NMR of 3-22</th>
<th>NMR of 3-26</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-4</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-5</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-6</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-7</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-8</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-9</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-10</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
<tr>
<td>A-11</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
<td>.................................................................</td>
</tr>
</tbody>
</table>
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G*</td>
<td>Gaussian basis set with diffuse functions on atoms other than hydrogen</td>
</tr>
<tr>
<td>AM1</td>
<td>Austin model 1, semi-empirical method</td>
</tr>
<tr>
<td>Am(III)</td>
<td>Trivalent americium</td>
</tr>
<tr>
<td>An(III)</td>
<td>Trivalent actinides</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke 3 parameter, Lee, Yang, Parr functional</td>
</tr>
<tr>
<td>BTP</td>
<td>bis-triazinyl pyridine</td>
</tr>
<tr>
<td>CMPO</td>
<td>N,N-diisobutylcarbamoyl-methyl-octylphenyl-phosphineoxide</td>
</tr>
<tr>
<td>Cyanex 301</td>
<td>(bis(2,4,4-trimethylpentyl)dithiophosphinic acid)</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DIAMEX</td>
<td>Diamide Extraction</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DGA</td>
<td>Digycolamides</td>
</tr>
<tr>
<td>DMDBTDMA</td>
<td>Dimethyl-dibutyl-tetradecyl-malonamide</td>
</tr>
<tr>
<td>DMDOHEMA</td>
<td>Dimethyl-dioctyl-hexylethoxy-malonamide</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N dimethyl formamide</td>
</tr>
<tr>
<td>%E</td>
<td>Extraction efficiency</td>
</tr>
<tr>
<td>ECP</td>
<td>Effective core potential</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray mass spectrometry</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>Trivalent europium</td>
</tr>
<tr>
<td>HOFO</td>
<td>Highest occupied fragment orbital</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>L</td>
<td>Ligand</td>
</tr>
<tr>
<td>LANL2DZ</td>
<td>Los Alamos national lab double zeta density functional basis set</td>
</tr>
<tr>
<td>Ln(III)</td>
<td>Trivalent lanthanides</td>
</tr>
</tbody>
</table>
LUFO  Lowest unoccupied fragment orbital
LUMO  Lowest unoccupied molecular orbital
M     Metal
MO    Molecular orbital
MOPAC Molecular Orbital Package
NMR   Nuclear magnetic resonance spectroscopy
PM3   Parameterized model number 3, semi-empirical method
PM6   Parameterized model number 6, semi-empirical method
PUREX Plutonium uranium extraction
PyBOP benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate
RECP  Relativistic effective core potential
SANEX Selective actinide extraction
SCF   Self-consistent field
SE    Semi-empirical
S_{\text{N}2} bimolecular substitution reaction
SPARKLE A semi-empirical method for treating trivalent lanthnides. The "SPARKLE" refers to the 3\(^+\) oxidation state of lanthanides
TBP   Tributyl Phosphate
THF   Tetrahydrofuran
Tf    Trifluoromethanesulfonate aka Triflate
TRUEX Trans-uranium extraction
TTP   Tricapped trigonal prismatic geometry
Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

DEVELOPMENT OF NONADENTATE LIGANDS FOR THE SELECTIVE SEPARATION
OF LANTHANIDES AND ACTINIDES: A COMPUTATIONAL AND SYNTHETIC
INVESTIGATION

By

Ivan Fabe Dempsey Hyatt

December 2010

Chair: Mike Scott
Major: Chemistry

To meet the energy demands of the future, nuclear power provides one of the best options for providing electricity. The encumbrance that nuclear power bears is that the radioactive waste must be stored for many thousands of years. To counteract the problems associated with radioactive waste, the actinides can be separated from the waste stream in order to decrease waste volume and, after transmutation, decrease storage time of the hazardous materials.

Transmutation of actinides is hindered by the presence of lanthanides lowering the efficiency of the process. The following work presents ligands that can separate these two groups of metals from each other. The design of the ligands is based on radioactive stability, hard-soft acid-base principles, and the use of environmentally friendly elements. Tridentate ligands with nitrogen donor groups can then be attached to a triphenoxymethane scaffold to make a rigid structure that bonds metals in a nonadentate fashion. Several computational methods were also used to investigate the geometric and electronic structure of the metal complexes.
CHAPTER 1
INTRODUCTION

1.1 The Current Status of Nuclear Power

Nuclear power currently provides approximately 16% of the world’s electricity from about 441 nuclear reactors. In the United States 103 of these reactors provide us with 20% of our electricity.¹ By the year 2030 there will be a 57% increase in worldwide energy consumption with a significant fraction coming from developing nations.² Currently, the world does not have enough power plants available to generate the required electricity and with the rising cost of oil and concern about carbon dioxide emissions, the burning of fossil fuels may not be the best method to supply the energy demand. In contrast, there is an ample supply of uranium to fuel nuclear power and the entire process from mining to electricity distribution, generates less greenhouse gas than burning fossil fuels. The main detriment to nuclear power is the generation of radioactive waste which must be disposed of and stored in order to prevent contamination.³

1.2 Nuclear Waste Reprocessing

Since 1968 the United States has produced over 47,000 metric tonnes of spent fuel.⁴ Without a national repository, the radioactive waste is usually stored onsite at the reactor facility from which it was generated. In countries such as France, nuclear power provides around 80% of the electricity and produces approximately 1,135 tonnes of waste each year, but they have developed reprocessing methods that can recover reusable materials thus lowering the volume of waste. The commercial reprocessing plant in La Hague can reprocess up to 1,700 tonnes of spent fuel each year.⁵ A simplified closed fuel cycle is shown in Figure 1-1.⁶ All current methods being employed
do not separate the radiotoxic minor actinides (Np, Am, Cm) from the waste stream. These minor actinides account for the most dangerous waste source after removal of U and Pu.\textsuperscript{7}

Figure 1-1. The nuclear fuel cycle. Filled boxes represent the currently used open fuel cycle and unfilled boxes represent the proposed closed fuel cycle.

The main waste product in a nuclear reactor is the spent fuel rod. Nuclear fuel rods are made from various forms of uranium ore which is processed and enriched to contain 3-4% radioactive \textsuperscript{235}U. After three years of use, the rod must be replaced. The spent fuel rod contains 95.5% uranium, 3.1% other stable isotopes and 1.4% harmful radioactive elements including the minor actinides, \textsuperscript{99}Tc, \textsuperscript{129}I, \textsuperscript{90}Sr, and \textsuperscript{135}Cs.\textsuperscript{8} The spent
fuel rod is vitrified in 1-3M nitric acid and from here the separation of all waste products from the remaining uranium can begin.

The most radiotoxic elements in the waste are plutonium and the minor actinides. The radiotoxicity of these elements can be significantly reduced by transmutation. During transmutation the elements are bombarded with neutrons, which cause them to undergo fission reactions. Once the fission process is complete the daughter products that are generated from the process are either quickly eliminated by nuclear decay or are stable non-radioactive materials. Transmutation is severely impeded if there is a mixture of lanthanides [Ln(III)] and actinides [An(III)] because the Ln(III) have a higher neutron capture cross section. When bombarded with neutrons, the Ln(III) ions more readily absorb the neutrons thus the An(III) are not transmuted efficiently.\textsuperscript{9,10} If these waste products could be effectively separated and transmuted there would be significant reduction in waste volume and the radioactive components leftover would require much less storage time of hundreds rather than thousands of years. With a shorter amount of time required for safe storage, there is much less chance of damaging an underground repository from a geological change.\textsuperscript{11}

1.2.1 Plutonium Uranium Recovery by Extraction Method

The Plutonium Uranium Recovery by Extraction (PUREX) method is used to extract the plutonium and uranium for the waste stream. PUREX is a liquid-liquid extraction technique that uses tributylphosphate (TBP), shown in Figure 1-3, in an inert diluent (kerosene or dodecane) as the organic phase and nitric acid as the aqueous phase. First the fuel rod assembly is dismantled and the fuel pellets are dissolved in hot nitric acid. The U and Pu are then extracted from the acidic solution and then separated from each other to be either used as fuel or disposed.\textsuperscript{12} The key issue in PUREX is the
recovery of solvent. The solvent is contaminated by degradation and radiolysis of TBP which in turn causes emulsions that inhibit extraction effectiveness. The emulsion is counteracted by adding alkaline, carbonate, and water washes to remove the degradation products.\textsuperscript{13}

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

Figure 1-3. Structure of tributylphosphate (TBP), an extractant used in the PUREX process

\textbf{1.2.2 Transuranium Extraction Method}

Another method that has shown to be capable at removing the tri-, tetra-, and hexavalent actinides and lanthanides is called the Transuranium Extraction (TRUEX) process. The TRUEX process is similar to PUREX in that it also works by a solvation mechanism but it uses a combination of N,N-diisobutylcarbamoyl-methyl-octylphenyl-phosphineoxide (CMPO), shown in Figure 1-4, and TBP in an organic solvent. In acidic solutions the TRUEX process still works well and eliminates the need for pH adjustments thus the volume of waste generated is decreased. Although it is selective in extracting these products it cannot separate the trivalent lanthanides from the trivalent actinides. Another problem with the TRUEX method also contains phosphorus since hazardous secondary waste is produced upon incineration the process is far from ideal.\textsuperscript{11}
1.2.3 Diamide Extraction Method

In congruence with the TRUEX process, the Diamide Extraction (DIAMEX) process was conceived. Both methods have the same purpose but DIAMEX follows the CHON – principle (ligands only contain carbon, hydrogen, oxygen and nitrogen) thus it can be incinerated with less hazardous byproducts. Two ligands used for the DIAMEX process are dimethyl-dioctyl-hexylethoxy-malonamide (DMDOHEMA) and dimethyl-dibutyl-tetradecyl-malonamide (DMDBTDMA) and are shown in Figure 1-5.

Figure 1-5. Structure of DMDOHEMA and DMDBTDMA, extractants used in the DIAMEX process

DMDOHEMA bonds bidentate and the efficiency of these ligands are greatly influenced on the position of the N-substituents due to the fact that they can affect the
The basicity of the carbonyl oxygens.\textsuperscript{15, 16} The hard oxygen donors in DIAMEX ligands do not distinguish the actinides from the lanthanides thus another process is needed to separate the Ln(III) from the minor actinides in the raffinate.

1.2.4 Selective Actinide Extraction Method

The Selective Actinide Extraction (SANEX) process tries to separate the Ln(III) from the minor actinides by using ligands that contain acidic sulfur or heterocyclic nitrogen donors. There are several methods for measuring the ability of extractants for Ln(III)/An(III) separation in the literature.\textsuperscript{11} To quantify the ability of an extractant the distribution coefficient is used. The distribution coefficient is a measure of the metal concentration in the organic phase divided by the metal concentration in the aqueous phase of an extraction. Another common term used in measuring the ability of an extractant to selectively extract actinides over lanthanides is the separation factor. The separation factor is defined as the distribution coefficient of the actinide divided by the distribution coefficient of the lanthanide. The most common metals used to show separation factors are the comparison between europium and americium.

Dithiophosphonic acids such as Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid), shown in Figure 1-6, exhibits high selectivity for Am over the lanthanides. Unfortunately, the ligand generates secondary waste due to the presence of sulfur and phosphorus and it is susceptible to radiation damage. Additionally, the pH of the waste stream must be adjusted to ~3, requiring significant dilution in order to extract efficiently.\textsuperscript{17, 18} Recently, interest has focused on ligands with multidentate heterocyclic nitrogen donor atoms, using Eu(III) to represent the lanthanide series in test scenarios.\textsuperscript{11} It has been theorized that the electron density and the basicity of the nitrogen donor atom influences how the ligand interacts with the metal cation.\textsuperscript{19}
The most thoroughly investigated and highest Am(III)/Eu(III) separation factors (SF) ligands with heterocyclic nitrogen donor atoms has been 2,6-bis(1,2,4-triazin-3-yl)pyridines (BTP) and is shown in Figure 1-6. The scrutinization of BTP also revealed that it is susceptible to hydrolysis and radiolysis which makes them a poor choice for an industrial process.\textsuperscript{20} The work described herein uses multi-coordinate benzimidazole bearing ligands because it is known that they do not suffer from hydrolysis, are stable at high temperature, and have been shown to bind lanthanides and actinides although limited data on their extraction efficiency is available.\textsuperscript{21, 22}

![Figure 1-6. Structure of Cyanex 301 and BTP, extractants used in the TRUEX process.](image)

**1.3 Separation of Lanthanides and Actinides**

The similarities between An(III) and Ln(III) make separation an arduous task.

An(III) and Ln(III) cations are classified as hard acids by the HSAB-principle, hence their bonding is primarily ionic and mainly governed by charge density.\textsuperscript{23} Separation by exploiting their common bonding principles also proves difficult due to the similar ionic radii from the f-element contractions and the identical oxidation state. One difference that can be exploited is that the An(III) favor covalent bonds more than Ln(III).

Therefore, many successful ligands employ bonding of atoms softer than oxygen. The
advantageous covalency of the An(III) is due to the 5f orbitals being more spatially extended than the 4f orbitals. The extension leads to better overlap if the f orbitals are involved in bonding. Whether or not the 5f orbitals are involved in bonding has been disputed with some implying that the s orbital is the contributor due to the many coordination geometries and others attributing high separation factors to the difference in covalency.\textsuperscript{24,25}

To facilitate bonding multicoordinate ligands that have preorganized chelating groups have been synthesized to selectively separate lanthanides and actinides. Since trivalent f-elements have high coordination numbers of eight or greater and prefer a tricapped trigonal prismatic (TTP) geometry shown in Figure 1-7. If the binding ligands are preorganized to facilitate the TTP geometry the result would be better extractions and possibly higher metal selectivities. The preorganized platforms provide opportunities for different stoichiometric ligand amounts for complete complexation and different steric requirements.

Figure 1-7. Tricapped trigonal prismatic (TTP) geometry

1.4 Benefits of Preorganization on a Molecular Platform

Many groups have developed ligands based on using molecular platforms. One of the first synthetic accomplishments involved attaching multiple CMPO moieties to a
variety of calixarenes (Figure 1-8). The calixarene platform can be functionalized on the narrow lower rim and at the wide upper rim of the platform. The functionalization can also be used to tune solubility and attach different chelating groups (Figure 1-9).

