AWARD NUMBER: DE-FC07-05ID14896
AWARDEE NAME: Washington State University

PROJECT TITLE: **Advanced Aqueous Separation Systems for Actinide Partitioning**

Report category: Scientific/Technical
Report name: Final Scientific/Technical Report, with DOE F 241.3
Frequency: Final
Period covered: 09/30/2007 thru 09/29/2011 Due date: 12/28/2011

Final Report: University Nuclear Energy Research Initiative Project number DE-FC07-05ID14896

Project Duration: 09/30/2007 thru 09/29/2011

Final report due: 12/28/2011

Project Title: Advanced Aqueous Separation Systems for Actinide Partitioning

Principle Investigator Kenneth L. Nash
Chemistry Department
Washington State University
PO Box 99164-4630
Pullman, WA 99164-4630
Phone: 509-335-2654, Fax: 509-335-8867, e mail: knash@wsu.edu
Congressional District: Fifth (5th) Congressional District, Washington

Collaborators Sue Clark, Chemistry Department, WSU
G. Patrick Meier, Chemistry Department, WSU
Spiro Alexandratos, Chemistry Department, Hunter College, CUNY
Robert T. Paine, Chemistry Department, University of New Mexico
Robert Hancock, Chemistry Department, University of North Carolina, Wilmington
Dale D. Ensor, Chemistry Department, Tennessee Technological University

National Lab Partners:
R. Scott Herbst, Idaho National Lab
Gregg J. Lumetta, Pacific Northwest National Lab
Linfeng Rao, Lawrence Berkeley National Lab

Table of Contents

Abstract:

One of the most challenging aspects of advanced processing of spent nuclear fuel is the need to isolate transuranium elements from fission product lanthanides. This project expanded the scope of earlier investigations of americium (Am) partitioning from the lanthanides with the synthesis of new separations materials and a centralized focus on radiochemical characterization of the separation systems that could be developed based on these new materials. The primary objective of this program was to explore alternative materials for actinide separations and to link the design of new reagents for actinide separations to characterizations based on actinide chemistry. In the predominant trivalent oxidation state, the chemistry of lanthanides overlaps substantially with that of the trivalent actinides and their mutual separation is quite challenging. The two aqueous processing strategies recognized to have the greatest probability of success are: 1) application of complexing agents containing ligand donor atoms that are softer than oxygen (e.g., N, S, Cl^-) and 2) changing the oxidation state of americium to IV, V, or VI to increase the inherent differences in the chemistries of the groups. Unfortunately, the softer donor atoms interact less strongly than does oxygen with the hard acid lanthanide and actinide cations (though slightly more so with actinides than lanthanides), and the upper oxidation states of Am are all moderately strong oxidants, hence unstable in typical media. Neither of these factors represents an insurmountable obstacle to developing a successful separation, but creative and perhaps unconventional approaches will be needed to overcome these limitations. The members of this consortium bring a synergistic blend of specialized expertise and facilities to these challenging tasks. Several of the university-based partners (Hunter College, University of New Mexico, University of North Carolina, Wilmington, and Washington State University) dedicated their efforts to providing new separations materials. The separation potential of these materials were assessed in radiochemistry laboratories at WSU and Tennessee Technological University. National lab scientists will contribute specialized facilities, dedicated staff with relevant expertise and internship opportunities for students. Feedback between the materials design experts and the actinide separations experts provided iterative approaches to developing new materials. The program was coordinated by researchers at WSU. During the four year duration of this program, a total of 34 open literature publications were completes, at least twice that number of technical presentations were made, a total of five new Ph.D. actinide separations chemistry experts have graduated to positions at U.S. DOE National labs, a similar number of postdoctoral research associates have refined their skills and assumed positions in the field in Europe and Japan and seven M.S. level chemists with specific experience in inorganic coordination chemistry have also entered the professional workforce. Though no new application-ready processes have been developed, the state of knowledge on lanthanide and actinide interactions with a variety of different classes of complexing agents has been advanced. At several junctures in this research, suggestions are made for further fruitful investigations.

Final Report: Nuclear Energy Research Initiative – Consortium (NERI-C)

Project number DE-FC07-05ID14896

Project Duration: 09/30/2007 thru 09/29/2011

Final report due: 12/28/2011

Project Title: Advanced Aqueous Separation Systems for Actinide Partitioning

Principal Investigator: Kenneth L. Nash, Chemistry Department, Washington State University, Pullman, WA 99164-4630

Accomplishments:

In addition to the scientific accomplishments to be discussed below, the following potentially long-term tangible impacts arising from this project can be enumerated:

- WSU student Dr. Mark D. Ogden completed a Ph.D. Dissertation entitled ***THE EFFECT OF STRUCTURAL HINDRANCE ON THE COMPLEXATION OF ACTINIDES AND LANTHANIDES BY LIGANDS CONTAINING SOFT NITROGEN DONORS,*** based on work conducted partially within the envelope of this project. After a time as a Postdoctoral Research Associate at the Idaho National Lab, Dr. Ogden is now a Staff Scientist at ANSTO Minerals in Australia.
- WSU student Dr. Jenifer C. Braley completed a Ph.D. Dissertation entitled ***THE USE OF ORGANOPHOSPHORUS EXTRACTANTS IN f-ELEMENT SEPARATIONS,*** based on work conducted in this project. Dr .Braley is now a Staff Scientist at the Pacific Northwest National Lab in the Chemical Separations Group.
- WSU student Dr. Travis S. Grimes completed a Ph.D. Dissertation entitled ***COORDINATION CHEMISTRY OF f-ELEMENTS IN THE TALSPEAK PROCESS*** based in part on research conducted with support from this project. Dr. Grimes is now a Postdoctoral Research Associate at the Idaho National Laboratory in the Chemical Separations Group.
- WSU student Dr. Melissa E. Freiderich completed a Ph.D. dissertation entitled ***FUNDAMENTAL STUDIES AND POTENTIAL APPLICATIONS OF CLOUD POINT EXTRACTION*** based on research conducted in part under the auspices of this Project. Dr. Freiderich is now a Postdoctoral Research Associate at the Oak Ridge National Lab in the Chemical Separations Group.
- One additional WSU student is nearing completion of a Ph.D. based on research conducted in part under the auspices of this investigation.
- One Postdoctoral Research Associate and two visiting scientists supported externally have also contributed to the success of this project
- At TTU, K. Fred York – 4 semesters of support, worked on the NOPO resin preparation and absorption studies. Fred decided not to finish his M.S. degree for personal reasons. He is now teaching High School Chemistry.
- At TTU, Matt Gott – 2 semesters of support, worked on the preparation of chromatographic materials for the separation of various radionuclides. Attended the summer school for

Nuclear Forensics and worked for Sue Clark at WSU. Finished his M.S. in 2010 and is currently working on Ph.D. in radiochemistry/nuclear medicine at Univ. of Missouri, Columbia.

- At UNC-W this research project involved twelve MS graduate students, seven of whom have graduated, as well as two undergraduate students: **MS students:** David Buist, Daniel Kissel, Adam Brenneman, Neil J. Williams, Amy Mroz, Danielle Merrill, T. Neal Triplett, Daniel G. Ballance, Francheska Vasquez, Galen C. Littman, Ryan Tillman, Ashley N. Carolan. **Undergraduate students:** Joanna M. Hamilton, Ashley E. Hames.

Publications:

1) M. Nilsson, K. L. Nash, Trans-lanthanide extraction studies in the TALSPEAK system: investigatinig the effect of acidity and temperature, *Solvent Extraction & Ion Exchange* 27(3) 354-377 (2009).
2) Zhang, Z., Helms, G., Nash, K. L., Clark, S. B. Uranyl photochemistry: decarboxylation of gluconic acid, Radiochimica Acta (2010), 98(9-11), 589-594.
3) Grimes, Travis S., Nilsson, Mikael A., Nash, Kenneth L. Lactic acid partitioning in TALSPEAK extraction systems, Separation Science and Technology (2010), 45(12-13), 1725-1732.
4) Ogden, Mark D., Hoch, Cortney L., Sinkov, Serguei I., Meier, G. Patrick, Lumetta, Gregg J., Nash, Kenneth L. Complexation studies of bidentate heterocyclic n-donor ligands with Nd(III) and Am(III)_, Journal of Solution Chemistry (2011), 40(11), 1874-1888.
5) Braley, Jenifer C.; Grimes, Travis S.; Nash, Kenneth L. _Alternatives to HDEHP and DTPA for simplified TALSPEAK separations,_Industrial & Engineering Chemistry Research, ACS ASAP. (2011)
6) Brigham, Derek, Badajoz, Coralie, Cote, Gerard, Nash, Kenneth L. Extraction of trivalent lanthanides and americium by tri-n-octylphosphine oxide from ammonium thiocyanate media Solvent Extraction and Ion Exchange (2011), 29(2), 270-291.
7) J. Sulakova, R.T. Paine, M. Chakravarty, K.L. Nash, Extraction of lanthanide and actinide nitrate and thiocyanate salts by 2,6-bis[(bis(2- n-octyl)phosphino)methyl]pyridine n,p,p`-trioxide in toluene, Submitted for publication, Separation Science and Technology, November, 2011
8) K.L. Nash, T.S. Grimes, M. Nilsson Fundamental studies of TALSPEAK chemistry for trivalent actinide – Lanthanide separations in advanced nuclear fuel cycles in Global 2009 Conference, September 6-11, 2009, Paris, France, pp. 1099-1106.
9) Nash, K. L., Braley, J. C., Chemistry of radioactive materials in the nuclear fuel cycle In Woodhead Publishing Series in Energy (2011), 2 (Advanced Separation Techniques for Nuclear Fuel Reprocessing and Radioactive Waste Treatment), pp, 3-22.
10) Kenneth L. Nash, Cecile Marie, Mark D. Ogden and Derek Brigham Soft-donor extractants vs. Aqueous complexants in trivalent lanthanide/actinide separations in 19th International Solvent Extraction Conference Proceedings, October 3-7, 2011, Santiago, Chile, Ch 3, paper 77.

11) Kenneth L. Nash, Mikael Nilsson, Travis Grimes, Jenifer Braley, Kazuyoshi Uruga and Cecile Marie, Complex interactions in solvent extraction—biphasic speciation in the TALSPEAK process 19th International Solvent Extraction Conference Proceedings, October 3-7, 2011, Santiago, Chile, Ch 3, paper 85.

12) Jenifer C. Braley, Daniel McAlister, E. Philip Horwitz, Kenneth Nash, Explorations of TALSPEAK chemistry in extraction chromatography: Comparisons of TTHA with DTPA and HDEHP with [HEH]EHP, Submitted for publication, Solvent Extraction & Ion Exchange 2011

13) Travis S. Grimes and Kenneth L. Nash Acid dissociation and rare earth stability constants for DTPA at 2.0 M ionic strength in preparation for submission, Thermochimica Acta

14) Asako Shimada, Jana Sulakova, Kenneth L Nash, Yijia Yang, Spiro Alexandratos Study on the extraction properties of Eu, Th, U and Am with tetramethylmalonamide resin and column chromatographic separation in preparation for submission to Separation Science and Technology 2011.

15) Mark D. Ogden, Serguei I. Sinkov, G. Patrick Meier, Gregg J. Lumetta, Kenneth L. Nash, Complexation of N_4-Tetradentate Ligands with Nd(III) and Am(III) Journal of Solution Chemistry, in press 2011

16) Mark D. Ogden, Sergey I. Sinkov, Mikael Nilson, Gregg J. Lumetta, Robert D. Hancock, and Kenneth L. Nash, “Complexation of Am(III) and Nd(III) by 1,10-Phenanthroline-2,9-diacetic acid”, *J. Soln. Chem*, in press.

17) Cortney L. Hoch, Matthias Zeller, G. Patrick Meier, Kenneth L. Nash, First row transition metal complexes with 2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine: crystal structures and spectroscopic properties, in preparation for publication in Inorganica Chimica Acta, 2011.

18) Neil J. Williams, Nolan E. Dean, Donald G. VanDerveer, Robert C. Luckay and Robert D. Hancock, **“**Strong Metal Ion Size-based Selectivity of the Highly Preorganized ligand PDA (1,10-phenanthroline-2,9-dicarboxylic acid) with Trivalent Metal Ions. A Crystallographic, Fluorometric, and Thermodynamic Study”. *Inorg. Chem*., Vol. 48, pp. 7853-7863 (**2009**).

19) Raymond T. Gephart III, Neil J. Williams, Joseph H. Reibenspies, Alvaro S. de Sousa, and Robert D. Hancock, “Complexation of metal ions of higher charge by the highly preorganized ligand 2,9-bis(hydroxy-methyl)-1,10-phenanthroline. A crystallographic and thermodynamic study”. *Inorg. Chem.* Vol. 48, pp. 8201-8209 (**2009**).

20) David Buist, Neil J. Williams, Joseph H. Reibenspies, and Robert D. Hancock, “Control of metal ion size-based selectivity through chelate ring geometry. Metal ion complexing properties of bis-imidazole”, *Inorg. Chem.*, Vol. 49, pp 5033-5039 (**2010**).

21) Neil J. Williams, Daniel G. Ballance, Joseph H. Reibenspies, and Robert D. Hancock, “The complexes of the highly preorganized ligand PDALC (2,9-bis(hydroxymethyl)-1,10-phenanthroline) with trivalent Lanthanides. A Thermodynamic and Crystallographic Study.” *Inorg. Chim. Acta,* Vol. 363, pp. 3694–3699 (**2010**).

22) Sylvie Pailloux, Cornel Edicome Shirima, Karen Ann Smith, Eileen N. Duesler, Robert T. Paine, Neil J. Williams, and Robert D. Hancock, "Synthesis and Reactivity of (Benzoxazol-2-ylmethyl)phosphonic Acid**"**, *Inorg. Chem.,* Vol. 49, pp. 9369-9379 (**2010**).

23) Danielle Merrill and Robert D. Hancock, "Metal Ion Selectivities of the Highly preorganized tetradentate ligand 1,10-phenanthroline-2,9-dicarboxamide with Lanthanide(III) ions and some Actinide ions", *Radiochim. Acta,* Vol. 99, pp. 161-166 (**2011**).

24) Joanna M. Hamilton, Michael J. Anhorn, Karen A. Oscarson, Joseph H. Reibenspies, and Robert D. Hancock, "Complexation of Metal Ions, including Alkali Earth and Lanthanide(III) Ions, in Aqueous Solution by the Ligand Terpy (2,2',6',2"-terpyridyl)", *Inorg. Chem*., Vol. 50(7), pp. 2764-2770 (**2011**).

25) Joanna M. Hamilton, Jason R. Whitehead, Neil J. Williams, Maya El Ojaimi , Randolph P. Thummel, and Robert D. Hancock, "Metal Ion Complexing Properties of Dipyridoacridine, a Highly Preorganized Tridentate Homologue of 1,10-Phenanthroline", *Inorg. Chem*., Vol. 50(8), 3785-3790 (**2011**).

26) Lindsay L. Boone, Amy E. Mroz, Donald G. VanDerveer, and Robert D. Hancock, "Metal Ion Coordinating Properties of the highly preorganized tetradentate ligand 1,10-phenanthroline-2,9-dicarboxaldehyde-2,9-dioxime. *Eur. J. Inorg. Chem*., Vol. 99, pp. 161-166 (**2011**).

27) Danielle Merrill, James M. Harrington, Hee-Seung Lee, and Robert D. Hancock, "Unusual Metal Ion Selectivities of the Highly Preorganized Tetradentrate Ligand 1,10-phenanthroline-2,9-dicarboxamide. A Thermodynamic and Fluorescence Study." *Inorg. Chem.*, Vol. 50, pp. 8348-8355 (**2011**).

28) Ashley N. Carolan, Amy E. Mroz, Maya El Ojaimi, Donald G. VanDerveer, Randolph P. Thummel, and Robert D. Hancock, "Metal Ion complexing properties of 2,2'-pyridyl-1,10-phenanthroline, a more Preorganized analogue of Terpyridyl. A Crystallographic, Fluorescence, and Thermodynamic study." *Inorg. Chem.* submitted.

29) Neil J. Williams, Danielle Merrill, Daniel Ballance, and Robert D. Hancock, 'The stability of complexes of trivalent Lanthanides with the highly preorganized ligand PDA (1,10-phenanthroline-2,9-dicarboxylic acid)", *Radiochim. Acta*, to be submitted

30) Ashley N. Carolan, Gregory M. Cockrell, Neil J. Williams, Gang Zhang, Donald G. VanDerveer, Randolph P. Thummel, and Robert D. Hancock, "Affinity of the Highly Preorganized Tetradentate Ligand 2,9-Di-(pyrid-2-yl)-1,10-phenanthroline for Metal ions in Aqueous Solution, including Lanthanide(III) ions and Thorium(IV). A Thermodynamic and Crystallographic Study." *Inorg. Chem.* to be submitted.

31) Ashley N. Carolan and Robert D. Hancock, "The affinity of Lanthanide(III) ions for Nitrogen donor ligands of the polypyridyl type" *Radiochim. Acta*, to be submitted.

32) G. C. Littmann, I. V. Nikolayenko, and Robert D. Hancock. "The Metal Ion selectivity patterns induced by the triazine group of tripyridyl triazine (TPTZ). A thermodynamic and DFT study", *Inorg. Chem*. to be submitted.

33) Robert D. Hancock and Igor V. Nikolayenko "Do Non-bonded H--H Interactions in Phenanthrene Stabilize it Relative to Anthracene? A Possible Resolution to this Question, and its Implications for Ligands such as 2,2'-Bipyridyl." *Inorg. Chem.*, to be submitted.

34) Daniel G. Ballance, and Robert D. Hancock, "Metal ion complexing properties of Quaterpy (2,2':6',2' ':6' ',2' ''-quaterpyridine) with metal ions in solution. A Thermodynamic and Fluorescence study." *Polyhedron*, to be submitted.

Presentations: Numerous at the following meetings

American Chemical Society National meetings 2009-2011
American Chemical Society Regional meetings 2009-2011
Actinide Separations Conferences, 2009, 2010, 2011
Separation Science and Technology for Energy Applications 2009, 2011
Global 2009
Global 2011
International Solvent Extraction Conference 2011, Santiago, Chile
DOE-NE Fuel Cycle Research and Development information exchange meetings
Journee de Science de Marcoule, France, 2011

Introduction: Ligand design challenges in actinide process chemistry

Despite decades of research, the selective separation of the minor actinides Am and Cm from fission product lanthanides (predominantly La-Dy) with decontamination factors of $> 10^4$ remains an elusive target. However, several new extractant systems have been identified and characterized during the past decade. Some of these systems promise to yield such separation performance. In addition, there are several notable examples of successful approaches to trivalent actinide/lanthanide separations that have been brought forward and in some cases extensively characterized though never deployed in spent fuel processing [1]. The most important among these earlier studies involve ternary or quaternary amine extractants contacted with concentrated lithium chloride solutions (the TRAMEX process [2]) and aminopolycarboxylic acid complexants used in combination with acidic organophosphorus extractants (the TALSPEAK process [3]). The basic principals of these processes are the foundation of ongoing investigations, as in the SETFICS process [4-6] proposed by Japanese scientists. TRAMEX is an essential component of the production of transplutonium actinides for research application and the preparation of ^{252}Cf neutron irradiation sources carried out at the High Flux Isotope Reactor (HFIR) and Radiological Engineering Development Center (REDC) at Oak Ridge National Lab [2].

All successful aqueous processing options for group separation of fission product lanthanides from trivalent actinides have relied on the applications of ligand donor atoms “softer” than oxygen (N, S, Cl^-) [1], following the lead of the earliest reports of this effect from Diamond et al.[7]. The slightly greater strength of the complexation of trivalent actinides with these donor atoms than that exhibited by the corresponding lanthanides (believed to be derived from a greater covalent contribution to the bonding in the actinide systems) provides adequate thermodynamic driving force for the separation to occur. Though the effects are difficult to quantify, an apparent correlation exists between the numbers of soft donor atoms that can be coordinated to the trivalent cation and the separation factors. However, the appearance of hard donor oxygen atoms (resulting from degradation of the soft-donor extractant molecule) has been shown to significantly degrade the effectiveness of many soft donor separation systems [8].

Various protocols based on the application of soft donor ligands containing nitrogenous (amines, pyridines, imidazole, triazine,…) functional groups have been developed recently[9] that achieve single stage mutual separation factors of 10 to 100. Am/Eu separation factors of more than 5000 have been reported for selected dithiophosphinic acid extractants [10, 11]. Other derivatives of this general class of extractant molecules bearing aromatic substituents sacrifice some separation efficiency for a higher degree of radiation stability and the ability to conduct separations operations in more acidic solutions [12-14]. The success of separation processes based on either of these classes of reagents in pilot scale demonstrations has been limited by extractant purity problems and by unacceptable radiation or hydrolytic stability of the reagents [15-17]. It can be inferred from this observation that reagent stability is as important an aspect of ligand design for nuclear fuels processing as is the configuration of the cation binding site or control of ligand/complex solubility in the extractant phase.