Calixarenes also facilitate the extraction of metal cations by inhibiting the approach of water molecules to the metal coordination site. Calixarenes have been extensively studied for the preorganization of chelating groups and can range from a three phenyl to an eight membered macrocycle. Some problems with calixarenes include solubility, not being easily modified, and inability to provide \( C_3 \) symmetry due to steric strain.

Another class of molecules that is used as a molecular platform is the \( C_3 \)-symmetric triphenoxyethylene scaffold shown in Figure 1-10. Using three tridentate
ligands attached to the platform will build a nonadentate ligand capable of bonding in a tricapped trigonal prismatic geometry. Upon the addition of the multi-coordinate ligand to the extraction medium any water or nitrates that are bonded to the inner coordination sphere of the metal are displaced. The removal of the nine water or nitrate molecules by one nonadentate ligand leads to an increase in the spontaneity of reaction by increasing entropy. A thermodynamic study has shown that for the heavier lanthanides the complexation reaction is mainly driven by entropy thus the predicted entropic gain of a preorganized molecular platform correlates with their data.\textsuperscript{33, 34}

An important feature of triphenoxymethane is that it can be conformationally locked so that three hydroxyl groups point in the same direction. The rigid “all-up” orientation of the hydroxyl groups facilitate preorganization of the final nonadentate ligand in that the phenyl rings do not rotate around the central carbon of triphenoxymethane. The substituents on the phenyl rings can be changed to tune solubility, cavity size and influence other steric properties. The solubility of the ligand can be set early in the synthesis by altering groups at the 2 and 4 positions of the phenols. With the ability to change these groups, the interaction of the molecule at the extraction phase boundary can be tuned to facilitate the transfer of the metal from the aqueous to organic phase. The entropic gain, preorganization and tunable solubility engender the triphenoxymethane platform with useful attributes for the development of extraction agents. Many variations using triphenoxymethane have been experimented on by changing the substituents and trying different chelating groups.\textsuperscript{35, 36, 37}
Kornelia Matolka, a previous member of the Scott group, prepared a triphenoxymethane based ligand using three tridentate chelating groups. The chelating group used different moieties of diglycolamides (DGA) as shown in Figure 1-11.

The ligand chelating groups used oxygen donors to bind the metal and showed tolerance to acidic solutions. The ligand showed increased affinity for the later lanthanides and maintained good extraction ability even with a 1:1 ligand:Ln(III) ratio, where normally a 10:1 ratio is required to achieve such results. Unfortunately, the hard donors in DGA hindered it from binding actinides selectively. In an attempt to decrease the hardness of the donors, the oxygen atoms were replaced by sulfur atoms. Inclusion
of softer sulfur atoms lead to poor extraction efficiency. The Scott group has since put considerable effort into exploring ligands that incorporate nitrogen donor atoms. The nitrogen donor atoms should still have the relative softness when compared the DGA oxygen donors but still be hard enough to bond selectively to the actinides.

1.5 Experimental Research Objectives

Based on the knowledge gained from earlier work in the Scott group, a new class of ligands with pyridyl-benzimidazole donors was designed to selectively separate the lanthanides and actinides. The choice of donor atoms was guided by computational chemistry results in order to correlate a predictive analysis to experimental data. When applicable, biphasic extraction experiments were performed using the synthesized ligand and lanthanide elements in a nitric acid solution in order to simulate the industrial separation process. The common moiety used for each ligand is shown in Figure 1-12 and relies on the synthetic procedures developed by Piguet et al. but has never been attached to any variation of triphenoxymethane.$^{39}$

![Figure 1-12](image-url)

Figure 1-12. Common moiety used in all synthesized ligands. The groups R, R’ and R” refer to the various linkages, donor groups and solubility modifiers.

1.6 Computation Research Objectives

Computational chemistry was used for this project to establish a predictive method for screening possible ligands and to investigate what electronic properties facilitate the
selective separation of lanthanides and actinides. The screening process used semi-empirical calculations to evaluate the structure and symmetry of several ligands and based on this information, synthetic targets were chosen. DFT calculations were not performed on the full nonadentate structures because of the intensive computation time and resources needed. Instead, DFT calculations were utilized to investigate the electronic structure of a truncated version of the ligands. The accuracy of DFT became necessary for calculating the energy level matching and HOMO – LUMO gap energies of the metal – ligand complexes. The electronic structure properties that facilitate the selective separation of lanthanides and actinides were investigated and correlated to experimental data when applicable.

1.6.1 Semi-Empirical Calculations

The laborious multi-step procedure needed to synthesize a nonadentate ligand capable of fully encapsulating a lanthanide or actinide often requires many moiety variations to optimize the bonding geometry. By performing quantum chemical calculations on the ligands and metal complexes, one can predict whether the synthetic effort will be fruitful. In order to accurately predict whether a ligand will be a good extractant, some chemical property must be evaluated that correlates to it. In previous work completed by the Scott group, any deviation from TTP geometry and concomitant increase in twist angle correlated with decrease in extraction efficiency. The twist angle is defined as the angle to which the two triangles in the TTP are deviated from their eclipsed geometry. Thus, in theory, the TTP geometry can be modeled from an optimized geometry calculation. With this calculation, one can predict the extraction efficiency.
Recently, the SPARKLE/AM1 model was developed and it showed the model could give accurate results for Ln(III) complexes. SPARKLE/AM1 is a semi-empirical method that is exclusively implemented in the free software package, MOPAC2009. SPARKLE refers to the parameterization of the trivalent lanthanides and AM1 is the actually level of theory being used in the calculation. Several papers show results using the AM1 method and the more recently developed PM6 method are comparable to \textit{ab initio} DFT calculations and to crystallographic data from the Cambridge Structural Database. Because the method is semi-empirical, it uses a simple Hamiltonian as well as parameters obtained from experimental results or \textit{ab initio} calculations to quickly calculate molecular properties including geometry. The only feasible means of optimizing the geometry of large (250 atoms or more) lanthanide complexes is to use the SPARKLE/AM1 method. In this study many structures are computed to assess the twist angle and the semi-empirical method is evaluated across lanthanide series to its accuracy with our specific compounds.

\textbf{1.6.2 Density Functional Theory Calculations}

Due to the radiotoxicity, and expense of working with actinides many groups in this field have begun to use Density Functional Theory (DFT) in order to investigate how to better design ligands for Ln(III)/An(III) separation. Calculations of Ln(III) and An(III) complexes is not as perspicuous as other structures because the large number of electrons at the metal requires relativistic effects must be taken into consideration. The average radius of an atom is proportional to the Bohr radius $a_0$, and $a_0$ is inversely proportional to the electron mass. Therefore, the relativistic increase of mass with velocity decreases the radius of the inner s orbitals in a heavy atom. To maintain orthogonality with the inner s orbitals, the outer s orbitals must also decrease in radius.
The retraction of s orbitals causes all of the p orbitals to shrink as well but to a lesser degree. As the s and p orbitals get smaller they screen the nucleus more effectively than nonrelativistic atoms thus causing an expansion of the d and f orbitals. All-electron calculations of relativistic molecules are time consuming so to increase the speed the calculations the use a relativistic effective core potential (RECP) is employed. RECP freezes the core electrons based on one all-electron iteration and then only the valence electrons are treated explicitly. Accounting for relativistic effects with an effective core potential has been shown to give accurate data while minimizing refinement time.

The most prominent calculation methods to aid in the development of extraction complexes include using either Gaussian or the Amsterdam Density Functional (ADF) program package. In order to run a calculation on Ln(III) complexes, a generated basis set must be used to include relativistic effects. In addition, the common practice is to use the generated basis set on just the metal and much lower level (i.e. 6-31G*) basis set on the rest of the atoms. The lower level of theory is used for all other atoms in order to decrease the calculation time. This method gives accurate data for both packages but the calculation time is quite long. In this study, DFT methods were utilized to investigate the properties of several heterocyclic nitrogen donor ligands bound to either Eu, Am, or Cm. The calculations performed used three terdentate ligands in order to simulate the environment provided by the nonadentate triphenoxymethane ligand. The triphenoxymethane platform was truncated in order to decrease the computational time. The molecules underwent geometry optimizations and their molecular orbitals evaluated.
CHAPTER 2
STRUCTURAL ANALYSIS OF NONADENTATE LANTHANIDE COMPLEXES USING SEMI-EMPIRICAL METHODS

2.1 Introduction

Semi-empirical (SE) calculations have long been used to evaluate chemical systems that contain too many electrons to calculate by normal Hatree-Fock methods or DFT. SE methods use an approximated Hamiltonian operator that estimates integrals using experimental and ab initio calculation data in order to avoid cumbersome all electron calculations. Recently, the semi-empirical program MOPAC incorporated the SPARKLE model which allows for trivalent lanthanide complexes to be calculated with impressive accuracy.$^{40,41,46}$ In an independent review, the SPARKLE model was said to be “very useful for the design and rational development of functional lanthanoid complexes.”$^{47}$ due to the accuracy in which it can estimate bond lengths. These reviews made MOPAC a logical choice for full geometry optimization of the structures before synthetic efforts were attempted. The rapid speed of the calculations also provides immediate structural information to help modulate ligand design instead of exploring time consuming and expensive synthesis.

There are many benefits to using SE methods for ligand design of which the most significant is that the full nonadentate ligand using the triphenoxymethane scaffold can be incorporated whereas with any other method the triphenoxymethane scaffold must be truncated and the structure evaluated as three separated tridentate ligands. One of the largest drawbacks to using SE methods is the known inaccuracy for calculating amide bonds geometries.$^{48}$ This is problematic for this project since the most successful synthetic method of joining the metal binding units to triphenoxymethane is through an amide linkage. Inspection of amide bond rotation was closely monitored for deviations in
Another issue is that the actinides are not able to be calculated with SE methods because the lack of data on them and complex electronic structure of their diffuse 5f orbitals.

In this chapter, SE calculations are used to develop a means of visualizing the structure of nonadentate ligands formed by triphenoxymethane derivatives as molecular scaffolds. The twist angle for each calculated structure is evaluated in order to obtain information on ideal bonding geometries. Finally, the method is tested to assess how precisely it predicts the lanthanide contraction. The SE optimized structures also offer a starting geometry for further DFT optimization. The main goal of this project is to model and evaluate the structures to predict the most viable ligand design that facilitates bonding. The structures that exhibit the best results were then deemed worthy of synthetic efforts.

2.2 Computed Structures

The following structures in Figure 2-1 were computed in MOPAC using SPARKLE/PM6 method and showed the most promising results when assessing their structural properties. The ligand design followed the strict criteria of only using C, H, O and N atoms, triphenoxymethane to form a nonadentate structure upon complexation and containing synthons that have been previously published. The benzimidazole containing ligand arm was based on the benzimidazole-lanthanide complex work performed by Piguet et al. and the triphenoxymethane work from the Scott group.\textsuperscript{49, 50} Structures 2-1, 2-3, 2-4, 2-6 and 2-7 used linkages previously explored by the Scott group to attach the ligand arm to triphenoxymethane. The synthetic linkages that have not been attempted before include structures 2-2, 2-5, 2-8 and 2-9.
Figure 2-1. Semi-empirical calculation structures
Figure 2-2. Semi-empirical geometry optimization of structure 2-7
Figure 2-3. Semi-empirical geometry optimization of structure 2-8
The length of the arm linking the donor groups to the platform was also varied with either two or three carbon atoms. The extra CH$_2$ group was included to test whether the increase in flexibility would influence the binding of the three arms to the metal. Different alkyl groups were used to ascertain if bulky substituents would affect the bonding environment. Since the alkyl groups on triphenoxymethane are the main factor influencing solubility, knowledge of their steric effects on metal binding is important. Europium was used for each structure due to its importance in lanthanide – actinide separation but also because it represents the average size and charge of the lanthanide series. The calculated structures of 2-7 and 2-8 are shown in Figure 2-2 and Figure 2-3, respectively.

### 2.3 Structural Evaluation

The metal to ligand bond distances, twist angles, and the standard deviation (STD) of the twist angles are shown in Table 2-1 and 2-2. The values listed in the tables represent the main parameters on which ligand design was evaluated with SE calculations. Visual inspection of the geometry optimization also was useful but not easily quantifiable due to the many subtle differences between each structure.

<table>
<thead>
<tr>
<th></th>
<th>O</th>
<th>N$_{py}$</th>
<th>N$_{bzd}$</th>
<th>Twist Angle</th>
<th>STD Twist Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>2.43</td>
<td>2.56</td>
<td>2.47</td>
<td>12.94</td>
<td>1.15</td>
</tr>
<tr>
<td>2-2</td>
<td>2.43</td>
<td>2.56</td>
<td>2.47</td>
<td>11.33</td>
<td>0.30</td>
</tr>
<tr>
<td>2-3</td>
<td>2.43</td>
<td>2.56</td>
<td>2.47</td>
<td>13.27</td>
<td>0.80</td>
</tr>
<tr>
<td>2-4</td>
<td>2.43</td>
<td>2.56</td>
<td>2.47</td>
<td>12.48</td>
<td>0.51</td>
</tr>
<tr>
<td>2-5</td>
<td>2.45</td>
<td>2.53</td>
<td>2.46</td>
<td>15.70</td>
<td>1.29</td>
</tr>
<tr>
<td>2-6</td>
<td>2.43</td>
<td>2.56</td>
<td>2.47</td>
<td>14.09</td>
<td>1.77</td>
</tr>
<tr>
<td>2-7</td>
<td>2.45</td>
<td>2.53</td>
<td>2.46</td>
<td>16.02</td>
<td>4.81</td>
</tr>
</tbody>
</table>

The oxygen donor of the amide, nitrogen donor of the pyridine and nitrogen donor of the benzimidazole are notated as O, N$_{py}$ and N$_{bzd}$, respectively.
Table 2-2. Average Metal Bond Lengths (Å) and Twist Angles (˚) of Triazole Structures

<table>
<thead>
<tr>
<th></th>
<th>N_{tz}</th>
<th>N_{py}</th>
<th>N_{bzd}</th>
<th>Twist Angle</th>
<th>STD Twist Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-8</td>
<td>2.51</td>
<td>2.52</td>
<td>2.47</td>
<td>10.36</td>
<td>0.58</td>
</tr>
<tr>
<td>2-9</td>
<td>2.50</td>
<td>2.52</td>
<td>2.47</td>
<td>10.36</td>
<td>0.58</td>
</tr>
</tbody>
</table>

The nitrogen donor of the triazole, nitrogen donor of the pyridine and nitrogen donor of the benzimidazole are notated as N_{tz}, N_{py} and N_{bzd}, respectively.

The twist angle for each complex was obtained by calculating the centroid of each triangle of the TTP geometry and averaging the three dihedral angles of donor atom (top), centroid (top), centroid (bottom), donor atom (bottom). All of the amide type ligands have similar bond lengths with an exception of structures 2-5 and 2-7. It is likely that the small deviation is due to the steric strain with the short acyl linkage in 2-5 and the amide linkage containing the donor oxygen in 2-7. The triazole type ligands have approximately the same bond length to the benzimidazole as the amide type ligands but the triazole moiety accounts for a longer bond as opposed to the oxygen donating atom of the amide type ligands.

The twist angle for each complex fell within a narrow range of 10.36 to 16.02 degrees and additional analysis were performed to extract more discerning data from each structure. The standard deviation for each of the three twist angles in the structures was calculated in order to evaluate the symmetry of each molecule. A higher standard deviation between twist angles for any given structure implies more asymmetry in the optimized geometry and a lower theorized extraction efficiency. Using the twist angle and the standard deviation as criteria the SE calculations predicted that 2-2, 2-4, 2-8, and 2-9 would be possible candidates for synthetic efforts. Structures 2-2 and 2-4 both used a three carbon linker validating that the additional flexibility gives a more symmetric structure than their two carbon linking counterparts, 2-1 and 2-3. In contrast, structures 2-8 and 2-9 had the exact same twist angle values despite one
being two carbon linker and the other a three carbon linker. It is possible that something specific to the planarity and direct donation of the triazole moiety or a combination of many effects caused 2-8 and 2-9 to be different from the rest of the calculations. Structure 2-7 had the largest twist angle but also a significantly higher standard deviation compared to the other structures. The inability of SE calculations to accurately define the conjugated planarity of amide bonds is most directly seen in structure 2-7 thus it was chosen as a possible candidate for synthesis because of the inconclusive evidence provided by the calculation.

SE calculations were completed using different alkyl groups on triphenoxymethane but there was no change in metal ligand bond lengths or twist angles thus the wide variety of groups at these positions in structure 2-1 through 2-9 were deemed negligible. It is unfortunate that the alkyl groups of methyl, tert-butyl, tert-pentyl were ineffective in changing the bonding environment of the metal because it represents a possible parameter to alter selectivity but experimentally it is a positive result with regards to modifying solubility without possible fluctuations to the metal – ligand bond. Other possible alkyl groups were not calculated because at the time no synthetic procedures were established for their synthesis.

2.4 Lanthanide Contraction

A self consistent process of analyzing the accuracy of the method is to use the same ligand but change the lanthanide for each calculation. Across the lanthanide series there should be a decrease in bond length of the metal - ligand bond due to the fact that the ionic radius gets smaller. When increasing electrons on the metal there is an increase in shielding and decreases ionic radius following the trend of the lanthanide
contraction. From Figure 2-4 and Figure 2-5 it is shown that ligand 2-4 and 2-7 both have a decrease in bond length across the lanthanide series, respectively.

![Bond lengths of structure 2-4](image1)

Figure 2-4. The graph shows the metal to donor atom bond lengths for structure 2-4.

![Bond lengths of structure 2-7](image2)

Figure 2-5. The graph shows the metal to donor atom bond lengths for structure 2-7.
In Figure 2-4 and 2-5 the oxygen donor of the amide, nitrogen donor of the pyridine and nitrogen donor of the benzimidazole are notated as O, Npy and Nbzd, respectively. The degree of error becomes apparent when comparing lanthanides that are adjacent to each other in the periodic table suggesting the method cannot accurately reproduce such small variations in size. Interestingly, the ligand used for structure 2-7 represented the lanthanide contraction even though the large fluctuations in twist angle persisted. One could speculate that the SE method used has a much higher accuracy for the ligand – lanthanide bonds than it does with other atomic interaction in the molecule. Despite the minor deviations with adjacent metals the method accurately represented the lanthanide contraction and affirmed its ability to accurately measure trends for the nonadentate complexes calculated in this study.

2.4 Conclusions

In this study semi-empirical calculations were used to assist in practical ligand design. The main objective was to eliminate possible ligand structures using computational data and symmetry arguments. Out of nine possible ligands five were chosen to be worthy of synthetic efforts. The decision was based on the analysis of the twist angle of each calculated structure. Varying the alkyl groups on triphenoxymethane did not have an effect on the twist angle and deemed to have negligible effect on the metal bonding environment. The lanthanide contraction was reproduced for two representative ligands thus giving validity to the method for the uncommon structures computed in this study.
2.5 Computational Details

All semi-empirical calculations were performed within MOPAC on PC with a Windows operating system. The level of theory used was PM6 and trivalent lanthanides used the SPARKLE model.
CHAPTER 3
SYNTHESIS OF BENZIMIDAZOLE-PRIDYL FUNCTIONALIZED NONADENTATE LIGANDS

3.1 Introduction

In this study the synthesis of several benzimidazole-pyridyl functionalized ligands was attempted. The basic procedure was to first synthesize the ligand arm which usually contained two or three possible chelating groups then attaching three of the ligand arms to triphenoxymethane in order to form a nonadentate ligand. Several synthetic procedures developed by Piguet et al. were employed and improved upon to achieve the benzimidazole-pyridyl functionality that they use for luminescence experiments. Although they have not attached their ligands to triphenoxymethane they have been able to attach the ligand arms to another type of tripodal platform shown in Figure 3-1. The ligand in Figure 3-1 lacked rigidity and had limited solubility modifiers thus limiting its use in An(III)/Ln(III) extractions. However, when three of the arms are attached to triphenoxymethane the close proximity leads to a more preorganized structure for the binding of the metal. The goal for the synthetic project was to obtain several nonadentate ligands containing benzimidazole-pyridyl moieties in as high yield and lowest number of steps as possible in order to be applicable to an industrial process.

The synthetic targets were chosen based on semi-empirical calculations.

3.2 Synthetic Difficulties of Ether Linkage Ligands

With the knowledge that the ligands synthesized by Piguet et al. could be attached to a tripodal platform through an ether linkage and the information gathered by the predictive semi-empirical calculations discussed in the previous chapter attempts were made to substitute in triphenoxymethane as the molecular platform via ether linkage. The first steps taken involved the synthesis of ligand arm as shown in Figure 3-2.
Figure 3-1. Tripodal helicate ligand developed by Piguet et al.

Figure 3-2. Synthesis of ligand arm 3-10, which contains the chloride functionality needed to attach triphenoxymethane via Williamson ether synthesis.
The synthesis began with commercially available starting materials and proceeded smoothly except for the formation of product 3-8. It was found that the benzimidazole nitrogen was susceptible to nitrone formation during the procedure used to remove the excess iron from the reaction. EDTA was used to remove the iron by varying the pH and adding hydrogen peroxide. The hydrogen peroxide was assumed to be the culprit for the nitrone formation and the placement of the nitrone on the benzimidazole was determined by obtaining an X-ray crystal structure of the unwanted byproduct. Other than the nitrone formation, the synthesis does not deviate much from the literature procedure with the exception that the yield on 3-3 was increased from 85% to 100% by reacting for two weeks at room temperature instead one hour in a reaction vessel and that the yield on 3-9 was never reproduced in the claimed 94% yield.

The discovery that 3-3 could be synthesized from a reaction time of two weeks was made by analyzing the reaction by TLC. Once the ligand arm (3-10) was synthesized the two carbon linker triphenoxymethane (3-15a) was synthesized by the procedure in Figure 3-3. Even though the three carbon ether linkage displayed better twist angle parameters from semi-empirical calculations the two carbon ether linkage to triphenoxymethane was used because of the previously established synthetic procedure developed by Matloka.

To attach 3-10 to 3-15a NaH was used to deprotonate the hydroxyl group on 3-15a but the subsequent SN2 reaction on 3-10 was unsuccessful using a variety of solvents and reaction conditions. Another attempt was made by adding a tosyl leaving group on 3-15a to make 3-16a and reacting it with 3-9 in the presence of base but this reaction failed to attach the two reactants and form the desired product. After
exhaustive reaction conditions were explored for the ether linkage it became apparent that some other means of tethering the ligand arm to triphenoxy methane would be required.

![Chemical Reaction Diagram]

Figure 3-3. Synthesis of two carbon linker triphenoxy methane.

### 3.3 Synthesis of Amide Linkage Ligands

Another method that had been established to attach a ligand arm to triphenoxy methane was to use an amide linkage. The Scott group had already explored how to synthesize a two and three carbon amine functionalized triphenoxy methane and subsequently attach a ligand arm with a carboxylic acid functionality by using the reagent benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP).

The three carbon amine triphenoxy methane was chosen for the synthesis due to the favorable twist angle data obtained from the semi-empirical calculations comparing 2-3 and 2-4. The synthesis for the three carbon linker amine, 3-18, shown in Figure 3-4, was published by Matloka. The synthesis also incorporated di-t-butyl groups on
triphenoxymethane due to solubility issues involved with the methyl-t-butyl triphenoxymethane (3-13a).

Figure 3-4. Synthesis of the three carbon linker amine triphenoxymethane, 3-18

3.3.1 Carboxylic Acid Functionalization of the Ligand Arm

The ligand arm was modified to a novel carboxylic acid moiety using two separate procedures shown in Figure 3-5. All reactions using chromium reagents, hydrogen peroxide, and sodium hypochlorite to oxidize 3-8 or 3-9 directly to the carboxylic acid failed. The acid was formed after preparation of aldehyde, 3-19, followed by oxidation with Tollen’s reagent.

Figure 3-5. Synthesis of carboxylic acid functionalized ligand arm, 3-20
Due to the low yield to form 3-9 and 3-20, efforts to improve the protocol were undertaken to increase the yield of the overall synthesis. The elimination of the methyl deprotection step in the synthesis of 3-9, and direct oxidation of the ether (3-8) to an ester (3-21) increased the overall yield to the carboxylic acid from 3.3% to 22%. The overall yield for the synthesis of the nonadentate ligand, 3-22, was 9.4% in 16 steps.

Figure 3-6. Synthesis of the nonadentate ligand, 3-22

The low yield for the amide linkage and benzimidazole formation of 3-23 and 3-24 was due to side reactions that occurred from using the weak methyl ester protection group. In addition, 3-24, resulted in a mixture of methyl and ethyl esters due to the use of ethanol as a solvent but it is inconsequential since the ester is hydrolyzed in the subsequent step. With a carboxylic acid directly attached to the ortho position of the pyridine the coupling reaction with PyBOP forms the link to triphenoxy methane and the amide metal donor group in one synthetic step (Figure 3-8). The overall yield for the final nonadentate ligand, 3-26, is 2.2% with a total of eleven steps.
3.3.2 Incorporation of the Amide Linkage as a Donor Group for Metal Binding

To improve upon the final structure the amide linkage was included as a donor group to the metal. The synthetic target was chosen to be the inconclusive semi-empirical calculated structure, 2-7. To obtain the targeted ligand 3-18 was used as the molecular platform but a new ligand arm was needed. The synthesis of the new amide ligand arm is shown in Figure 3-7.

Figure 3-7. Synthesis of the carboxylic acid functionalized benzimidazole-pridyl ligand arm, 3-25

Figure 3-8. Synthesis of the nonadentate ligand, 3-26
3.4 Synthesis of Triazole Linkage Ligands

Since the previous ligand arm synthetic protocols were complicated by low yields and a large number of steps, a completely new synthetic scheme was developed. In comparison to the other methods, Figure 3-9 shows a route that uses a different reagent to form the benzimidazole ring, offers highly combinatorial options through halogen exchange and cross coupling reactions, and ultimately creates a softer all nitrogen donating environment for metal complexation.

![Chemical structure](image)

Figure 3-9. Synthesis of the alkyne ligand arm, 3-31

The synthesis of 3-28 is from the literature procedure developed by Chuang et al.\(^{51}\) The commercially available reactant, 3-29, was substituted for 3-1 in order to limit the number of steps and increase the overall yield of the nonadentate ligand. The benzimidazole formation using Fe/HCl for 3-8 and 3-24 proved too harsh to retain the bromine of 3-28. Using Na\(_2\)S\(_2\)O\(_4\) as the benzimidazole ring closing reagent not only formed the targeted product but offered an easier purification procedure. The Sonogashira reaction introduced the alkyne to 3-30 by adding trimethylsilyl-acetylene in the presence of base and Cul. The overall yield for the ligand arm was 22% in five steps. It should be noted the compound 3-31 is likely photosensitive as it began to darken when stored in the presence of light.
The azide was substituted for the tosyl group of 3-16c as shown in Figure 3-10. Since semi-empirical calculations did not show a difference in twist angle between structures 2-8 and 2-9 and because there was no established procedure for a three carbon linker the two carbon linker was again utilized. The alkyl substituents on the triphenoxy methane rings were changed to di-tert-pentyl in order to attempt to alleviate solubility problems. The final step in the synthesis relies on the 1, 3 dipolar cycloaddition of the azide on triphenoxy methane and the alkyne on the ligand arm to produce 3-33. With nine total steps the overall yield for the nonadentate ligand, 3-33, was 8%.

![Chemical structure diagram](image)

Figure 3-10. Synthesis of the nonadentate triazole ligand, 3-33

3.5 Conclusions

In this chapter the synthesis of four types of nonadentate ligands were presented of which three were successfully completed. The first synthetic target was the structure
2-1 but the ether linkage failed to react and the product was not obtained even after leaving group changes and many attempts using various conditions.

The second synthetic target, 3-22, was produced in the highest yield of all the synthesized ligands but also the highest number of steps. The structure of the ligand used an amide linkage to connect the triphenoylmethane platform to the ligand arm but did not incorporate the amide linkage into metal binding.

The third synthetic target, 3-26, included the linking amide as a donor group for metal binding and eliminated five synthetic steps compared to 3-22, but due to the weak methyl ester protecting group and harsh reaction conditions, the yield was decreased.

The fourth synthetic target, 3-33, contained all heterocyclic nitrogen donors of benzimidazole, pyridine, and triazole. The ligand arm synthesis was completely changed in order to increase the overall yield, eliminate steps and to form an alkyne for the triazole linkage. The final nonadentate ligand, 3-33, was obtained in the highest yield and with the least number of steps than the other ligands.