For spent fuel separations applications, the design of chelating agents and the development of processes for their use must emphasize equally complex stability (derived from the creation of a binding site compatible with the structural requirements of the target metal ion), organic phase compatibility (derived from adjustment of the nature and positioning of the attached alkyl groups) and radiation/hydrolysis resistance. It is possible to build radiation tolerance into extractant molecules, though this may come at the expense of either or both of the other two elements of ligand design. Rather than focusing on a large scale program to develop new extractant formulations (which would require substantially greater amounts of effort and a longer time frame than was available in this program), this project emphasized ligand binding sites known to distinguish between trivalent lanthanides and actinides. The initial objectives of this program included a significant emphasis on radiation stability studies; developments in the science and in the larger Global Nuclear Energy Program (GNEP) and Advanced Fuel Cycle Initiative (AFCI) led to a shift in emphasis from some aspects of the original scope of this work. The two primary tasks completed in this investigation focused on the preparation and characterization of tetraaza complexing agents and fundamental studies of the TALSPEAK Process. Scoping experiments were done on the planned work on radiation stability of the complexants, but ultimately the bulk of this work was postponed due to the perception that focusing on nitrogen-based ligand design and TALSPEAK studies were higher priority activities.

Project Objectives: In earlier research on the subject of minor actinide separations (funded within the U-NERI program), the PI's research team: investigated in some detail the separations chemistry of the TALSPEAK process, including thermodynamic and kinetic features of the reactions that define the performance envelope of the process; developed a series of new polyaza complexants potentially suited to the mutual partitioning of Am and Cm from lanthanides; prepared critical reviews of the TALSPEAK process and a complementary experimental investigation of features of TALSPEAK; begun an examination of the separation potential of unconventional systems including those based on cloud point extraction and ionic liquids; examined selected features of solid-liquid partitioning of Am from lanthanides using non-standard aqueous media. Within that program, work completed by a WSU student working at the Idaho National Lab produced two different solid/liquid separation methods based on oxidation of Am to the penta- or hexavalent oxidation states.

In this (NERI-C) continuation of the prior work, the scope of the studies was modified and broadened with the addition of external collaborators bringing complementary expertise to the conduct of this investigation of actinide separation science. The collaborating investigators in this extension of the previous study bring specific expertise in:

1) Soft donor ligand design, characterization and synthesis (Hancock, UNC-W),

2) The ability to functionalize polymeric materials that will reduce reagent phase partitioning issues in several extractant systems (Alexandratos, CUNY),

3) The design of organophosphorus extractants based on pyridine derivatives, likely to exhibit improved radiation stability in harsh environments (Paine, UNM),

4) Enhanced in-house organic synthesis capabilities (Meier, WSU) for the creation of relevant structurally hindered aliphatic complexant molecules differing from the Hancock ligands,

5) Expansion of radiochemistry support function with the addition of Ensor at Tennessee Technological University to contribute to the assessment of new chromatographic materials.

The collaborators in this project were initially integrated vertically, that is with a focus on direct communication of new materials from the partner labs to WSU. As the project progressed, horizontal cooperation between the partners was encouraged. The roster of National Laboratory partnering institutions was expanded from the prior study (adding L. F. Rao from LNBL to R. S.

Herbst at INL and G. J. Lumetta at PNNL) to bring the specific expertise of those investigators into the educational experience, and to provide ready access to facilities and capabilities not available at the partner universities, in particular, larger quantities of long–lived isotopes of Am and Cm, the facilities to safely handle them and ready access to DOE user facilities. Several WSU students completed some portion of their Ph.D. research at each of the three institutions.

At the initiation of this program we established an initial network of predominantly (or exclusively) undergraduate institutions whose students and faculties were to be invited to WSU for a one-week tutorial on actinide chemistry, nuclear science, chemical separations and the nuclear fuel cycle. With unexpectedly fruitful entry of new graduate students into our program, this particular feature of the program was shelved due to laboratory space and budgetary pressures. We plan to revisit this possibility at a later date. This decision allowed a deeper focus on advancing the science. Increased enrollment in the WSU graduate radiochemistry program continues without the external stimulus that this undergraduate institution strategy intended. The objective of providing training, orientation and educational materials to faculty members who will then be able to incorporate this science into the curriculum at their home institutions remains a worthy objective, but it was not pursued in this project.

The overall organization of this program featured a central role for the actinide - radiochemistry program at WSU for primary evaluation of the actinide coordination chemistry and separations potential of the new materials that were created in the consortium partner laboratories. The complementary radiotracer work conducted in Ensor's lab focused on the assessment of the separations performance of chromatographic materials emphasizing the application of radioanalytical chemistry techniques. One tangible result of this program was the successful completion of four Ph.D. dissertations, with a fifth Ph.D. student continuing toward completion of her degree supported by other funding. The graduates have accepted either Postdoctoral Research or permanent staff positions at DOE labs – their current work focuses on applications of radiochemistry in fuel-cycle relevant research.

References part 1.

1) Nash., K.L., *A Review of the Basic Chemistry and Recent Developments in Trivalent f-Element Separations.* Solvent Extr. Ion Exch., 1993. **11**: 729-768.

2) Bond, W.D. and R.E. Leuze, *Removal of Americium and Curium from High-Level Wastes*, in *Actinide Separations*, J.D. Navratil and W.W. Schulz, Editors. 1980, American Chemical Society: Washington, D. C. p. 441.

3) Weaver, B. and F.A. Kappelmann, Journal Inorg. Nucl. Chem., 1968. **30**: 263.

4) Koma, Y., M. Watanabe, S. Nemoto, and Y. Tanaka, *A counter current experiment for the separation of trivalent actinides and lanthanides by the SETFICS process.* Solvent Extr. Ion Exch., 1998. **16**(6): 1357-1367.

5) Ozawa, M., Y. Koma, K. Nomura, and Y. Tanaka, *Separation of actinides and fission products in high-level liquid wastes by the improved TRUEX process.* J. Alloys and Compounds, 1998. **271-273**: 538-543.

6) Morita, Y., S. Tachimori, Y. Koma, and A. Aoshima, *Studies on actinide separation process from high-level liquid waste.* 2002, Department of Materials Science, Tokai Research Establishment, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, Japan. p. i-iv, 1-20.

7) Diamond, R.M., J. K. Street, and G.T. Seaborg, *An ion-exchange study of possible hybridized 5f bonding in the actinides.* J. Am. Chem. Soc., 1954. **76**: 1461.

8) Modolo, G. and R. Odoj, *Influence of the purity and irradiation stability of Cyanex 301 on the separation of trivalent actinides from lanthanides by solvent extraction.* J. Radioanalytical Nucl. Chem., 1998. **228**(1-2): 83-88.

9) Kolarik, Z., U. Mullich, and F. Gassner, *Extraction of Am(III)and Eu(III) nitrates by 2,6-di-(5,6-dipropyl-1,2,4-triazin-3-yl) pyridines.* Solvent Extr. Ion Exch., 1999. **17**: 1155.

10) Tian, G., Y. Zhu, and J. Xu, Solvent Extr. Ion Exch., 2001. **19**: 993-1015.

11) Chen, J., G. Tian, R. Jiao, and Y. Zhu, *A hot test for separating americium from fission product lanthanides by purified Cyanex 301 extraction in centrifugal contactors.* J. of Nucl. Science Technol. 2002(Suppl. 3): 325-327.

Summary of the Work Completed:

- Hancock completed at UNC-W the synthesis of several derivatives of 2,9-substituted phenanthroline and completed detailed characterization studies of these compounds in aqueous media. Spectrophotometric titrations of phenanthroline-2,9-dicarboxylic acid (PDA) establish the relative complexing strength for this compound. As a cation receptor, the PDA bonding pocket is well suited to actinide bonding. In separations testing, the solubility remained too low to enable the development of viable separations applications of PDA as a holdback reagent for solvent extraction applications, though An(III)/Ln(III) selectivity indicators were positive.
- A sample of an alcoholic analog to PDA (PDAlc) in separation testing proved too weak for appreciable partitioning of lanthanides or actinides as a stand alone extractant. When combined with the cation exchanging extraction agent, 1-bromodecanoic acid, the extraction results indicated some participation of PDAlc were consistent with the formation of an ester between the two extractant molecules. This reagent likewise proved unsuitable for the intended application
- A third option for improving solubility of PDA that was explored was the creation amides. The Hancock group prepared samples of symmetrical di-octyl(diamide) PDA derivatives, but this adjustment also failed to produce a reagent with adequate organic phase solubility. Further adjustments to prepare a tetraoctyl diamide proved difficult to synthesize, though this species remains a worthy target for study.
- The Paine group attempted preparation of the tetra(2-ethyl)hexyl derivative of the TEHNOPOPO extractant to support a more thorough examination of the actinide extraction properties of this derivative that had been the subject of an earlier examination. Due to problems with the purity of starting materials, this synthesis produced material that was difficult to purify.
- With the TEHNOPOPO removed from further consideration, the project was moved forward with the analogous tetraoctyl derivative which was prepared in good yield and high purity. Though there were some solubility restrictions imposed by the substitution of octyl for 2-ethyl(hexyl) groups, a complete study of actinide uptake from nitrate and thiocyanate media was completed and a manuscript submitted for publication.
- Discussions were also conducted between Paine, Alexandratos and the PI regarding the appropriate functionalization of the NOPOPO cation receptor to enable its immobilization of a polystyrene backbone to allow development of the chromatographic sorbent option for use of this class of cation receptors. A suitable pathway to creating this material was not established.
- The Alexandratos group first prepared samples of a collection of three different neutral phosphate based polystyrene resin materials for actinide nitrate uptake studies, featuring mainly uranium. A complex series of characterization experiments were conducted to characterize the cation uptake performance on these materials. Some experiments indicated a possibility of ester hydrolysis in the phosphate group.
- The Alexandratos group also prepared significant quantities of polystyrene resin beads functionalized with dimethyl malonamide groups. Actinide and lanthanide uptake characteristics of the DMMA resins were investigated in detail. Promising results were

seen for all species of interest. Continuing work on this system is planned, for which funding will be sought.

- The Meier group developed synthesis protocols for applying Sharpless' Click chemistry to the preparation of pyridine and bipyridine triazole ligands. Bidentate (N2), tridentate (N3) and tetradentate (N4) varieties of ligands were prepared. Solvent extraction studies provided occasional useful insights, but no clear conclusions on the value of these reagents in lanthanide-actinide separations. Crystals of several transition metal complexes were grown and characterized structurally, at a minimum confirming the synthesis of the proposed extractant molecules. Studies of the thermal and hydrolytic stability of the pyridine bis-triazole ligands were done.