Each consecutive ligand had an improvement in yield or synthetic steps but the overall yield is still questionable in terms of an industrial process. It appears that further optimization of the reactions or alternate synthetic pathways would be needed for large scale production. For an industrial extraction process they have the advantage of encompassing the metal at a 1:1 ligand to metal ratio whereas three tridentate ligands would need a 3:1 ratio. When comparing nonadentate ligands to three tridentate ligands the reaction yield needs to be three times as high for the three tridentate ligands to fit the appropriate stoichiometry. For instance the best yield obtained was for 3-22 at 9% so any tridentate synthesis would need at least 28% overall yield to be competitive.
The objective of the synthetic project was to synthesize nonadentate ligands using a triphenoxymethane platform and to expand upon previously developed methods for obtaining benzimidazole-pridyl containing ligand arms. Three novel nonadentate ligands were synthesized and their procedures were optimized to achieve the highest yields.

### 3.6 Experimental Section

Starting materials (3-1, 3-4, 3-11a,b,c, 3-propylbromo phthalimide, N-methyl-2-nitroaniline, 2,6 dibromopyridine) were purchased through Sigma-Aldrich. The synthetic methodology for the preparation of compounds 3-2, 3-5, 3-6, 3-7, 3-8, 3-9, and 3-10, were adapted from literature procedures. Synthesis of 3-27 used the procedure of Chuang et al. Methods for the synthesis of triphenoxymethane followed literature procedures. All of the \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Varian VXR-300 or Mercury-300 spectrometer at 299.95 MHz. Each mass spec sample was dissolved in appropriate solvent and underwent direct-injection through an autosampler, followed by ESI or APCI analysis with methanol (with or without 0.2% FA) as mobile phase. Solvent is used only when necessary for DART. The ions were detected with the Agilent 6210 TOF-MS while the data was processed with the MassHunterTM software.

**methyl 2-(6-(diethylcarbamoyl)pyridin-2-yl)-1-ethyl-1H-benzo[d]imidazole-5-carboxylate (3-21):**

N,N-diethyl-6-(1-ethyl-5-(methoxymethyl)-1H-benzo[d]imidazol-2-yl)picolinamide (3-8) (1.08 g, 2.95 mmol), KMnO\(_4\) (4.66 g, 29.5 mmol), and triethylbenzylammonium chloride (9.50 g, 29.5 mmol) were refluxed in dichloromethane (100 mL) for 24 hours. The excess KMnO\(_4\) was removed by the addition of a concentrated solution of sodium bisulfite. The organic phase was separated and the aqueous layer was extracted with
dichloromethane. The organic phases were combined, dried with sodium sulfate, filtered and concentrated until crystallization occurred to afford 0.906 g (81%) of 3-21. $^1$H NMR (CDCl$_3$): $\delta = 1.07$ (t, 3H, $J=7.0$ Hz, CH$_3$), 1.28 (t, 3H, $J=1.0$ Hz), 1.48 (t, 3H, $J=6.9$ Hz), 3.34 (q, 2H, $J=1.0$ Hz), 3.62 (q, 2H, $J=6.9$ Hz), 3.96 (s, 3H), 4.78 (q, 2H, $J=7.1$ Hz), 7.48 (d, 1H, $J=8.7$ Hz), 7.58 (d, 1H, $J=7.8$ Hz), 7.97 (t, 1H, $J=7.8$ Hz), 8.07 (d, 1H, $J=8.7$ Hz), 8.41 (d, 1H, $J=7.9$ Hz), 8.55 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta = 12.60$, 14.10, 15.13, 39.32, 40.67, 42.59, 51.88, 109.59, 122.37, 124.67, 124.93, 137.91, 139.20, 142.03, 148.72, 150.78, 154.37, 167.25, 168.07 ppm. ESI-MS m/z: 381.1914 [M + H]$^+$, 403.1753 [M + Na]$^+$, 783.3591 [2M + Na]$^+$

2-(6-(diethylcarbamoyl)pyridin-2-yl)-1-ethyl-1H-benzimidazole-5-carboxylic acid (3-20):

Compound 3-21 (0.50 g, 1.3 mmol) and NaOH (0.1 g, 2.5 mmol) were refluxed in methanol/water (20 mL/20 mL) for 30 mins. The mixture was then concentrated under vacuum, precipitated with concentrated hydrochloric acid (35%), and filtered. The white solid was dried under vacuum to give 0.48 g (99% yield) of 3-22. $^1$H NMR (CDCl$_3$): $\delta = 1.10$ (t, 3H, $J=7.2$ Hz), 1.30 (t, 3H, $J=7.1$ Hz), 1.52 (t, 3H, $J=7.0$ Hz), 3.37 (d, 2H, $J=7.0$ Hz), 3.64 (d, 2H, $J=7.2$ Hz), 4.81 (d, 2H, $J=7.3$ Hz), 7.54 (d, 1H, $J=8.6$ Hz), 7.63 (dd, 1H, $J=7.7$, 0.9 Hz), 8.03 (t, 1H, $J=7.9$ Hz), 8.17 (dd, 1H, $J=8.6$, 1.5 Hz), 8.50 (dd, 1H, $J=8.0$, 0.8 Hz), 8.71 (d, 1H, $J=1.3$ Hz), 9.89 - 10.92 (bs, 1H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta = 13.03$, 14.53, 15.54, 39.84, 41.28, 43.10, 110.21, 123.24, 123.38, 125.11, 125.80, 125.88, 138.58, 139.62, 141.59, 148.49, 151.10, 154.78, 168.55, 171.36. ESI-MS m/z: 367.1787 [M + H]$^+$, 389.1584 [M + Na]$^+$, 733.3445 [2M + H]$^+$, 755.3262 [2M + Na]$^+$
methyl 6-(ethyl(4-(methoxymethyl)-2-nitrophenyl)carbamoyl)picolinate (3-23):

A mixture of 3-5 (13.00 g, 71.8 mmol), CH₂Cl₂ (120 mL), thionyl chloride (20.8 mL, 285 mmol), and DMF (0.1 mL) was refluxed for 1.5 h under a nitrogen atmosphere and evaporated to dryness. The white residue was dried under vacuum for 30 min, dissolved in CH₂Cl₂ (60 mL), and cooled to 0 °C. A mixture of 3-3 (15.34 g, 73.0 mmol), triethylamine (44 mL), and CH₂Cl₂ (100 mL) was added dropwise. The resulting solution was stirred for 10 min at 0°C, refluxed for 2 h, and evaporated to dryness. The residual brown oil was dissolved in CH₂Cl₂/aqueous half-saturated NH₄Cl, the organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂. The combined organic phases were washed with deionized water, dried over MgSO₄, filtered, and evaporated to dryness. The resulting crude compound was purified by column chromatography using 100% DCM to 96% DCM/4% MeOH gradient to afford 3-23 as a brown oil (11.4 g, 24.6 mmol, 42%). ¹H NMR (CDCl₃): δ = 1.25 (t, 3H, J=7.2 Hz), 3.41 (s, 3H), 3.72 (dq, 1H, J=13.9, 7.2 Hz), 3.80 (s, 3H), 4.23 (dq, 1H, J=13.9, 7.1 Hz), 4.47 (s, 2H), 7.35 (d, 1H, J=8.2 Hz), 7.51 (dd, 1H, J=8.4, 1.8 Hz), 7.82 (t, 1H, J=1.0 Hz), 7.89 - 7.99 (m, 2H), 8.06 (dd, 1H, J=7.8, 1.2 Hz) ppm. ¹³C NMR (CDCl₃): δ = 12.66, 31.11, 46.40, 52.52, 58.73, 72.95, 124.31, 125.94, 127.89, 132.10, 136.43, 138.05, 139.45, 145.73, 145.96, 152.56, 164.94, 165.91 ppm. ESI-MS m/z: 374.1342 [M + H]⁺, 396.1184 [M + Na]⁺, 769.2426 [2M + Na]⁺

6-(1-ethyl-5-(methoxymethyl)-1H-benzo[d]imidazol-2-yl)picolinic acid (3-25):

A mixture of 3-23 (9.19 g, 24.6 mmol), ethanol (750 mL), water (200 mL), powdered iron (11.0 g, 197 mmol), and concentrated hydrochloric acid (37%, 50 mL) was refluxed for 18 h under a nitrogen atmosphere, filtered, and concentrated under vacuum. The residual aqueous layer was poured into a mixture of CH₂Cl₂ (200 mL),
water (370 mL) and Na$_2$H$_2$EDTA·2H$_2$O (132 g, 393 mmol). The pH was adjusted to 7 with a 25% aqueous ammonia solution then 30% hydrogen peroxide solution (7 mL, 68.8 mmol) was very slowly added and the mixture was stirred for 15 min. The pH was adjusted to 8.5 with a 25% aqueous ammonia solution, the aqueous layer was extracted with CH$_2$Cl$_2$, and the combined organic layers were washed with deionized water until neutral, dried over MgSO$_4$, filtered, and evaporated to dryness to afford compound 2-24. The mixture of methyl and ethyl esters was then hydrolyzed by KOH (2.76 g, 49.2 mmol) in 75 mL of water at reflux for 1 hour. Concentrated HCl was added until pH=2 and a white precipitate formed which was collected by filtration to give 3-25 (2.60 g, 8.36 mmol, 34% yield.) 1H NMR (CDCl$_3$): $\delta$ = 1.52 (t, 3H, J=6.9 Hz), 3.33 (s, 3H), 4.59 (s, 2H), 4.95 (q, 2H, J=1.0 Hz), 7.53 (d, 1H, J=8.6 Hz), 7.81 (s, 1H), 7.98 (d, 1H, J=8.6 Hz), 8.23 - 8.42 (m, 2H), 8.73 (d, 1H, J=7.7 Hz) ppm. 13C NMR (CDCl$_3$): $\delta$ = 14.88, 41.92, 57.65, 73.18, 112.53, 114.28, 125.56, 126.70, 128.29, 132.89, 133.45, 136.78, 139.55, 144.49, 145.72, 148.51, 165.34 ppm. DART-MS m/z: 312.1350 [M + H]+, 623.2613 [2M+ H]+

2-(6-bromopyridin-2-yl)-1-methyl-1H-benzo[d]imidazole (3-30):

Under a nitrogen atmosphere 6-bromopicolinaldehyde (3.2 g) and N-methyl-2-nitroaniline (2.6 g) were stirred in a degassed mixture of ethanol (256 mL) and water (64 mL) at 100°C until all solids completely dissolved. To this solution, solid Na$_2$S$_2$O$_4$ (9.6 g) was added in one portion and the mixture was stirred at 100°C for 24 hr to give a yellow solution. The solution was concentrated under vacuum and extracted with ethyl acetate/water. The organic phases were combined, dried with sodium sulfate, and evaporated. Purification was achieved by column chromatography using a 100% DCM to 95% DCM/ 5% MeOH gradient and gave 2.0 g of product (41%). $^1$H NMR (CDCl$_3$): $\delta$
= 4.13 (s, 3H), 7.18 - 7.36 (m, 3H), 7.39 (d, 1H, J=7.9 Hz), 7.55 (t, 1H, J=7.8 Hz), 7.68 - 7.77 (m, 1H), 8.26 (d, 1H, J=7.7 Hz) ppm. 13C NMR (CDCl3): δ = 32.56, 109.85, 119.85, 122.67, 122.95, 123.55, 127.74, 137.00, 138.85, 140.30, 142.04, 148.07, 150.77 ppm.

ESI-MS m/z: 288.0140 [M + H]+

1-methyl-2-(6-((trimethylsilyl)ethynyl)pyridin-2-yl)-1H-benzo[d]imidazole (3-31a):

The following Sonogashira coupling reaction took place under a nitrogen atmosphere. Compound 3-30 (1.59 g, 8.57 mmol), Pd(PPh2)Cl2 (0.301 g, 5 mol %), trimethylsilylacetylene (1.4 mL, 9.43 mmol) and CuI (0.082 g, 5 mol %), were added to a solution of anhydrous DMF. To this solution dry, degassed triethylamine (5 mL, 35.6 mmol) was added and allowed to stir for 2 hours at room temperature. After the reaction was complete the mixture was filtered over Celite and the filter pad was rinsed with a small amount of THF. The filtrate was then acidified with 1M HCl and extracted with DCM. The organic phase was washed with water, dried, and evaporated. Purification was achieved by column chromatography using 100% DCM to afford 0.83 g of product (70%). 1H NMR (CDCl3): δ = 0.30 (s, 9H), 4.29 (s, 3H), 7.29 - 7.38 (m, 2H), 7.40 - 7.46 (m, 1H), 7.51 (d, 1H, J=1.0 Hz), 7.74 - 7.86 (m, 2H, J=7.9 Hz), 8.32 (d, 1H, J=1.0 Hz) ppm. 13C NMR (CDCl3): δ = 0.00, 32.97, 95.22, 103.84, 110.20, 120.31, 122.88, 123.69, 124.30, 127.67, 137.17, 137.52, 142.14, 142.70, 149.84, 151.03 ppm. C18H19N3Si calculated: C, 70.78; H, 6.27; N, 13.76. found: C, 70.40; H, 6.21; N, 13.50.