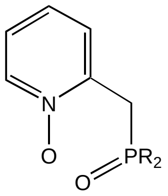
Technical Progress. In the following section, project plans and results of the new materials creation sections of this project are discussed organized according to separate subtasks.

Subtask 1. Organophosphorus and Organoamide Extractant Development

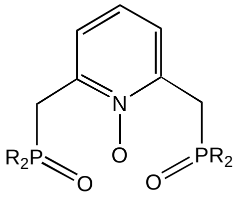
R. T. Paine, University of New Mexico

Background: The Paine group has focused attention on the design and development of ligands that would potentially serve as selective solvent extraction reagents for f-block ions in contact with highly acidic solutions typically encountered in fuel reprocessing. For this application, ligand targets need to be not only selective in their recognition of one or a small group of ions, but they must also display long term stability toward harsh process conditions (strong mineral acid, high radiation fields and the presence of powerful oxidants), as well as good solubility in hydrocarbon diluents. In addition, they must display rapid metal-ligand binding and release kinetics, as well as favorable phase transfer performance without third-phase formation. Finally, because of the scales implicit in spent fuel reprocessing, an "ideal ligand" that meets target process performance goals must also be relatively cheap and easy to make.

Based on knowledge of cation-solvating solvent extraction reagents, the Paine group has sought to develop new classes of multifunctional ligands having combinations of two or more oxygen donor groups assembled on an organic backbone that facilitates chelating interactions with transuranium element cations. For example, with DOE-Basic Energy Sciences support, they have discovered that the combination of P=O and pyridine N-oxide donors on the organic frameworks shown in **1** (NOPO) and **2** (NOPOPO) provide for strong bidentate and tridentate chelate interactions on f-element cations. Actinide extraction properties have been reported indicating that these reagents might exhibit actinide partitioning performance comparable to that of the CMPO extractant family. The multi-functional nature of the extractant is central to this behavior. These results led to the initiation of a DOE U-NERI program [P.I. Paine; co-P.I.s Nash (WSU) and Herbst (INL)] in 2006 that focused on the further practical development of the NOPO and NOPOPO ligands for use in minor actinide/lanthanide fission product separations. As part of this ongoing interaction, work has also been done on water-soluble (phosphonic acid) structural analogs of **1** and **2.** This ligand architecture thus can be deployed in a variety of different processing applications.



1



2

In this program the synthesis of an aliphatic hydrocarbon-soluble derivative of a variety of NOPOPO derivatives was proposed, including an example that might be suited to immobilization on a polymeric resin. These ligands are all variants on the successful NOPO/NOPOPO themes represented by **1** and **2.** Due to the inherent stability of these frameworks to acid and oxidation and the expectation of rapid phase transfer kinetics, it was expected that these ligands would be most useful for extractions of the high oxidation state americium species [Am(IV), Am(VI)]. In addition, functionalization of the pyridine ring at the 4-position is possible. Ultimately, the 4-position functionalization of pyridine derivatives was in part reserved to the polymer functionalization section of this project and in part conducted under a parallel project. This adjustment of direction enabled a more detailed focus on the preparation and characterization of tetra ethyl(hexyl) (TEHNOPOPO) and tetra octyl (TONOPOPO) derivatives of NOPOPO for more complete characterization of actinide uptake performance. Interactions between the UNM group and INL focused on studies of radiation stability of the NOPOPO ligands. Proposed work on di- and tetra-amides analogs of NOPO and NOPOPO proved more challenging synthesis problems than anticipated than the potential payoff of such species merited, so that portion of the planned effort was shelved for consideration at a later date. Similarly, possible extended studies of thiolated analogs of NOPOPO were abandoned as the initial samples prepared demonstrated minimal extraction efficiency. Samples of NOPOPO extractants were provided to the Tennessee Tech group for studies of extraction chromatography applications.

Sub-Task 1 Scope of Work: The research effort at the University of New Mexico (UNM) was directed by Prof. R.T. Paine in the Chemistry Department. His group provided a focused effort to develop new phosphine oxide and amide-based organic ligands designed to have favorable chelation properties for trivalent *f*-block ions that would facilitate practical, selective actinide ion partitioning. Small, laboratory-scale syntheses for target ligands were developed and optimized, purification protocols were devised, the ligands were characterized spectroscopically and survey lanthanide(III) coordination chemistry was completed. The program identified several candidates that would be appropriate for future solvent extraction studies and that activity will be continued if follow-on funding can be obtained.

Sub-Task 1 Final Report: The justification for this sub-task originated from prior synthetic development of NOPO (**1**) and NOPOPO (**2**) ligands with R = aryl (Ar) and alkoxide (RO) substituent groups at UNM [1-4]. Initial evaluation of the solvent extraction performance of **1** and **2** with R = Ph using chlorocarbon solvents was completed under our DoE-BES program at UNM [5, 6]. That work showed that **1** and **2** (R = Ph) behaved much like the well studied CMP and CMPO ligands extracting trivalent lanthanides and actinides effectively at high HNO_3 and HCl concentrations. Subsequent extraction studies of hydrocarbon soluble derivatives of **1** and **2** (R = 2-EtHx) [7] encouraged additional extraction characterization as well as acid and radiation stability testing that was accomplished under a DoE-U-NERI project [8].

In the current project, a rather expansive exploration of new but related ligand architectures was examined. This investigation was expected to provide a second generation of NOPO and NOPOPO-like ligands engineered to produce favorable chelation fields but potentially with greater selectivity for trivalent actinides over trivalent lanthanide fission product ions and perhaps selectivity for Am/Cm partitioning. Two general approaches were explored. One involved architectural modification of the base NOPO and NOPOPO platforms by inclusion of additional pyridine, pyridine N-oxide and phosphine oxide donors that could potentially provide increased ligand denticity and coordination complex stability. The second approach involved partial donor group “softening” through replacement of one hard donor site with a softer donor or by addition of a soft donor to the base NOPO and NOPOPO structures. Alternate donor fragments for this study included pyridine, organoamides, thiophosphoryl and dithiophosphinic acid. Example ligands that have been successfully obtained include those shown in structures **3-16**. The development of this collection of ligands required a large synthetic effort that benefitted greatly from synergy with our DoE-BES program at UNM in which syntheses and coordination chemistry for related ligands with R = (Ar) and (RO) were being pursued. Unfortunately, ligands with aryl or alkoxy substituents are not particularly soluble in alkane diluents used in practical solvent extractions. Therefore, the effort in this project involved derivation of ligands with alkyl substituents that are typically much more alkane soluble but also more difficult to make and purify. In several cases quite different synthetic approaches were required in order to obtain the targets with good yield and purity. Some specific comments regarding the progress made and potential of these ligands for future practical separation studies are summarized below.

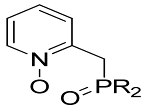
NOPO and NOPOPO Platform Derivatives

Ligand 2. It was discovered during our previous U-NERI project that, somewhat unexpectedly, the ligands **2** with R = n-octyl and dodecyl, are easier to purify than the 2-EtHx derivative that was used initially to do hydrocarbon solvent-based extractions [6]. Hence, optimized syntheses for these two molecules were developed in the early stages of the current project and large (> 5 g) samples were prepared for further solution thermodynamic analyses and extraction characterization in Prof. Nash's group. The work with **2** (R = n-octyl) will continue beyond the close of the current project.

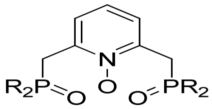
Ligands 3-8. These ligands were developed as direct extensions of **1** and **2**. The intent was to modify the coordination fields exerted by **1** and **2** by placement of one or more additional pyridine, pyridine N-oxide and/or phosphine oxide fragments on the base pyridin-2-yl and pyridin-2, 6-diyl backbones. Such substitutions would be expected to strengthen the coordination interaction by increasing the ligand denticity, soften or harden the coordination field depending upon the soft/hard character of the third donor and enhance the hydrophobicity of the extracted complex. These goals were achieved, at least in part, with the synthesis and complete characterization of examples of **4-7** (R = Ar). Each ligand forms very stable Ln(III) complexes, and infrared spectroscopy suggests that the ligands are forming tridentate chelate structures. Unfortunately, at this point, X-ray quality crystals of the complexes have not been obtained so the precise nature of the chelate interactions has not been verified. Nonetheless, this encouraged development of analogs of **4-7** with n-octyl groups. As expected, these ligands have improved hydrocarbon solvent solubility and the extraction performance could be gainfully evaluated at sometime in the future. Attempts were also made to place another donor group arm on the trifunctional pyridin-2-yl carbon atom of **4-7**. The target tetrafunctional ligands, if fully chelating could produce novel, highly hydrophobic coordination environments. At the close of the project only one of these tetrafunctional ligands has been fully characterized, namely 4-$CH_2C_5H_4N$. Attempts to N-oxidize the molecule have not yet been fruitful. Work will continue on these systems as additional funding is secured. A manuscript describing the work to date is under preparation.

CMPO Modified Platform Ligands

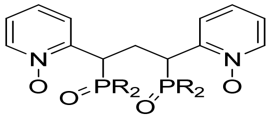
Ligands 9 and 10. These molecules can be considered to be CMP or CMPO-like ligands that have been modified at the central methylene carbon with a pyridin-2-yl fragment. In earlier work we had developed routes to placing alkylphosphine oxide, alkylamide and alkylester functional arms on the methylene carbon atom [9-15] and the substitution of the pyridine-2-yl was a logical if not straight forward extension for obtaining an enhanced chelating ligand. The syntheses of **9** and **10** with R = Ph and R' =Et were accomplished as well as the related molecules with the pyridine fragment not oxidized. The coordination chemistry of the ligands on Ln(III) ions was explored and found to give a variety of complexes. Most notably, the crystal structure determination for one of these, [Pr(**10**)(NO_3)$_3$], shows **10** acting as a tetradentate NOPOPOCO chelate. The second amide carbonyl is not bound to the central Pr(III). This finding suggests further ligand and complexation modifications that may lead to an unprecedented pentadentate coordination environment. Not surprisingly, **9** and **10** with R = Ph and R' = Et are not significantly soluble in hydrocarbon solvents. Hence, advancement of these ligands as extractants requires development of "greasy" analogs and this has been completed by synthesis of R = n-octyl derivatives that have limited solubility.