2-(6-ethynylpyridin-2-yl)-1-methyl-1H-benzo[d]imidazole (3-31b):

A solution of 3-31a (0.734 g, 3.62 mmol), CsF (0.365 g, 4.34 mmol), MeOH (25 mL), and THF (25 mL) was stirred for 4 hours. After the reaction was complete the mixture was evaporated and then a 1M HCl solution was added. The solution was extracted with DCM, the organic phases combined and washed with water. The organic
phase was then dried with sodium sulfate, filtered, and evaporated. The crude product was then recrystallized from minimal diethyl ether to afford 0.515 g product (92%). $^1$H NMR (CDCl$_3$): $\delta = 3.18$ (s, 1H), 4.26 (s, 3H), 7.27 - 7.36 (m, 2H), 7.37 - 7.44 (m, 1H), 7.49 (d, 1H, $J$=7.6 Hz), 7.73 - 7.85 (m, 2H), 8.36 (d, 1H, $J$=7.9 Hz) ppm. $^{13}$C NMR (CDCl$_3$): $\delta = 33.03$, 77.38, 82.90, 110.24, 120.29, 122.96, 123.79, 124.63, 127.67, 137.31, 137.50, 141.30, 142.57, 149.52, 151.09 ppm. ESI-MS m/z: 234.10 [M + H]$^+$, 467.1976 [2M + H]$^+$

**Tris(2-ethylacetoxy-3-methyl-5-tert-pentylphenyl)methane (3-14c):**

Under a nitrogen atmosphere 0.50 g of 3-13c was dissolved in dry acetone and 0.40 g of ethyl bromoacetate and 0.91 g of Cs$_2$CO$_3$ was added. The mixture was refluxed for 12-15 h and then cooled to room temperature. The acetone was removed under vacuum and the solids dissolved in diethyl ether. Solid MgSO$_4$ was added and the insoluble salts and drying agent were filtered off. The ether was removed from the filtrate and to give the crude product. The white solid was recrystallized in ethanol to give 0.49 g (71%) of product, 3-14c. $^1$H NMR (CDCl$_3$): $\delta = 0.46$ - 0.63 (m, 18H), 1.14 (s, 18H), 1.27 (t, 9H, $J$=7.2 Hz), 1.32 (s, 18H), 1.48 (q, 6H, $J$=7.3 Hz), 1.68 (q, 6H, $J$=7.3 Hz), 4.16 (s, 4H), 4.24 (q, 6H, $J$=7.2 Hz), 6.31 (s, 1H), 6.99 (s, 2H), 7.07 (s, 3H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta = 9.34$, 9.71, 14.33, 28.72, 29.16, 34.62, 37.11, 37.86, 39.26, 60.85, 68.38, 69.61, 125.12, 127.42, 136.98, 140.51, 143.39, 152.54, 169.10 ppm. Yield = 71%, ESI-MS m/z: 971.6936 [M + H]$^+$, 989.7055 [M + H$_3$O]$^+$

**Tris[2-(2-hydroxyethoxy)-3-methyl-5-tert-pentylphenyl)methane (3-15c):**

A dry diethyl ether solution of 3-14c was added over 1-2h with an addition funnel to a slurry of LiAlH$_4$ (0.49 g, 0.503 mmol) in 100 mL dry diethyl ether cooled to 0 °C. The mixture was then warmed to room temperature and stirred 12-15 h. The excess
reductant was destroyed with 1 M HCl (100 mL). The ether layer was separated and further extracted with 1 M HCl (2 x 100 mL) and brine (100 mL). The ether was then dried with MgSO₄. After filtration of the drying agent, the ether was removed to give 0.38 g (90%) of white crystalline material. ¹H NMR (CDCl₃): δ = 0.53 (m, 18H), 1.18 (s, 18H), 1.32 (s, 18H), 1.50 (s, 6H), 1.70 (m, 6H), 3.50 (m, 2H), 3.74 (m, 4H), 3.98 (m, 4H), 4.23 (m, 2H), 6.43 (s, 1H), 7.06 (s, 3H), 7.21 (s, 3H) ppm. ¹³C NMR (CDCl₃): δ = 9.09, 9.48, 34.78, 36.94, 37.64, 39.10, 62.07, 73.12, 124.83, 127.72, 137.31, 139.92, 142.74, 152.12 ppm. Yield = 90%. ESI-MS m/z: 845.6654 [M + H]⁺, 862.6916 [M + NH₄]⁺, 1690.3219 [2M]⁺, 1707.3464 [2M+NH₄]⁺

**Tris[2-(2-toluenesulfonyloxy)ethoxy]-3-methyl-5-tert-pentylphenyl]methane (3-16c):**

In a dry flask 0.283 g (0.334 mmol) of 3-15c was dissolved in 100 mL of dry pyridine and cooled to 0 °C in an ice bath. A 0.254 g (1.33 mmol) portion of toluene sulfonyl chloride was added and the reaction mixture was stirred for 2 h at 0 °C and then for 12-15 h at room temperature. The pyridine was removed under vacuum and the solid material dissolved in 100 mL methylene chloride and the extracted with 1 M HCl (2 x 100 mL). The organic phase was the dried with MgSO₄, filtered, and the solvent removed. Methanol was added and the white solid product filtered off and washed with more dry methanol to afford 0.41 g (93%) of 3-16c. ¹H NMR (CDCl₃): δ = 0.36 - 0.60 (m, 18H), 1.12 (s., 18H), 1.23 (s, 18H), 1.38 - 1.51 (m, 6H), 1.54 - 1.77 (m, 6H), 2.43 (s, 9H), 3.13 - 3.46 (m, 2H), 3.51 - 3.80 (m, 2H), 3.83 - 4.20 (m, 4H), 4.36 - 4.83 (m, 4H), 6.19 (s, 1H), 7.02 (s, 3H), 7.09 (s, 3H), 7.37 (d, 6H, J=8.2 Hz), 7.85 (d, 6H, J=7.9 Hz) ppm. ¹³C NMR (CDCl₃): δ = 9.03, 9.32, 21.57, 29.26, 29.67, 34.83, 36.81, 37.62, 39.12, 69.46, 70.00, 125.10, 127.54, 127.95, 129.91, 132.99, 137.01, 140.32, 143.31, 144.63.
152.14 ppm. C$_{76}$H$_{106}$O$_{12}$S$_3$ calculated: C, 69.80; H, 8.17; found: C, 69.32; H, 8.39. Yield = 93%.

**Tris(2-(2-azidoethoxy)-3,5-di-tert-pentylphenyl)methane (3-32):**

3-16c (15.31g, 11.7mmol) was combined with sodium azide (6.85g, 105mmol) in 325mL of DMF in a dry 500mL Schlenk flask fitted with a reflux condenser. The reaction mixture was heated to reflux overnight. The solution was allowed to cool to room temperature when 250mL of water was added and the solution extracted with dichloromethane (3 x 100mL). The combined organics were washed with water (3 x 100mL) and brine (1 x 100mL). The organics were then dried with sodium sulfate and the solvent removed under reduced pressure yielding pure 3-32 (10.82g, 99%). $^1$H NMR (CDCl$_3$): δ = 0.52 (t, 9H, J=7.5 Hz), 0.58 (t, 9H, J=7.5 Hz), 1.15 (s, 18H), 1.39 (s, 18H), 1.44 - 1.57 (m, 6H), 1.64 - 1.90 (m, 6H), 3.10 - 4.06 (m, 9H), 6.40 (s, 1H), 7.08 (s, 3H), 7.12 (s, 3H) ppm. $^{13}$C NMR (CDCl$_3$) δ = 9.06, 9.51, 29.42, 35.18, 36.83, 37.66, 38.57, 39.17, 51.80, 70.52, 125.12, 127.80, 137.44, 140.25, 143.20, 152.59 ppm. C$_{55}$H$_{85}$N$_9$O$_3$ calculated: C, 71.78; H, 9.31; N, 13.70; found: C, 71.87; H, 9.62; N, 13.50.

**tris(2-(2-(4-(6-(1-methyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)-1H-1,2,3-triazol-1-yl)ethoxy)-3,5-di-tert-pentylphenyl)methane (3-33):**

A solution of tris(2-(2-azidoethoxy)-3,5-di-tert-pentylphenyl)methane (3-32) (0.458 g, 0.497 mmol), 3-31b (0.406 g, 1.74 mmol), Cul (0.01 g, 10 mol%), and Et$_3$N (0.55 mL, 3.98 mmol) were combined in THF (30 mL) under a nitrogen atmosphere. The solution was stirred for 24 hours and turned dark brown over time. The resulting mixture was poured into a half-saturated ammonium chloride solution and then extracted with DCM and subsequently evaporated. Diethyl ether was poured into the dark mixture and filtered. The filtrate was then evaporated and purified by column chromatography (100%
DCM to 4% MeOH : 96% DCM gradient) to afford 0.492 g of product (61%). $^1$H NMR (CDCl$_3$): $\delta = 0.52$ (m, 18H), 1.00 - 1.29 (m, 36H), 1.41 (d, 6H, J=7.3 Hz), 1.52 (d, 6H, J=7.0 Hz), 3.75 - 3.92 (m, 6H), 3.96 (s, 9H), 4.52 (m, 3H), 4.95 (m, 1H), 6.55 (s, 1H), 7.03 - 7.24 (m, 12H), 7.31 (br. s., 3H), 7.67 (td, 3H, J=7.9, 1.5 Hz), 7.74 (d, 3H, J=7.9 Hz), 8.11 (d, 3H, J=7.9 Hz), 8.20 (d, 3H, J=7.9 Hz), 8.69 (s, 3H) ppm. $^{13}$C NMR (CDCl$_3$): $\delta = 9.01$, 9.40, 28.00, 28.81, 28.93, 29.05, 32.10, 34.32, 36.71, 37.71, 38.95, 51.05, 53.34, 69.96, 109.65, 119.79, 119.96, 122.45, 123.17, 123.61, 124.35, 125.24, 128.14, 136.89, 136.96, 137.54, 140.37, 142.21, 143.92, 148.03, 148.88, 149.73, 150.02, 151.94 ppm. APCI-MS m/z: 1619.9719 [M + H]$^+$

**General Procedure for the Synthesis of 3-22 and 3-26**

A DMF solution of 1.0 equiv of carboxylic acid, 1.1 equiv PyBOP, and 2 equiv of diethyl-isopropylamine was stirred together for 30 minutes at room temperature. To this solution was added 0.3 equiv of the triphenoxymethane amine and was stirred for 24 hours. After the reaction was complete 10% HCl solution was added and then extracted with either dichloromethane or diethyl ether. The organic phases were combined and underwent several water washes to removed residual DMF. The organic phase were then dried with sodium sulfate, filtered. and evaporated to affored the product.

**Analysis of Compound 3-22:**

$^1$H NMR (CDCl$_3$): $\delta = 1.23$ (s, 27H), 1.37 (s, 36H), 1.90 - 2.08 (m, 3H), 2.10 - 2.36 (m, 9H), 3.36 (s, 9H), 3.52 - 3.70 (m, 6H), 3.82 - 4.01 (m, 6H), 4.50 (s, 6H), 4.53 - 4.75 (m, 6H), 6.54 (s, 1H), 7.17 - 7.26 (m, 6H), 7.28 - 7.37 (m, 6H), 7.57 (t, 3H, J=7.9 Hz), 7.68 (s, 3H), 7.73 (dd, 3H, J=7.6, 1.1 Hz), 8.08 - 8.17 (m, 3H), 8.21 (dd, 3H, J=7.8, 1.0 Hz) ppm. $^{13}$C NMR (CDCl$_3$): $\delta = 15.38$, 30.69, 31.38, 31.48, 34.50, 35.49, 37.61, 40.24, 57.77, 70.15, 74.93, 109.75, 119.65, 121.98, 122.35, 123.83, 126.85, 127.23, 132.94,
135.49, 137.58, 137.98, 141.77, 142.45, 144.60 ppm. ESI-MS m/z: 840.5151 [M + 2H]^{2+}, 851.5058 [M + H + Na]^{2+}, 1701.9972 [M + Na]^+. Yield: 85%

**Analysis of Compound 3-26:**

^{1}H NMR (CDCl\textsubscript{3}): δ = 0.98 (t, 9H, J=7.2 Hz), 1.06 - 1.54 (m, 72H, M13), 1.94 - 2.49 (m, 6H), 3.23 (q, 6H, J=7.1 Hz), 3.51 (q, 12H, J=7.4 Hz), 3.67 - 3.91 (m, 6H), 4.30 - 4.74 (m, 6H), 6.51 (s, 1H), 7.12 (s, 6H), 7.17 - 7.32 (m, 3H), 7.41 (d, 3H, J=7.4 Hz), 7.62 - 7.82 (m, 6H), 8.01 (d, 3H, J=7.7 Hz), 8.21 (s, 3H) ppm. ^{13}C NMR (CDCl\textsubscript{3}): δ = 13.00, 14.50, 15.30, 31.06, 31.73, 31.80, 34.72, 35.75, 38.88, 39.70, 41.28, 42.98, 70.87, 110.68, 118.54, 122.52, 123.29, 123.90, 125.19, 127.40, 130.90, 137.47, 137.73, 138.47, 140.10, 142.06, 144.63, 147.55, 149.91, 153.74, 154.91, 168.14, 168.42 ppm.

APCI-MS m/z: 1845.1415 [M + H]^+, 1867.1237 [M + Na]^+. Yield: 80%
CHAPTER 4
METAL COMPLEXATION EXPERIMENTS OF LANTHANIDES USING
BENZIMIDAZOLE-PRIDYL FUNCTIONALIZED NONADENTATE LIGANDS

4.1 Introduction

In this chapter the extraction results and crystal structure of the ligands synthesized in chapter three are discussed. The objective of the experimentation was to analyze each ligands’ extraction efficiency for lanthanides and to evaluate the crystal structure of the ligands after metal complexation.

The solvent extraction study used ligands 3-22, 3-26, and 3-33 to examine how relatively soft nitrogen donor atoms played a role in lanthanide extraction. In each study dichloromethane containing a $10^{-3}$ M solution of ligand was used as the organic phase and 1 M nitric acid containing $10^{-4}$ M Ln(III) nitrate was used as the aqueous phase. Once the extraction event was performed, UV-Vis spectrophotometry was used to measure the ability of each ligand to extract the lanthanides. The extraction efficiency of each trivalent lanthanide was calculated as $\%E = 100/(A_1 - A)/ (A_1 - A_0)$, where $A$ is the absorbance of the extracted aqueous phase, $A_1$ is the absorbance of the aqueous phase before extraction, and $A_0$ is the absorbance of metal free 1 M nitric acid solution.

The crystal structures of 3-26 and 3-33 both with ytterbium were obtained. Both crystals were formed from ytterbium (III) triflate. The triflate anion balances the trivalent cation of the complex. Structural parameters are reported and the crystal structure is compared to computational data.