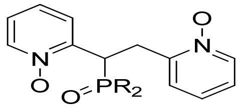
1



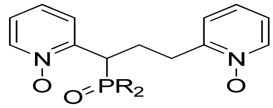
2



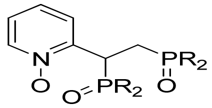
3



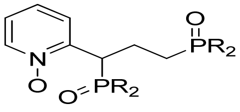
4



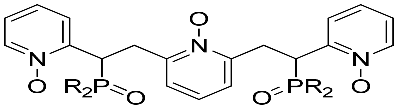
5



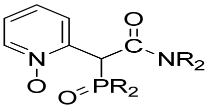
6



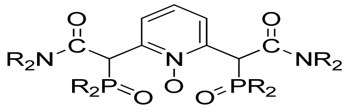
7



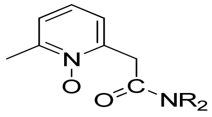
8



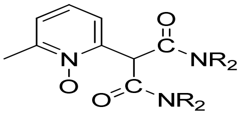
9



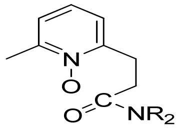
10



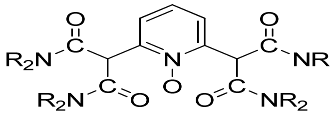
11



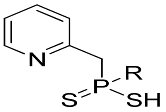
12



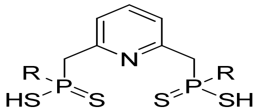
13



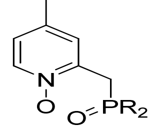
14



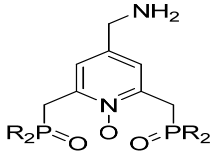
15



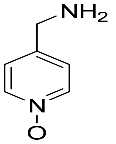
16



17



18



19

CHON Amide Platform Ligands

Ligands 11-14. A very large effort during the project was given to the development of these so-called "CHON" analogs of NOPO and NOPOPO. Of course a variety of "CHON"-ligands have been under development in several European laboratories since they offer the potential to be more environmentally friendly with regard to their final incineration properties compared to phosphorus-bearing extractants. They also do not produce phosphonic acid impurities that can interfere with desired extraction performance. Each of the ligands was first prepared with R = Ph as the amide substituent. This choice was made in anticipation of easier purification and characterization compared to alkyl substituent analogs. This proved correct; however, the resulting ligands show poor solubility properties except in chlorocarbon solvents. Nonetheless, the ligands have interesting coordination properties forming NOCO and NOCOCO chelate structures. The results were sufficiently promising that we next attempted to make alkyl analogs (R = Me, Et, *i*-Pr, *i*-Bu) with the intent to obtain hydrocarbon solvent soluble derivatives. On a positive note these ligands proved to be somewhat more easily made and purified; however, the solubilities in hexane, for example, were minimal. One derivative (**11**, R = Me) was sent to WSU for extraction analysis and the results were unremarkable. Further work with this family of ligands is warranted after further consideration of the ligand construction details. A manuscript describing the current ligand synthesis story is in progress and it will be submitted for publication later.

Thiophosphinic Acid Ligands

Ligands 15 and 16. At the start of this project there was interest within the actinide separations community in organodithiophosphinic acids as potential extractants for Am/Cm partitioning (e.g, Cyanex 301). We had previously prepared several CMPO-like sulfinyl and sulfonyl phosphine oxides [16], CMPS [17] and NOPS [18] ligands so with that experience we turned attention to constructing examples of 15 and 16. For synthetic simplicity we initially targeted the compounds with R = Ph. The synthesis of **15** (R = Ph) proved manageable and it was isolated in good yield as a crystalline solid. Interestingly, the much greater base strength of the pyridine fragment compared to the phenyldithiophosphinite fragment lead to isolation of the compound not as the dithiophosphinic acid but as the zwitterions. This was discovered initially via the x-ray crystal structure determination for the free ligand. In collaboration with our co-investigator Prof R. Hancock the ligand pK_a's were determined spectrophotometrically in water solution. Further, metal binding studies with La(III), Zn(II) and Cd(II) in water were examined. La(III) and Zn(II) were found to bind very weakly while Cd(II) formed a much more stable complex. Subsequently, coordination compounds with Cd(II) and Pt(II) were isolated and structurally characterized by x-ray crystallography. A manuscript describing these results in detail has been submitted for publication.The synthesis of **16** procved to be a bit more challenging although small samples of the compound have been isolated. With some alternative funding we will attempt to optimize the synthesis of this molecule and then begin studies of alkyl derivatives that may prove to be more robust toward decomposition.

Immobilized Extractants

Ligands 17-19. In recent years our co-investigator, Prof S. Alexandratos, has greatly advanced the field of ligand attachment chemistry on solid supports, and they have produced a number of useful phosphine oxide functionalized solid state separation materials. We have also had a much smaller effort in place to prepare ligand immobilized extraction materials, and we have produced supports functionalized with CMPO [19, 20]. This experience lead us to join together with the goal of devising approaches for immobilizing the NOPO and NOPOPO fragments on solid supports. Several modes of ligand-support attachment were considered and it was decided to focus on an amide coupling scheme that required the synthesis of **17** and **18**. Both ligands have been prepared during the project although both reaction schemes contain one step that results in low overall yields of the targets. Since **17** and **18** are somewhat precious, it was decided to explore the attachment chemistry with a model ligand that would be easier to make. That ligand is **19**. This compound has been made in 3-5 g quantities and it has been supplied to the Alexandratos group for attachment development and extraction testing. If the model chemistry is successful we will plan to explore the attachment coupling chemistry with **17** and **18**.

References This Section.

1. McCabe, D. J., Russell, A. A., Karthikeyan, S., Paine, R. T., Ryan, R. R., Smith, B. Inorg. Chem. **1987**, *26*, 1230.
2. Rapko, B. M., Duesler, E. N., Smith, P. H., Paine, R. T., Ryan, R. R. Inorg. Chem 1993, 32, 2164.
3. Engelhardt, U., Rapko, B. M., Duesler, E. N., Frutos, D., Paine, R. T. Polyhedron 1995, 14, 2361.
4. Gan, X.-M., Duesler, E. N., Paine, R. T. Inorg. Chem. 2001, 40, 4420.
5. Bond, E. M., Engelhardt, U., Deere, T. P., Rapko, B. M., Paine, R. T., FitzPatrick, J. R. Solv. Extr. Ion Exch. 1997, 15, 381.
6. Bond, E. M., Engelhardt, U., Deere, T. P., Rapko, B. M., Paine, R. T., FitzPatrick, J. R. Solv. Extr. Ion Exch. 1998, 16, 967.
7. Nash, K. L., Lavellette, C., Borkowski, M., Paine, R. T., Gan, X.-M. Inorg Chem. 2002, 41, 5849.
8. Swancutt, K. L., Mezyk, S. P., Martin, L. R., Tillotson, R. D., Pailloux, S., Chakravarty, M., Paine, R. T. ACS Symp. Ser. 2010, 1046, 231.
9. McCabe, D. J., Duesler, E. N., Paine, R. T. Inorg. Chem. 1985, 24, 4626.
10. McCabe, D. J., Bowen, S. M., Paine, R. T. Synthesis, 1986, 319.
11. McCabe, D. J., Duesler, E.N., Paine, R. T. Inorg. Chem. 1988, 27, 1220.
12. McCabe, D. J., Duesler, E. N., Paine, R. T. Inorg. Chim. Acta 1988, 147, 265.
13. Conary, G. S., Meline, R. L., Schaeffer, R., Duesler, E. N., Paine, R. T. Inorg. Chim. Acta 1992, 201, 165.
14. Conary, G. S., McCabe, D. J., Meline, R. L., Duesler, E. N., Paine, R. T. Inorg. Chim. Acta 1993, 203, 11.
15. Conary, G. S., McCabe, D. J., Caudle, L. J., Duesler, E. N., Paine, R. T. Inorg. Chim. Acta 1993, 207, 213.
16. Karthikeyan, S., Ryan, R. R., Paine, R. T. Inorg. Chem. 1989, 28, 1989.
17. McCabe, D. J., Duesler, E. N., Paine, R. T. Inorg. Chem.1987, 26, 2300.
18. Gan, X.-M., Paine, R. T. unpublished results
19. Paine, R. T., Blaha, S. L., Russell, A. A., Conary, G. S. Solv. Extr. Ion Exch. 1989, 7, 925.
20. Blaha, S. L., Caudle, L. J., Conary, G. S., Paine, R. T., Thomas, K. W. Radiochim. Acta 1989, 48, 59.

Chromatographic studies of NOPOPO uptake of metal ions.

Ensor Group at Tennessee Technological University

Summary:

The laboratory at Tennessee Technological University has evaluated potential complexants for the separation of elements important in nuclear fuel processing. These complexants were incorporated into an inert polymeric support using a dichloromethane as the solvent. The three complexants were 2,6-bis[(diphenylphosphino) methyl]pyridine N,P,P'-trioxide (NOPOPO), Cyanex 923® (a mixture of alkylphosphine oxides, and triphenyl phosphine oxide (TPPO). An initial evaluation of the three materials for the uptake of Am(III) from [HNO_3] showed only the NOPOPO had significant uptake (Figure 1). Based on the results from the study in Figure 1 most of the subsequent work focused on the NOPOPO resin.

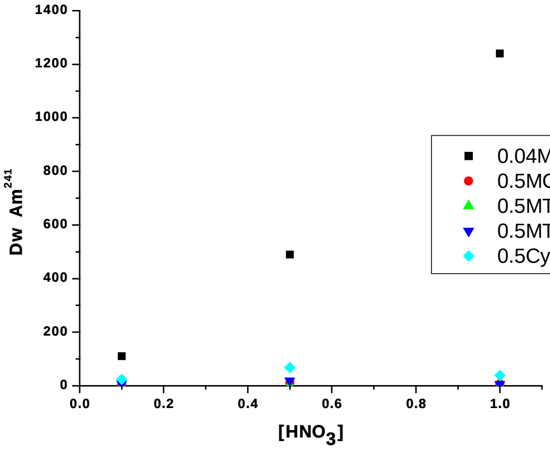


Figure 1.

The kinetics of the NOPOPO material was excellent. Equilibrium was obtained within 15 minutes using a batch contact method. Figure 2 shows the uptake of Eu(III) from 0.50 M HNO_3 over time.