4.2 Extraction Results

The data in Table 4-1 shows that ligands 3-22 and 3-26 gave the highest $\%E$ while 3-33 gives $\%E$ values within the error limits of the analysis method.
Table 4-1. Extraction Efficiency

<table>
<thead>
<tr>
<th>Ligand</th>
<th>3-22</th>
<th>3-26</th>
<th>3-33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>%E</td>
<td>%E</td>
<td>%E</td>
</tr>
<tr>
<td>La(III)</td>
<td>5.7</td>
<td>5.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Ce(III)</td>
<td>3.9</td>
<td>4.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>Pr(III)</td>
<td>2.7</td>
<td>4.2</td>
<td>n.d.</td>
</tr>
<tr>
<td>Nd(III)</td>
<td>5.7</td>
<td>4.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>5.0</td>
<td>3.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Gd(III)</td>
<td>4.2</td>
<td>4.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>Tb(III)</td>
<td>4.6</td>
<td>4.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>Dy(III)</td>
<td>5.1</td>
<td>5.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Er(III)</td>
<td>5.3</td>
<td>5.4</td>
<td>n.d.</td>
</tr>
<tr>
<td>Tm(III)</td>
<td>10.8</td>
<td>12.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>Yb(III)</td>
<td>6.2</td>
<td>7.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

It is not surprising that the hard oxygen donors of the amide functional group in ligands 3-22 and 3-26 had a greater affinity for lanthanides in comparison to the softer triazole donor of 3-33 since the lanthanides themselves are classified as hard acids. The rigidity of the two carbon linker arm in 3-33 could hamper to metal complexation in comparison to the three carbon linker in 3-22 and 3-26 although semi-empirical calculations seem to suggest otherwise for this particular ligand. The lowered extraction efficiency of rigid two carbon linkers that connect the three ligand arms to the triphenoxymethane platform verses three carbon linkers was previously evaluated experimentally by the Scott group. With the exception of Tm and Yb all of the lanthanides had approximately 5% extraction efficiency. As previously stated, the increase in %E for the late lanthanides are mainly governed by entropic effects rather than enthalpy of complexation. It is also possible that the binding pocket of the ligands 3-22 and 3-26 are more favorable for smaller lanthanides. The similarity in %E between 3-22 and 3-26 demonstrates that the extra amide group in 3-26 does not drastically affect the bonding environment despite the increased opportunity for hydrogen bonding.
Since the %E for ligands 3-22 and 3-26 are still all less than 13% they may still prove viable to give high separation factors if actinide extraction studies were performed. The actinide extraction studies for this set of ligands were not performed because of the expense, radiotoxicity and government regulation of actinides.

The most structurally similar molecule to 3-33 that has undergone solvent extraction experiments consists of a bis-benzimidazole pridy skeletal and did not use a molecular scaffold. Drew et al. reported that their ligands containing this structure also showed comparably low distribution coefficients for Eu(III) although it should be noted that their extraction conditions are different than what is used in this study.\textsuperscript{19} They also reported an increase in distribution coefficients when using Am(III) leading to separation factors as high as 9 for Am(III)/Eu(III). Although this value is dwarfed by the BTP maximum separation factor of 150, it does show proof of concept that benzimidazole containing ligands may offer acceptable separation between lanthanides and actinides if conditions are optimized.

4.3 Crystal Structure

The crystals presented in this study were grown by the slow diffusion of methyl tert-butyl ether or diethyl ether into methanol. All efforts to crystallize lanthanide nitrate salts resulted in precipitation of a fine powder. Despite numerous attempts crystals of 3-22 could not be obtained. In a typical lanthanide complexation procedure, equal molar portions of a lanthanide salt were reacted with ligand in ethyl acetate for several hours. In the case of nitrate salts, the product immediately precipitated from the solution. The precipitate was filtered to obtain the metal-ligand complex. Triflate salt reactions were evaporated to dryness to obtain the complex. Figure 4-1 and Figure 4-2 show the crystal structure of ytterbium complexed by 3-26 and 3-33, respectively.
Figure 4-1. Crystal structure of Yb complexed by ligand 3-26 with ellipsoids at 50% probability
Figure 4-2. Crystal structure of Yb complexed by ligand 3-33 with ellipsoids at 50% probability
4.4 Conclusions

The extraction experiments using ligands 3-22, 3-26, and 3-33 were performed to test their ability to extract lanthanide ions from an acidic solution. If the extraction efficiency is too high for the lanthanides the selective separation of actinides would not be likely. The extraction efficiency for ligands 3-22, and 3-26 were approximately 5% and increased for the heavier lanthanides. The low extraction efficiency with lanthanides could be a positive result in that the selectivity of the lanthanides is low but it could also mean that the ligand is not bonding the metal or the solubility of the ligand in solution is poor.

The crystal structures of Yb(3-26) and Yb(3-33) demonstrated that the ligand can complex the metal. The crystal structures were evaluated for their bond lengths, twist angle and standard deviation (STD) of twist angle. The solid state structure was also compared to SE calculations to evaluate accuracy of the theoretical method. To analyze the agreement between the theoretical SE calculations and the experimentally obtained crystal structure a new set of calculations were performed that used the solid state geometry as the initial guess for the SE geometry optimization. The results are reported in Table 4-2 and 4-3.

Table 4-2. Comparison of bond lengths (Å) and twist angles (˚) between the crystal structure, SE calculation, and crystal SE calculation of Yb(3-26)

<table>
<thead>
<tr>
<th></th>
<th>Crystal Structure</th>
<th>SE calculation</th>
<th>SE calculation of crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2.31(7)</td>
<td>2.38</td>
<td>2.36</td>
</tr>
<tr>
<td>( N_{py} )</td>
<td>2.46(9)</td>
<td>2.43</td>
<td>2.44</td>
</tr>
<tr>
<td>( N_{bzd} )</td>
<td>2.55(9)</td>
<td>2.36</td>
<td>2.34</td>
</tr>
<tr>
<td>Twist Angle</td>
<td>9.08</td>
<td>8.57</td>
<td>4.04</td>
</tr>
<tr>
<td>STD Twist Angle</td>
<td>1.24</td>
<td>4.58</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The oxygen donor of the amide, nitrogen donor of the pyridine and nitrogen donor of the benzimidazole are notated as O, \( N_{py} \) and \( N_{bzd} \), respectively.
Table 4-3. Comparison of bond lengths (Å) and twist angles (°) between the crystal structure, SE calculation, and crystal SE calculation of Yb(3-33)

<table>
<thead>
<tr>
<th></th>
<th>Crystal Structure</th>
<th>SE calculation</th>
<th>SE calculation of crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{triazole}</td>
<td>2.47(6)</td>
<td>2.42</td>
<td>2.43</td>
</tr>
<tr>
<td>N\textsubscript{py}</td>
<td>2.51(7)</td>
<td>2.43</td>
<td>2.44</td>
</tr>
<tr>
<td>N\textsubscript{bzd}</td>
<td>2.47(6)</td>
<td>2.38</td>
<td>2.37</td>
</tr>
<tr>
<td>Twist Angle</td>
<td>8.92</td>
<td>5.53</td>
<td>5.18</td>
</tr>
<tr>
<td>STD Twist Angle</td>
<td>1.06</td>
<td>0.27</td>
<td>0.77</td>
</tr>
</tbody>
</table>

The nitrogen donor of the triazole, nitrogen donor of the pyridine and nitrogen donor of the benzimidazole are notated as N\textsubscript{triazole}, N\textsubscript{py} and N\textsubscript{bzd}, respectively.

The bond lengths in each structure were not accurately represented at the benzimidazole donor group and it is concluded that an alteration in the way that benzimidazole is treated in the SE calculations is needed. The SE calculation of Yb(3-26) was found to be in agreement with the crystal structure twist angle but this could be coincidental since the STD of the twist angles do not agree. When the crystal structure geometry of Yb(3-26) was used as a starting point for the SE geometry optimization, the structure was taken to a more symmetric minimum as shown by the decrease in STD. The SE calculations of Yb(3-33) were similar to those of Yb(3-26) in that the benzimidazole donor was not accurately represented. The twist angles of Yb(3-33) did not achieve the accuracy of Yb(3-26) but the STD value was in better agreement. When the crystal structure geometry of Yb(3-33) was used as a starting point for the SE geometry optimization, the structure was not significantly changed. Overall, the SE calculations are validated by comparison with the crystal structure with whatever starting geometry is chosen.
4.5 Experimental Section

4.5.1 Extraction Experiment

The lanthanide and actinide salts, La(NO$_3$)$_3$·6H$_2$O (Alpha Aesar), Ce(NO$_3$)$_3$·6H$_2$O, Pr(NO$_3$)$_3$·6H$_2$O, Nd(NO$_3$)$_3$·6H$_2$O, Eu(NO$_3$)$_3$·5H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O, Tb(NO$_3$)$_3$·6H$_2$O, Dy(NO$_3$)$_3$·5H$_2$O, Er(NO$_3$)$_3$·5H$_2$O, Tm(NO$_3$)$_3$·5H$_2$O, Yb(NO$_3$)$_3$·5H$_2$O, Yb(Tf)$_3$·5H$_2$O (Aldrich) were used as received. The solutions were prepared from 18 MΩ Millipore deionized water, TraceMetal-grade HNO$_3$ (Fisher Scientific), and HPLC-grade organic solvents. The extraction efficiency was measure by utilizing the Arsenazo(III) assay and was performed on a Varian Cary 50 UV-vis spectrophotometer. The metal extraction experiments followed previously reported procedure. Metal stock solutions were standardized by colorimetric titration with Na$_2$H$_2$EDTA and xylenol orange. All extraction experiments used 10$^{-3}$ M solutions of ligand in dichloromethane and a 10$^{-4}$ M solutions of Ln(III) nitrate in 1 M nitric acid. The extraction took place in a 10 mL sealed vial using 4 mL of organic solution and 4 mL of aqueous solution and agitated on an oscillating table for 24 hours. The errors, based on the precision of the spectrophotometer and the standard deviation from the mean of at least three measurements, were in most cases no higher than 1.5%. The distribution coefficients (defined as the ratio of concentrations of metal in the organic and aqueous layers) were obtained and reported.

4.5.2 Crystal Structure of Yb(3-26)$^{3+}$

X-Ray intensity data were collected at 100 K on a Bruker DUO diffractometer using MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization
effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. In the final cycle of refinement, 17922 reflections (of which 12086 are observed with $I > 2\sigma(I)$) were used to refine 1661 parameters and the resulting $R_1$, $wR_2$ and $S$ (goodness of fit) were 5.77%, 14.43% and 0.932, respectively. The refinement was carried out by minimizing the $wR_2$ function using $F^2$ rather than $F$ values. $R_1$ is calculated to provide a reference to the conventional $R$ value but its function is not minimized. Further parameters are reported in Table 4-4. Several solvent molecules were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

4.5.2 Crystal Structure of Yb(3-33)$^{3+}$

X-Ray Intensity data were collected at 100 K on a Bruker DUO diffractometer using MoKα radiation ($\lambda = 0.71073$ Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal
parameters and all of the H atoms were calculated in idealized positions and refined
riding on their parent atoms. In the final cycle of refinement, 19530 reflections (of which
15188 are observed with I > 2σ(I)) were used to refine 1260 parameters and the
resulting R₁, wR₂ and S (goodness of fit) were 7.96%, 20.13% and 1.027, respectively.
The refinement was carried out by minimizing the wR₂ function using F² rather than F
values. R₁ is calculated to provide a reference to the conventional R value but its
function is not minimized. Further parameters are reported in Table 4-4.

Several solvent molecules were disordered and could not be modeled properly,
thus program SQUEEZE, a part of the PLATON package of crystallographic software,
was used to calculate the solvent disorder area and remove its contribution to the
overall intensity data.⁵⁹ The largest residual electron density peak could not be properly
accounted for chemically and considering the amount of disorder in this structure, it is
very likely that it is the result of a slight lower quality data than expected.
Table 4-4. X-ray data for crystal structures Yb complexed by 3-22 and 3-33 using triflate counter ions grown from the diffusion of ether into methanol

<table>
<thead>
<tr>
<th></th>
<th>Yb(3-33)(^{3+})·(CF(_3)SO(_3))(_3)</th>
<th>Yb(3-26)(^{3+})·(CF(_3)SO(_3))(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Reflections</td>
<td>50337</td>
<td>17922</td>
</tr>
<tr>
<td>Unique Reflections</td>
<td>19530/15188</td>
<td>17922/12086</td>
</tr>
<tr>
<td>Reflections (\geq 2\sigma(I))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collection Range ('')</td>
<td>1.49 &lt; (\theta) &lt; 25.00</td>
<td>1.54 &lt; (\theta) &lt; 27.50</td>
</tr>
<tr>
<td>Formula</td>
<td>(\text{C}<em>{103}\text{H}</em>{118}\text{F}<em>{9}\text{N}</em>{18}\text{O}<em>{12}\text{S}</em>{3}\text{Yb})</td>
<td>(\text{C}<em>{106}\text{H}</em>{130}\text{F}<em>{9}\text{N}</em>{12}\text{O}<em>{18}\text{S}</em>{3}\text{Yb})</td>
</tr>
<tr>
<td>(M_r)</td>
<td>2240.37</td>
<td>2300.44</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Triclinic</td>
<td>Rhombohedral</td>
</tr>
<tr>
<td>Space Group</td>
<td>(P\bar{I})</td>
<td>(R3c)</td>
</tr>
<tr>
<td>(a) ((\text{Å}))</td>
<td>13.9187(16)</td>
<td>42.262(3)</td>
</tr>
<tr>
<td>(b) ((\text{Å}))</td>
<td>14.9433(18)</td>
<td></td>
</tr>
<tr>
<td>(c) ((\text{Å}))</td>
<td>29.236(4)</td>
<td>45.351(3)</td>
</tr>
<tr>
<td>(\alpha) ('')</td>
<td>90.593(2)</td>
<td></td>
</tr>
<tr>
<td>(\beta) ('')</td>
<td>91.506(2)</td>
<td></td>
</tr>
<tr>
<td>(\gamma) ('')</td>
<td>114.085(2)</td>
<td></td>
</tr>
<tr>
<td>(V_c) ((\text{Å}^3))</td>
<td>5548.0(11)</td>
<td>70148(8)</td>
</tr>
<tr>
<td>(D_c) ((g\ \text{cm}^{-1}))</td>
<td>1.341</td>
<td>1.307</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>(F(000))</td>
<td>2314</td>
<td>28632</td>
</tr>
<tr>
<td>(\mu[\text{Mo-K}\alpha]) ((\text{mm}^{-1}))</td>
<td>0.979</td>
<td>0.933</td>
</tr>
<tr>
<td>(R_1[\geq 2\sigma(I)\text{data}])</td>
<td>0.0796</td>
<td>0.0577</td>
</tr>
<tr>
<td>(wR_2[\geq 2\sigma(I)\text{data}])</td>
<td>0.2013</td>
<td>0.1443</td>
</tr>
<tr>
<td>GoF</td>
<td>1.027</td>
<td>1.089</td>
</tr>
<tr>
<td>Largest Peak, deepest trough</td>
<td>+4.588, -1.802</td>
<td>+1.081, -0.817</td>
</tr>
</tbody>
</table>

\(\text{a)}\) Obtained with monochromatic MoK\(\alpha\) radiation (\(\lambda = 0.71073\ \text{Å}\))

\(\text{b)}\) \(R_1 = \Sigma F_o - F_c / \Sigma F_o\).

\(\text{c)}\) \(wR_2 = \left[\Sigma [w(F_o^2 - F_c^2)^2 / \Sigma [w(F_o^2)]^2\right]^{1/2}\)
CHAPTER 5
ELECTRONIC STRUCTURE OF EUROPIUM, AMERICIUM, AND CURIUM COMPLEXES USING DENSITY FUNCTIONAL THEORY

5.1 Introduction

The complex bonding and radiotoxicity of actinides has spurred many theoretical investigations in recent years. The advent of cheap and available computing power has made many electron calculations involving heavy metals more feasible. Theoreticians have also invented effective core potentials (ECP) for heavy metals in which core electrons are calculated as part of the nuclei and treated as a rigid non-polarizable potential while the valence electrons are computed with a separate valence wavefunction. The approximation drastically decreases the amount of computational resources needed to calculate actinide complexes. In particular, the effective core potentials used in this study are relativistic effective core potentials (RECP) because they also account for the relativistic energy changes that occur as the innermost electrons start to approach the speed of light. For an accurate description of heavy metals, such as actinides, accounting for relativistic effects has been shown to be critical for computation.

The methods chosen for the calculations were based on computational resources, program availability, and literature results. All calculations were performed using the Gaussian 03 program package on the University of Florida High Performance Computing network. Each geometry optimization and single point calculation of a metal-ligand complex used a maximum of four processors and eight gigabytes of memory. The hybrid B3LYP functional was chosen over other DFT functionals in order to facilitate self-consistent field (SCF) convergence. Americium, Europium and Curium were chosen to be computed for their importance to lanthanide-actinide separation.
methods. A small-core relativistic effective core potential was used for the metals. The double zeta basis set, 6-31G*, was chosen for all other atoms as a triple zeta basis set proved to be too costly in computational resources. In accordance with literature data, high spin configuration was used for all computed complexes which corresponds to the following spin multiplicities for each metal: Eu = 7, Am = 7, Cm = 8.

In this study, calculations of the molecular orbital (MO) data produced large files of text and to facilitate interpretation the data was plotted graphically. The data for the MO diagrams in this chapter were processed in the AOMix program package. In order to decrease the complexity of the diagrams only MO contributions that are above 4% were included. The metal and ligand energies in the diagrams have been to highlight the frontier orbitals, but the metal-ligand complex energies have not been altered. Because of the many approximations used in the calculations, the results for the different elements can be compared but the energy values are not accurate.

The objective of the DFT study was to evaluate the geometry and electronics of the metallated complexes of the synthesized compounds. In order to decrease calculation time, the ligands were truncated to three independent terdentate ligands as opposed to one nonadentate ligand. For comparison, the BTP ligand was computed in the same manner since the actinide selectivity of it is often attributed to the orbital interactions. Since the structure has never been modeled with the B3LYP functional, Am(BTP)₃³⁺ was also included in the calculation in view of its relevance to the area of study.

5.2 Geometry Optimizations

Geometry optimizations were carried out using metals Eu³⁺, Am³⁺, and Cm³⁺ in combination with structures 5-1, 5-2, and 5-3 (Figure 5-1).
Figure 5-1. Simplified ligands computed by DFT. Each ligand was computed with Eu, Am, and Cm as the metal.

The optimizations for each structure were $D_3$ or $C_3$ symmetric with less than 2 kcal/mol difference in energy between the fully optimized and the symmetry restricted structure. Ligand 5-1 was computed for comparison, and the bond distances were similar to previously published reports using a similar method. Structure 5-2 represents a truncated version of 3-22 and 3-26 with the commonality of amide, pyridine, and benzimidazole donors. The triphenoxymethane and other atoms irrelevant to the electronic structure were removed. Structure 5-3 resembles the 3-33 donor atoms but the linkage to triphenoxymethane was replaced by a methyl group. In addition, the alkyl group of the benzimidazole nitrogen was been replaced with hydrogen in order to facilitate SCF convergence. The removal of the electron donating methyl group may cause small electronic differences to the experimental comparison.

The bond distances for the M-L bonds are reported in Table 5-1, 5-2, and 5-3 where the pyridine, triazine, benzimidazole, amide, and triazole donor atoms are labeled as $N_{py}$, $N_{triazine}$, $N_{bzd}$, $O_{amide}$, and $N_{triazole}$, respectively.

Table 5-1. Calculated M-N bond distances for structure 5-1

<table>
<thead>
<tr>
<th></th>
<th>$d(M-N_{py})$</th>
<th>$d(M-N_{triazine})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[Eu(5-1)_3]^{3+}$</td>
<td>2.61</td>
<td>2.60</td>
</tr>
<tr>
<td>$[Am(5-1)_3]^{3+}$</td>
<td>2.64</td>
<td>2.62</td>
</tr>
<tr>
<td>$[Cm(5-1)_3]^{3+}$</td>
<td>2.64</td>
<td>2.63</td>
</tr>
</tbody>
</table>
Table 5-2. Calculated M-N bond distances for structure 5-2

<table>
<thead>
<tr>
<th></th>
<th>(d(M-N_{py}))</th>
<th>(d(M-N_{bzd}))</th>
<th>(d(M-O_{amide}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Eu(5-2)_2]^3+)</td>
<td>2.69</td>
<td>2.68</td>
<td>2.45</td>
</tr>
<tr>
<td>([Am(5-2)_2]^3+)</td>
<td>2.69</td>
<td>2.69</td>
<td>2.47</td>
</tr>
<tr>
<td>([Cm(5-2)_2]^3+)</td>
<td>2.69</td>
<td>2.67</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 5-3. Calculated M-N bond distances for structure 5-3

<table>
<thead>
<tr>
<th></th>
<th>(d(M-N_{py}))</th>
<th>(d(M-N_{bzd}))</th>
<th>(d(M-N_{triazole}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Eu(5-3)_3]^3+)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>([Am(5-3)_3]^3+)</td>
<td>2.68</td>
<td>2.63</td>
<td>2.63</td>
</tr>
<tr>
<td>([Cm(5-3)_3]^3+)</td>
<td>2.70</td>
<td>2.64</td>
<td>2.64</td>
</tr>
</tbody>
</table>

There are only small differences in bond distances between Am and Cm complexes with each ligand. In each case the Cm distances were slightly longer but likely within the error of the calculation. The Eu complexes exhibit shorter bonds compared to the Am and Cm complexes emphasizing that separation based on size of the cation would not be efficient. The \([Eu(5-3)_3]^3+\) structure failed to converge and hence no data is reported. All N-heterocyclic nitrogen donors have very similar bond lengths which are divergent from the oxygen donor bond lengths. The increased hardness of the oxygen donors makes for a stronger bond and is reflected in the shorter bond distance. The solid state structure of \([Eu(5-1)_3]^3+\) and \([Cm(5-1)_3]^3+\) has been determined and the authors reported average nitrogen bond distances of 2.55 Å and 2.57 Å, respectively.\(^{61}\) The geometry optimizations had longer bond lengths but should not significantly affect the molecular orbital analysis.
5.3 Electronic Structure Analysis

5.3.1 Mulliken and Natural Charge Analysis

Mulliken charges can be used as a computational assessment of the degree of covalency between a metal-ligand bond. Generally, the increased covalency between a neutral ligand and metal suggests a stronger bond. The charge on the metal should be $3^+$ for each computed molecule and any deviation from that value equates to a change in electron density around the metal. A stronger electron density donation will lower the Mulliken charge. Mulliken charges are less intuitive if back-bonding is occurring in the metal-ligand interaction because when the metal donates electron density back to the ligand the Mulliken charge is increased. The Mulliken charges for each calculation are shown in Table 5-4. The $[\text{Eu}(5\text{-}3)_3]^{3+}$ structure failed to converge and hence no data is reported.

<table>
<thead>
<tr>
<th></th>
<th>5-1</th>
<th>5-2</th>
<th>5-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>1.75</td>
<td>1.65</td>
<td>n.d.</td>
</tr>
<tr>
<td>Am</td>
<td>1.61</td>
<td>1.33</td>
<td>1.52</td>
</tr>
<tr>
<td>Cm</td>
<td>1.44</td>
<td>1.28</td>
<td>1.40</td>
</tr>
</tbody>
</table>

The low value can be attributed to the fact that Mulliken charges generally suggest excessively covalent interactions, although global trends are accurate. From the MO analysis presented later it was determined that the structures do not display any substantial back-bonding thus the value shown is pure donation of the donor atom electrons into the metal. Higher values of Eu complexes imply a more covalent bond occurs with the actinides than the lanthanides. The increased covalency for actinides is in agreement with the fact that the diffuse 5f orbitals can contribute to bonding in actinides, whereas, the energetically buried 4f orbitals of the lanthanides do
not because the energy discrepancy between bonding orbitals is too high. The calculations also show increased covalency for ligand 5-2 which can be explained by the hard oxygen donor of the methyl-amide functional group. Since lanthanides and actinides are both considered hard acids it is not surprising that the largest charge donation occurs at the oxygen atom. The all nitrogen donor ligands, 5-1 and 5-3, show similar results with the more electronegative triazole moiety of 5-3 decreasing the Mulliken charge more than the triazinyl moiety of 5-1. Overall the Mulliken charges were effective at determining which metal has more covalency with the ligand set and which ligand donates the most electron density to the metal.

5.3.2 Molecular Orbital Analysis

The possible covalency of a ligand can be measured by absolute hardness. Since absolute hardness is proportional to the HOMO-LUMO gap the difference in energy between the HOMO and LUMO of a ligand can give insight into how the ligand will interact with a metal. The HOMO-LUMO gap for structures (5-1)$_3$, (5-2)$_3$, (5-3)$_3$ in their computed equilibrium geometry for binding is 88.2, 98.7, and 99.9 kcal/mol, respectively. This shows the expected softness of 5-1 in comparison to the other ligands. It is likely that the dominance of the benzimidazole moiety on the relative HOMO-LUMO energies is the reason why the gap energies for structure 5-2 and 5-3 are so similar. In fact, the MO for the AnL$_3^{3+}$ complexes of 5-2 and 5-3 are mainly comprised of ligand centered orbitals in the frontier orbital region. The electron density of the HOMO in structures 5-2 and 5-3 is not entirely comprised of the benzene ring but also of the nitrogen donor as seen in Figure 5-2. Since some of the HOMO is comprised of the nitrogen donor atom it is reasonable to assume that it could be used for bonding if the energetics and orbital symmetries of the metal and ligand were more congruent. To
alter energetic matching it might be possible to modify benzimidazole to a lower energy by replacing substituents. The likely areas of modification include N-alkylation or aromatic substitution on the benzene ring. Another modification could be to add more conjugation to the structure in order to lower the HOMO – LUMO gap.

Figure 5-2. Representation of benzimidazole centered HOMO of Cm(5-3)$_3$$^{3+}$

An example of good energetic matching occurs in the HOMO-9 of Am(5-1)$_3$$^{3+}$ which consists of 39.2% f-orbital interacting with 22.7% of the ligand where the remaining percentage of the MO is not involved with the ligand to metal donation. The MO representation of HOMO-9 is shown in Figure 5-3. The bonding interaction is tracked in the calculation as having a positive overlap population which is clearly seen in Figure 5-3 where the orbitals on one of the three ligands has the triazinyl nitrogens directly facing the $f_{xyz}$ orbital on Am.
An example of proper energetic matching is shown in Figure 5-4. The HOMO-1 composition of Am(5-1)$_3^{3+}$ is 42.8% ligand and 57.2% metal and the interaction occurs in the frontier orbitals. Even though there is a good energetic matching for the HOMO-1 there is no overlap of the orbitals. Figure 5-4 depicts a negative overlap population where the orbital on the triazinyl nitrogen is not directly facing the metal orbital in the sigma bonding arrangement one would expect. The multiple contributions that make up many of the molecular orbitals can create a complex bonding environment. For instance, the HOMO-1 consists of 52.1% f-orbital anti-bonding to 31.6% of the ligand, 2.6% f-orbital in an ionic interaction with the ligand, and 2.5% d-orbital overlapping with
the ligand in a ligand to metal donation. Since the dominating interaction of the MO is anti-bonding the representation of HOMO-1 shown in Figure 5-4 is mainly anti-bonding with the f-orbital slightly distorted from the d-orbital contribution.

Figure 5-4. The HOMO-1 of Am(5-1)₃³⁺. The black lines signify anti-bonding interactions.

Another instance that can be mistaken for a bonding interaction is when there is zero overlap population for the interaction. An example of zero overlap population occurs in the HOMO-12 of Am(5-1)₃³⁺ and is shown in Figure 5-5. The zero overlap population can be viewed as an ionic bond where the electrostatic interaction between
the negatively charged nitrogen and the positively charged metal are attracted to each other but no orbital overlap occurs. These non-covalent type interactions are similar in lanthanides and actinides thus are not tracked since they should not be an important factor in selectivity.

![Image of molecular structure]

Figure 5-5. The HOMO-12 of Am(5-1)_3^{3+} does not display any overlap of orbitals since the overlap population was computed as zero.

The MO interaction diagrams of Eu(5-1)_3^{3+}, Am(5-1)_3^{3+}, and Cm(5-1)_3^{3+} are shown in Figure 5-6. With the exception of Am(5-1)_3^{3+}, most frontier orbitals have 96% ligand composition. When viewing the MO interaction diagrams it is important to note that although there appears to be a bond forming it is also possible for the interaction to be anti-bonding or ionic bonding interaction where there is no overlap between the metal
and ligand orbitals. For clarity, all MO diagrams that have contributions below 4% do not have a line drawn as an interaction.

Figure 5-6. MO for Eu(5-1)\textsuperscript{3+}, Am(5-1)\textsuperscript{3+}, and Cm(5-1)\textsuperscript{3+}. Metal energy levels shifted by approximately 18 eV and ligand orbitals by -8 eV.