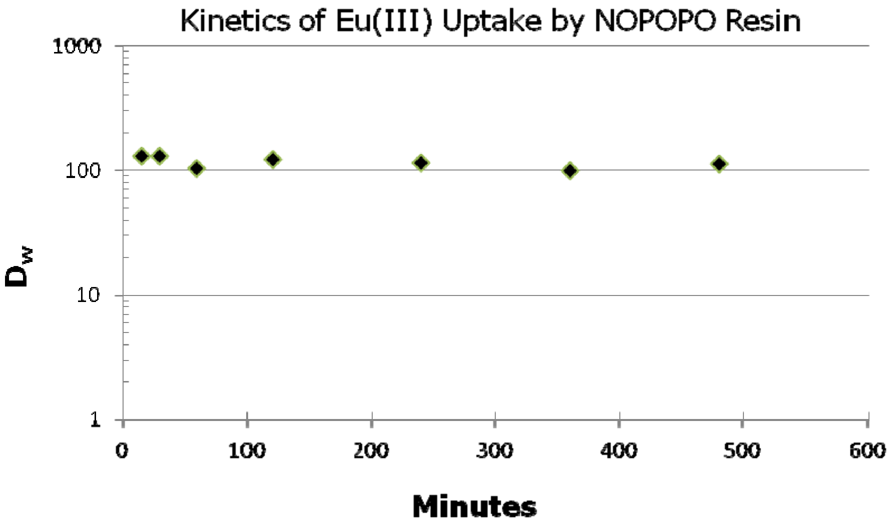


Figure 2

Chromatographic materials were prepared at 40% loading with 0.04 M extractant in DCM. The extractants used were NOPOPO and Cyanex 923. The uptake of these materials for a number of selected lanthanides and actinides from 0.05 M HNO_3 was measured at mM metal concentrations. The results showed that for all metals the NOPOPO was superior to the Cyanex 923. The selectivity of NOPOPO showed the overall order Th (IV) > UO_2(VI) > Ln(III). Figure 3 contains the distribution of these elements as a function of [HNO_3] with the highest uptake for most elements at 2.0 M acid. This is similar to results obtained by liquid-liquid extractions studies (*Inorg. Chem.*, 41(22), 5849 [2002]).

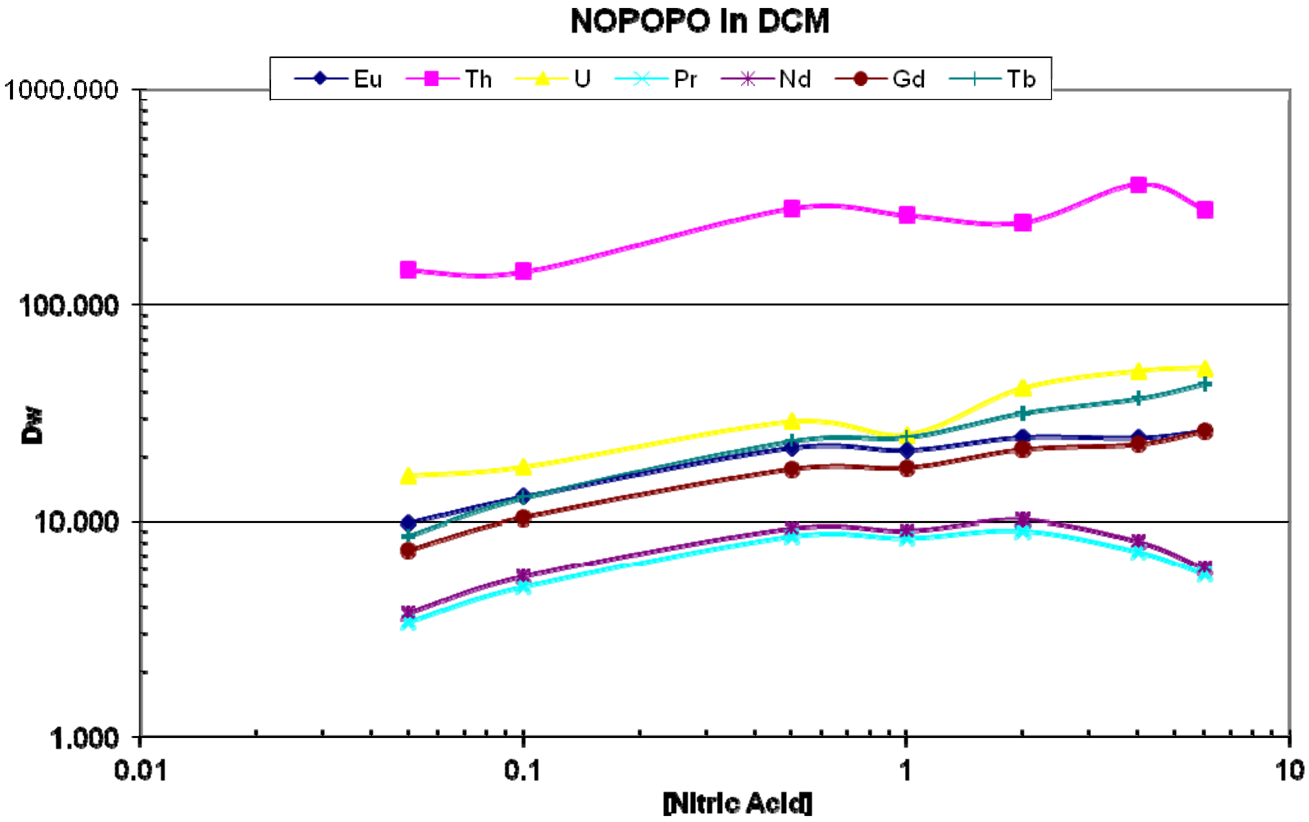


Figure 3

Finally radiotracer studies were performed with Am(III) as a function of $[HNO_3]$ which showed similar results to the other trivalent elements (Figure 4).

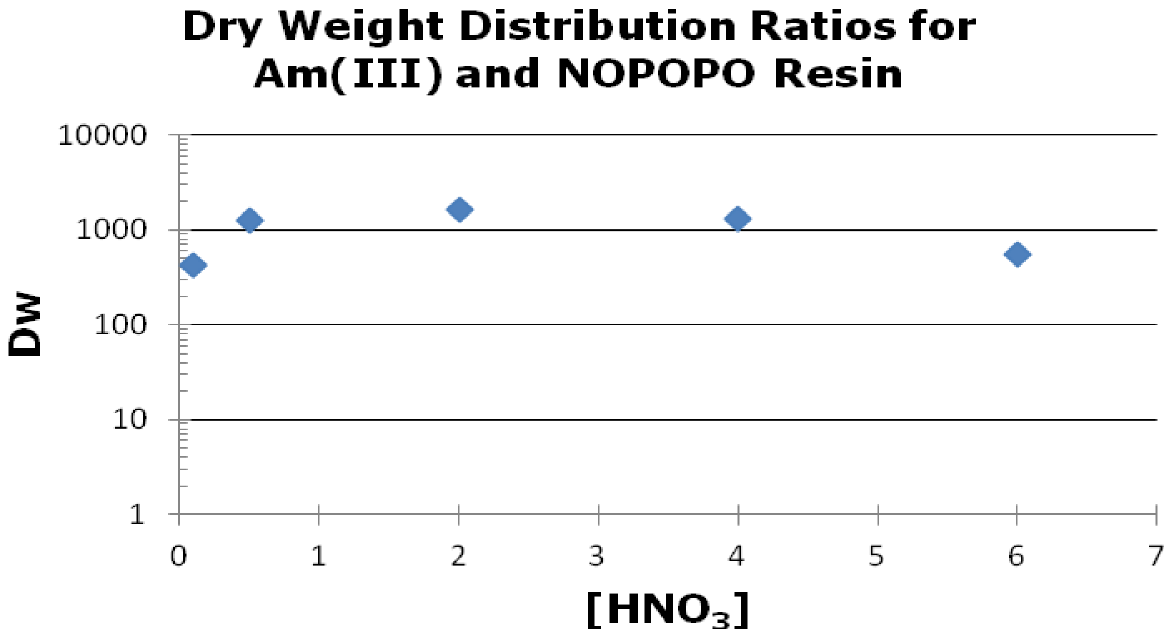


Figure 4.

Conclusions:

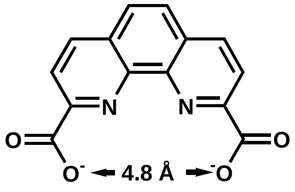
- The NOPOPO was the most effective complexant when impregnated onto a polymeric support.
- The NOPOPO molecule shows the general trend of higher D_w with higher concentration [M] nitric acid with a maximum at 1 – 2 M. This was similar to results from liquid-liquid extraction studies.
- The D_w of Am ≥ Eu.
- Grouping analytes show that D_w of Th>U~Tb ≥Eu>Gd≥Nd>La.
- Results are offer sufficient promise to establish potential value in continued investigation.

Additional discussion of solvent extraction results on TONOPOPO described in Subtask 5.

Subtask 2. Phenanthroline Derivatives

R. Hancock, University of North Carolina, Wilmington

Background. The ongoing WSU research on soft donor extractant/complexants systems has resulted in the synthesis of a number of new reagents, tetraaza extractant systems based on structural variants of ethylenediamine. Another class of ligands of promise for the separation of Am(III) and Cm(III) from fission product lanthanides are functionalized 1,10-phenanthroline species. The Hancock group has examined several of these systems and characterized their lanthanide complexes. Expanding on this research, the following work plan was proposed.

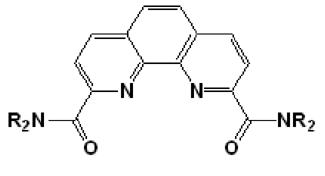


PDA

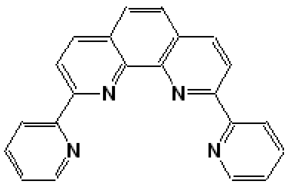
The ligand 1,10-phenanthroline-2,9-dicarboxylic acid (PDA) left has been investigated by the Hancock group, and found to have high affinity for Ln(III) ions. The 1,10-phenanthroline backbone of

PDA imparts great rigidity to the ligand, and the carboxylate groups are quite strongly constrained to lie in the plane of the ligand. This fixed geometry leads to a preference for metal ions with an ionic radius (r^+) of about 1.0 Å (Table 1). Selectivity against smaller and larger metal ions is notable (consider the series of alkaline earth complexes). The influence of covalency on the interaction strength is reflected in the $10^{6.5}$ stronger complexes of Zn^{2+} relative to similarly-sized Mg^{2+}. The influence of stronger electrostatic attraction is demonstrated in the series Ca(II) < La(III) < Th(IV). These cations are all about the same size, but K_1 increases by 10^6 from Ca(II) to La(III) and by 10^9 from La(III) to Th(IV). The equilibrium constants for the corresponding (hexadentate) EDTA complexes are $K_{Ca(EDTA)} = 10^{10.65}$, $K_{La(EDTA)} = 10^{15.36}$, $K_{Th(EDTA)} = 10^{23.2}$, a similar pattern of relative stability derived from a nominally stronger complexant. The Hancock group is currently attempting to characterize the UO_2^{2+} complexes, which appear to demonstrate an extraordinary affinity for PDA. The high affinity of PDA for metal ions of higher charge may turn out to assist in stabilizing the higher oxidation states of Am, noted to be very unstable. The simultaneous presence of soft donor nitrogen atoms and a geometry that favors binding to cations of approximately 1 Å radius suggests that this ligand system might have interesting effects on either soft donor or redox based separations of Am from lanthanides. It is noted also that the equilibrium constants (Table 1) for Cu^{2+} and La^{3+} are comparable in this system, supporting the use of Cu^{2+} as a tool for characterizing ligand interactions with Ln^{3+} and An^{3+}.