In particular, Eu(5-1)\textsuperscript{3+} shows poor energetic matching between the metal and ligand because of the energetically buried 4f orbitals of europium. The first positive overlap populated orbital of Eu(5-1)\textsuperscript{3+} occurs in the HOMO-35 with a composition of 3.4% d-orbital and 53.1% ligand. The small composition of the d-orbital in HOMO-35 implies that the energetics of the interaction is poor. There are no f-orbital contributions
found until the HOMO-120 at -33.414 eV with only a 1.1% composition, which is
deemed negligible in terms of covalency. In comparison Am(5-1)\textsubscript{3}\textsuperscript{3+} has the first f-orbital positive overlap population at HOMO-9 with 39.2% f-orbital interacting with 22.7% of the ligand. For the Cm(5-1)\textsubscript{3}\textsuperscript{3+} calculation the first f-orbital positive overlap population occurred at the HOMO-33 with 29.8% metal and 22.5% ligand. Even though the HOMO-32 is lower in energy it is a consequence of Cm being lower in energy than Am. The Cm(5-1)\textsubscript{3}\textsuperscript{3+} calculation also has several pairs of degenerate orbitals in the electronic structure (Figure 5-7). As previously mentioned, there is no significant back-bonding in the structures, therefore, there are no lines drawn from the HOMO to the LUFO of the ligand in the MO diagram (Figure 5-6).

Figure 5-7. Degenerate orbitals HOMO-43 and HOMO-44 of Cm(5-1)\textsubscript{3}\textsuperscript{3+} at -17.803 eV

The MO interaction diagram for metals Eu, Am, and Cm complexed by ligand 5-2 is shown in Figure 5-8. The first few ligand centered MOs of Eu(5-2)\textsubscript{3}\textsuperscript{3+}, Am(5-2)\textsubscript{3}\textsuperscript{3+}, and Cm(5-2)\textsubscript{3}\textsuperscript{3+} are comprised of benzimidazole character and look similar to the HOMO of
Cm(5-3)\(_3^{3+}\) shown in Figure 5-2. The Eu(5-2)\(_3^{3+}\) calculation is similar to Eu(5-1)\(_3^{3+}\) in that there are no f-orbital positive overlap populations in the frontier orbitals.

Figure 5-8. MO for Eu(5-2)\(_3^{3+}\), Am(5-2)\(_3^{3+}\), and Cm(5-2)\(_3^{3+}\). Metal energy levels shifted by approximately 18 eV and ligand orbitals by -8 eV.

When comparing the MO interaction diagram of Am(5-2)\(_3^{3+}\) with that of Am(5-1)\(_3^{3+}\) there are less interactions between Am and ligand (5-2)\(_3\) than with ligand (5-1)\(_3\). When the overlap population was analyzed it showed no f-orbital overlap in the frontier orbitals and only small bonding contributions from the d-orbitals. The lack of covalent interactions with Am(5-2)\(_3^{3+}\) is a sign that selectivity between Am and Eu might not be
achieved using ligand 5-2. Unlike Am(5-2)$_3^{3+}$ the calculation of Cm(5-2)$_3^{3+}$ does show positive overlap populations with the f-orbitals. An example of the ligand to metal donation for the HOMO-36 of Cm(5-2)$_3^{3+}$ is shown in Figure 5-9. The composition of HOMO-36 is 36.7% f-orbital and 19.7% ligand. The similar compositions mean the energetics are favorable for the interaction and that ligand 5-2 may be selective for Cm over Eu and possibly other lathanides. As with ligand 5-1, there is no substantial back-bonding in ligand 5-2.

![Figure 5-9. Representation of ligand to metal donation in the HOMO-36 of Cm(5-2)$_3^{3+}$](image)

The MO of ligand 5-3 shows many similarities to ligand 5-2 because of the common benzimidazole but the triazole moiety displayed unique properties as well. The MO diagrams for Am and Cm complexed by ligand 5-3 are shown in Figure 5-10.
Figure 5-10. MO for Am(5-3)$_3$$^{3+}$ and Cm(5-3)$_3$$^{3+}$. Metal energy levels shifted by approximately 18 eV and ligand orbitals by -8 eV.
As discussed previously the HOMO is dominated by the benzimidazole in both structures. When moving down in energy by approximately 1 eV from the HOMO interactions begin to appear in the Am complex and likewise in the Cm structure at approximately 2 eV from the HOMO. The calculation of Am(5-3)$_3^{3+}$ showed very similar results to Am(5-2)$_3^{3+}$ in that there was no positive overlap population with the f-orbitals. Likewise, the calculation of Cm(5-3)$_3^{3+}$ showed positive f-orbital overlap similar to the calculation of Cm(5-2)$_3^{3+}$ thus giving evidence for ligand 5-3 to be selective for Cm over Eu and possibly other lanthanides. One of the main differences of Cm(5-3)$_3^{3+}$ from the other calculations is that it was the only calculation of have an absence of d-orbital contribution in the frontier orbitals. All of the calculations showed at least small percentages of positive overlap populations of the d-orbitals. It is not likely that the absence of d-orbitals would cause changes in selectivity since the d-orbital contributions are so low.

5.4 Conclusions

The DFT study presented in this chapter calculated three ligand structures with Eu, Am, and Cm. Because of convergence problems two of the Eu complexes were not presented. The geometry optimization results were compared amongst the calculations and experimental structural data for Cm(5-1)$_3^{3+}$. The Mulliken charges of each computed structure were calculated. The Mulliken charges show that harder donors like oxygen donate more electron density to the metal than the nitrogen donor groups. The Mulliken charges on Eu were higher than Am and Cm because the energetic matching of orbitals did not facilitate donation. According to the MO analysis the Cm charges were slightly lower than Am despite Am complexes having more ligand to metal donations. The discrepancy between charges was increased when using the softer
ligand 5-1 and 5-3 as compared to 5-2 with harder donors. Since the softer ligands cause a larger difference between Am and Cm which implies back-donation from Am might be used to explain the difference but the population analysis did not uncover any large degree of back-donation. The other option to explain the difference in Mulliken charges is that the ECP for Cm uses 36 valance electrons while Eu and Am use an ECP with 35 electrons, therefore, the different basis set causes the minor discrepancy.

The population analysis investigated the orbital environment to try and evaluate what aspect of ligand design facilitates selective separation of lanthanides from actinides. The bonding in each structure is mainly ionic with covalency generated by ligand – metal donation. The ligand to metal σ donation consists of filled ligand MO’s populating empty metal ns, (n-1)d and (n-2)f orbitals where n=7 for actinides and n=6 for lanthanides. To help summarize the results of the population analysis Table 5-5 shows the average contributions of all the positive overlap populations in the frontier orbitals for each calculation.

<table>
<thead>
<tr>
<th>Table 5-5. Orbital compositions (%) of bonding interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>f-orbital</td>
</tr>
<tr>
<td>Ligand (f)</td>
</tr>
<tr>
<td>d-orbital</td>
</tr>
<tr>
<td>Ligand (d)</td>
</tr>
</tbody>
</table>

Table 5-5 has a dashed line for contributions that did not appear in the calculation but may be present in less than 1% contributions. The overall bonding for the frontier orbitals of Eu with any ligand is that it only has minimal d-orbital composition with large differences in composition of the metal and the ligand. The difference in composition implies that the energetics of the orbitals do not match and that the covalency is less
significant. The calculations show the Eu complexes are mainly comprised of ionic bonds. For the Am calculations ligand 5-1 was the only ligand that showed positive overlap populations for the f-orbitals. All of the Am calculations had small amounts of d-orbital bonding but since they are small in composition the covalency of the d-orbitals is not significant. The ligand analogs 5-2 and 5-3 did not show positive overlap populations with the f-orbitals, hence, they are likely not to be selective for Am over Eu.

The Cm calculations all have positive overlap populations with the f-orbitals. The MO compositions of Cm(5-1)\textsuperscript{3+} are not as high or evenly matched between metal and ligand as the Am(5-1)\textsuperscript{3+} calculation but they are likely to be significant for covalent interactions. The Cm(5-2)\textsuperscript{3+} and Cm(5-3)\textsuperscript{3+} calculations have an average ligand composition lower than the average metal compositions (Table 5-5) which might be altered with modifications that effect the energetics of the ligands. The Cm(5-3)\textsuperscript{3+} complex was the only calculation to not have d-orbital contributions in the frontier orbitals. The triazole moiety is the likely culprit but the low contributions of d-orbitals in the other structures indicate that it will not significantly alter potential selectivity.

### 5.5 Computational Details

All density functional theory (DFT) calculations were performed with the Gaussian '03 package. Spin-unrestricted multiplicities were used to account for the formal f\textsuperscript{n} configurations for lanthanides and actinides. Each complex had its geometry optimized by using the B3LYP functional, the 6-31G\textsuperscript{*} basis set for C, H, N, and O atoms and a small-core relativistic effective core potential (RECP) for Eu, Am, and Cm. The RECP data was taken from the EMSL basis set library which used work from the Stuttgart and Dresden groups. Subsequent single point calculations were performed with the optimized geometries in order to format them for input into the AOMix program package.
Using the AOMix program package the molecular orbitals, natural charges and populations were analyzed. Spin contamination was closely monitored and was found to be close to ideal values.
CHAPTER 6
SUMMARY

In this project ligands that facilitate the selective partitioning of lanthanides and actinides were designed, synthesized, and analyzed. The objectives of the project were to develop a rational means of ligand design through semi-empirical calculations, synthesize the desired ligands, collect experimental data from the synthesized ligands, and use DFT to model variations of the ligands and evaluate any features that appear to contribute to the selectivity of binding actinides over lanthanides. The penultimate goal was to produce ligands that had experimental and theoretical evidence supporting the selective separation of actinides from the nuclear waste stream.

The semi-empirical (SE) calculation project tested several metal-ligand complexes for their twist angles in order to predict which complex would be closer to the ideal TTP geometry. When comparing the calculated structures to the experimental data obtained from the crystal structures, the calculations only showed small differences in twist angle. The method was unable to reproduce accurate bond lengths for structure 2-7 with the major deviation coming from the benzimidazole nitrogen donor. For accurate bond lengths, DFT methods would be preferred in place of SE calculations but DFT becomes impractical with a large selection of ligands due to the increased computational demand. In this project the SE calculations outperform ab initio methods in predictive ligand design when deciding between multiple candidates.

The synthetic project investigated several synthetic pathways for producing ligands containing benzimidazole-pyridyl moieties attached to a triphenoxymethane molecular platform. The ligands synthesized were chosen based on SE calculation data obtained from a library of possible ligands. The synthesis of the ligands initially relied on
previously synthesized molecules as intermediates for the novel nonadentate final products. Overall, three ligands were successfully synthesized of which the two amide linkage ligands, 3-22 and 3-26, showed extraction efficiency of approximately 5% for the lanthanides. The triazole functionalized ligand, 3-33, showed less than 1% extraction efficiency for the lanthanides. Since the goal of the project is the selective binding of actinides low extraction efficiency of lanthanides is actually desirable. Theoretically, if the ligand can covalently bind a lanthanide it can likely bind actinides due to their extended 5f orbitals. All three ligands synthesized show promising initial results for selectively binding actinides over lanthanides although actinide experimentation is needed for confirmation.

In the DFT computational project the donor groups of the synthesized molecules are compared to structure 5-1. The selectivity exhibited by 5-1 toward trivalent lanthanides and actinides is complex, but through theoretical investigations trends are starting to appear that may help fine-tune ligand design for optimal performance. Since actinides contain more diffuse f-orbitals than lanthanides covalency can be exploited to separate Am and Cm from Eu. The highest degree of covalency would occur with ligands that facilitate back-bonding in addition to ligand to metal donation. Back-bonding was found to be inadequate for the ligands used in this study mainly because the hardness of the metals. Since the Am(5-1)₃³⁺ calculation did not show back-bonding even though ligand 5-1 demonstrates selectivity, it appears that back-bonding is only an ideality and not necessary for selectivity. Utility of using benzimidazole type ligands seem applicable if the metal – ligand energetics can be matched up through modification of the ligand. By tracking the positive overlap populations in the
calculations it was determined that ligands 5-2 and 5-3 could be selective for Cm. The calculations presented show a promising extrapolation to the synthetic nonadentate analogs and gives some validity to what experimental data would be expected with actinides.

The objectives for this project included the guided design, synthesis, analysis, and theoretical evaluation of a series of ligands for the selective separation of actinides over lanthanides for use in nuclear waste reprocessing. The work presented herein was able to complete all objectives except experimentation with the actinides. The SE calculations proved to be a worthy predictor for ligand design. Synthesis and subsequent experimentation of ligands was performed while DFT calculations provided a systematic theoretical approach for predicting selectivity between the lanthanides and actinides.
APPENDIX A
NUCLEAR MAGNETIC RESONANCE SPECTRA OF SYNTHESIZED COMPOUNDS

The following Nuclear Magnetic Resonance (NMR) spectra are provided as an assessment of purity for the synthesized compounds discussed in Chapter 3. Only the NMR spectra of compounds that did not include elemental analysis are shown.

Figure A-1. NMR of 3-21
Figure A-2. NMR of 3-20

Figure A-3. NMR of 3-23
Figure A-4. NMR of 3-25

Figure A-5. NMR of 3-30
Figure A-6. NMR of 3-31b

Figure A-7. NMR of 3-14c
Figure A-8. NMR of 3-15c

Figure A-9. NMR of 3-33
Figure A-10. NMR of 3-22

Figure A-11. NMR of 3-26
References

(1) John, Moens; U.S. Nuclear Generation of Electricity; EIA Survey Form 906; http://www.eia.doe.gov/cneaf/nuclear/page/nuc_generation/gensum.html.


(3) Madic, C.; Bourges, J.; J.F., D. In International Conference on Accelerator-Driven Transmutation Technology and Applications;.


(13) Pradel, P. In In The organic waste treatment in UP3 — La Hague; Proc. 3rd Int. Conf. on Nuclear Fuel Reprocessing and Waste Management; , pp 1101-1106.


(58) *SHELXTL6* (**2000**). Bruker-AXS, Madison, Wisconsin, USA.


BIOGRAPHICAL SKETCH

Ivan Fabe Dempsey Hyatt was born in Greensboro, North Carolina in the year of 1982. For the next eighteen years he lived in the small rural town of Staley, North Carolina and attended Eastern Randolph High School. In 2001, he began his undergraduate studies at East Carolina University under the supervision of Professor Andrew Sargent. His research consisted of computationally modeling the reaction mechanism of rhodium catalyzed hydroacylation. In 2005, he graduated with a Bachelor of Science in chemistry and a Bachelor in Arts in mathematics and enrolled into the University of Florida as a Grinter Fellow. He initially joined the physical chemistry division but after his first year in graduate school he switched to the inorganic chemistry division under the supervision of Dr. Michael J. Scott. He completed the requirements for the degree of Doctor in Philosophy in December 2010.