PDA is the first member of a family of ligands based on rigid 1,10-phen type reinforcing backbones that present the possibility of important metal ion affinities and selectivities. The Hancock group has started exploration of some examples below. PDAM has reasonable affinity for Ln(III) ions, with log K_1 for La(III) of 4.0, and like PDA shows strong selectivity towards metal ions of radius about 1.0 Å. Interestingly, PDAM is virtually non-protic, with a pK_a of 0.9. DPP has shown remarkable metal ion selectivities, and reasonably high log K_1 values with Ln(III) ions: log K_1 La(III) = 5.1, Gd(III) = 5.9. DPP is attractive because the larger number of N-donors should produce enhanced affinity for the more covalent Am(III) ion.



PDAM (R = H)

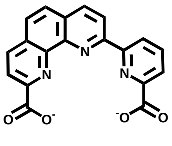


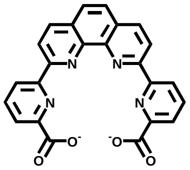
DPP

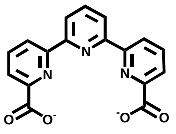
Table 1. The protonation and formation constants for a selection of metal ions with PDA (0.1 *M* $NaClO_4$, 25 ºC).

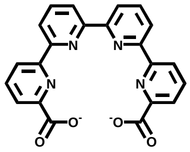
Lewis Acid	Ionic radius (Å) *(63)*	Equilibrium	log K_1(PDA)
H^+		$H^+ + L^{2-} \leftrightarrows HL^-$ $H^+ + LH^- \leftrightarrows H_2L$	4.75(2) 2.53(5)
Mg^{2+}	0.74	$Mg^{2+} + L^{2-} \leftrightarrows MgL$	3.53(5)
Ca^{2+}	1.00	$Ca^{2+} + L^{2-} \leftrightarrows CaL$	7.3(1)
Sr^{2+}	1.18	$Sr^{2+} + L^{2-} \leftrightarrows SrL$	5.61(4)
Ba^{2+}	1.36	$Ba^{2+} + L^{2-} \leftrightarrows BaL$	5.43(5)
La^{3+}	1.03	$La^{3+} + L^{2-} \leftrightarrows LaL^+$	13.5(1)
Gd^{3+}	0.94	$Gd^{3+} + L^{2-} \leftrightarrows GdL^+$	16.1(1)
Lu^{3+}	0.86	$Lu^{3+} + L^{2-} \leftrightarrows LuL^+$	17.5(1)
Th^{4+}	0.94	$Th^{4+} + L^{2-} \leftrightarrows ThL^{2+}$	24.0(1)
Zn^{2+}	0.74	$Zn^{2+} + L^{2-} \leftrightarrows ZnL$	11.0(1)
Cd^{2+}	0.96	$Cd^{2+} + L^{2-} \leftrightarrows CdL$	12.8(1)
Pb^{2+}	1.19	$Pb^{2+} + L^{2-} \leftrightarrows PbL$	11.4(1)
Cu^{2+}	0.57	$Cu^{2+} + L^{2-} \leftrightarrows CuL$	12.8(1)

The motif of a reinforced backbone based on an extended aromatic system such as 1,10-phen, with added donor groups, leads to a large number of possibilities of ligands promising for the selective complexation of Am(III), and perhaps also for higher oxidation states of Am. Clearly, one would wish to expand the number of N-donors further to enhance selectivity relative to the Ln(III) ions. Thus, L1 to L4 below should show enhanced selectivity for Am(III), and possibly also Am(VI). L3 and L4 are less rigid analogues of L1 and L2, and so should complex more weakly, which, could however be desirable if metal ions are to be removed from any potential extractants. It should be noted that adding carboxylates to the ortho positions of pyridyl groups is quite straightforward. As with the synthesis of PDA the polypyridyl ligand is synthesized with methyl groups ortho to the pyridyl N-donors, and then these are oxidized to carboxylate groups. L1 to L4 can also be turned into the amide analogues, which, like PDAM, should have good affinity for larger metal ions, and enhanced selectivity for Am(III) over the Ln(III) ions. The Hancock group has already synthesized a variety of poly-pyridyl-based ligands involving this type of chemistry *(65)*.


L_1

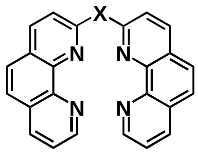

L_2


L_3

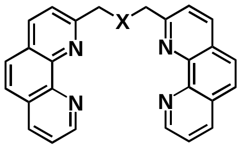

L_4

Clearly, a host of possibilities exists of polydentate ligands based on 1,10-phen. Particularly attractive from the synthetic point of view are coupled 1,10-phen ligands where the bridge is an S or an N (L5 and L6). These are made simply by reacting commercially available 2-chloro-1,10-phen with H_2S or ammonia under pressure.

Computer modeling of complexes of L5 and L6 suggests that the bridging S and N donors cannot coordinate to the metal ion when the 1,10-phen groups are coordinated. For incorporation of S-donors, in particular, to enhance selectivity for Am(III), ligand L7 would be suitable. The N-donor of L8 would allow for attachment of other coordinating groups such as a carboxylate, or long aliphatic groups to render the ligand water insoluble and suitable for use in solvent extraction. L7 and L8 would be synthesized from the 9-bromo-methyl 1,10-phen.



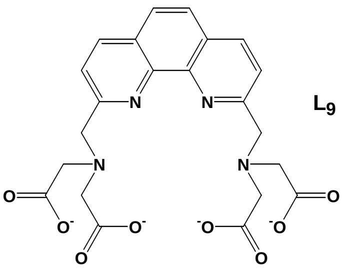
L_5, X = S
L_6, X = NR



L_7, X = S
L_8, X = NR

The reinforced backbone of the ligands discussed here can ultimately lead to ligands of unprecedented complexing power and metal ion selectivity. This motif could be used in a ligand such as L9, which would have enhanced selectivity for Am(III) over the Ln(III) ions, as compared to EDTA or DTPA. It should be noted that coordination of all of the nitrogen atoms in these complexants and those prepared in the prior work at WSU will lead to the formation of notably stable five-membered chelate rings. As will be noted in **Subtask 4**, these cation receptors are amenable to incorporation into polymeric matrices, which enables a variety of other separations applications.

Sub-Task 2 Scope of Work: The aim of this project was to understand the metal ion complexing patterns produced by ligands of the polypyridyl type, such as tpy (See Figure 1 for key to ligand abbreviations). The interest in polypyridyl ligands arises from their potential application in separating An(III) (An = Actinide) ions such as Am(III) and Cm(III) from Ln(III) (Ln = lanthanide) ions such as Gd(III) in the treatment of nuclear waste.[1] Interest in polypyridyl ligands that might form the functional groups of solvent extracts for such separations arises from the greater covalence[2,3] of the An-N than the Ln-N bond, which would be taken advantage of with the more covalently binding pyridyl-type donor group. Ligands and their less water soluble derivatives studied as potential extractants include BTP,[4] BTphen,[5] TPEN,[6] 4,7-diphenyl-phen,[7] TPTZ[8-12], and DPAM.[13] There is little in the way of formation constant data[14] available on polypyridyl type ligands with Ln(III) ions, or the less radioactive An cations such as Th(IV) or the UO_2^{2+} cations, so that a study of such complexes was undertaken.



L_9

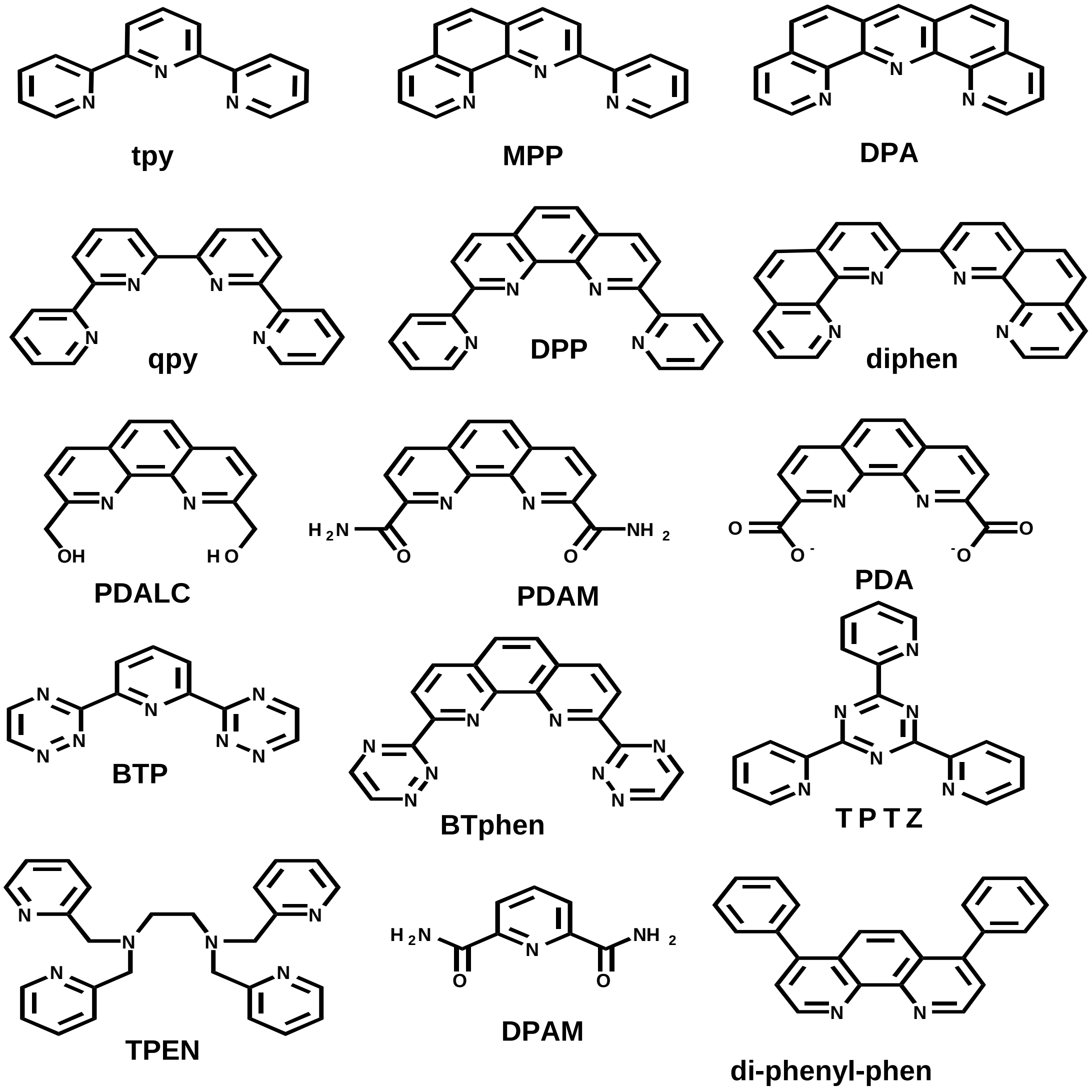


Figure 1. Ligands discussed in this report.

Sub-Task 2 Final Report: The starting point was the metal ion complexing properties of tpy[15] and qpy,[16] which have not been studied in aqueous solution with Ln(III) cations. The first problem was the difficulty of solubilization of these two ligands. It was found[15] that for tpy direct solution of the ligand in water at any pH, even after heating and sonication, resulted in solutions which were not complete as evidenced by large light-scattering peaks at about 200 nm. The approach that finally gave stable solutions without light-scattering peaks was to prepare a 10^{-5} M solution of tpy in pure MeOH, and then use this stock solution to prepare 10^{-5} M solutions of the ligand. The effect of the 1% of MeOH now present in such solutions was considered to be negligible. It was also found that background electrolytes such as 0.1 M $NaClO_4$ should be omitted, as these tended to salt the ligand out. The protonation equibria and metal complex-formation equilibria were then studied using the intense π-π^* transitions in the UV in the range 200-350 nm to follow the equilibria. In the case of qpy, solutions of only 2 x 10^{-7} M in water could be prepared, and the equilibria followed using a 1 meter long path-length cell or Fluorimetry, or else 10^{-5} M solutions in 50% MeOH/water could be studied by UV spectrophotometry. In Figure 2 is seen the variation of the absorbance spectra of the polypyridyl ligand DPP as a function of [Pr^{3+}] at pH 5.08. This set of spectra is typical of what is obtained with polypyridyl ligands, where rotation of the pyridyl group from *trans* in the free ligand to *cis* in the metal ion complex results in the appearance of sharp vibrational bands coupled to the π-π* electronic transitions of the ligand. These sharp bands are very useful diagnostic indicators of complex-formation. The formation constants were calculated from these sets of spectra using the Excel program,[17] with theoretical curves of absorbance *vs.* log [Pr^{3+}] fitted to the experimental values at six wavelengths as seen in Figure 3.

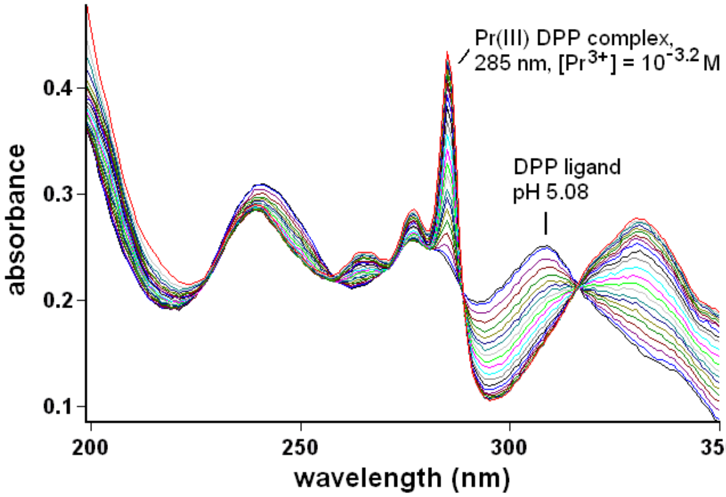


Figure 2. Variation of absorbance spectra of 10^{-5} M DPP ligand as a function of Pr^{3+} concentration at pH 5.08, which pH minimizes the occurrence of hydroxy species.

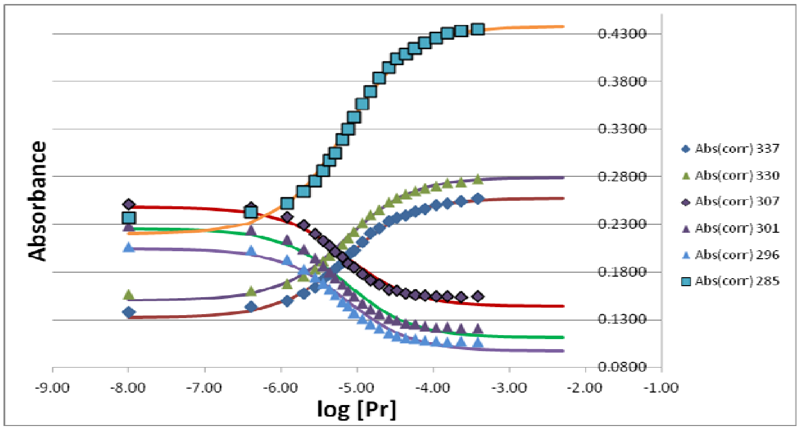
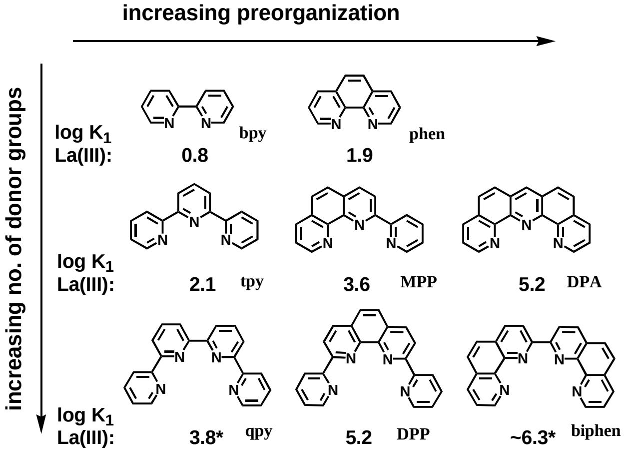


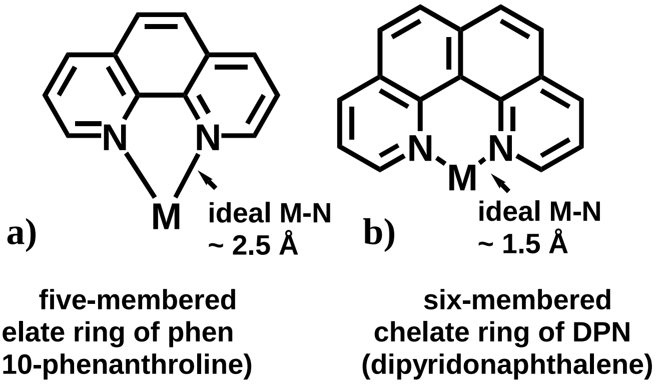
Figure 3. Variation of absorbance of 10^{-5} M DPP as a function of log [Pr^{3+}] at six different wavelengths. The points are the experimental values, while the solid lines are theoretical curves fitted using EXCEL[17] and a log K_1 value of 5.25.

The studies of polypyridyl ligands have focused on three structural features that may influence the stability of the complexes formed: 1) the number of pyridyl groups 2) the presence of reinforcing benzo groups which increase the preorganization[18] of the ligand, and 3) the presence of triazine groups as are found in TPTZ or BPphen. The effect of the first two factors on the stability of the complexes of Ln(III) can be summarized as in Scheme 1:



Scheme 1. Series of ligands showing how increased preorganization provided by reinforcing benzo groups, and increasing number of pyridyl donor groups, affects log K_1 for the complexes of the large La(III) metal ion. Log K_1 data references 15,16, 19-23. *50% MeOH.

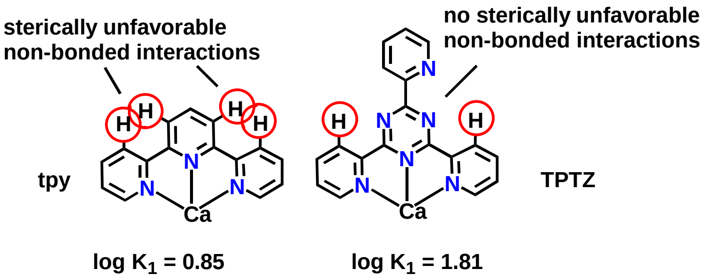
One sees the effect (1) on log K_1 for La(III) of adding extra pyridyl groups in sequences in scheme 1 such as bpy < tpy < qpy, or phen < MPP < DPP. Such increases in complex stability along these series are observed for virtually all metal ions. The effect (2) of reinforcing benzo- groups that increase the preorganization[18] of the ligand leads to increases in log K_1 for La(III) along series such as tpy < MPP < DPA. For large metal ions with ionic radii (r^+) close to 1.0 Å, such as Ln(III) ions or Ca(II), increasing such preorganization always leads to increasing log K_1 values. Since polypyridyl ligands usually form five-membered chelate rings, this leads to a preference for large metal ions, as summarized in scheme 2:



Scheme 2. Best-fit M-N lengths for metal ions coordinating in a) the five-membered chelate ring formed by phen, or b) the six-membered ring formed by DPN.

One thus finds that small metal ions such as Zn(II) or Cu(II) with $r^+ < 0.8$ Å do not show significant increases in log K_1 as ligand preorganization increases along series such as tpy < MPP < DPA. These smaller metal ions, and this applies also to a lesser extent to smaller Ln(III) ions such as Lu(III), experience increasing difficulty in coordinating with more rigid five-membered chelate rings. From these results, one can understand the superior metal ion extracting abilities of derivatives of BTphen,[5] since BTphen has four pyridyl-type donors, as well as a reinforcing benzo group.

The ligand BTphen brings one to factor (3) above, namely the effect on ligand complexing properties with metal ions produced by changing triazine groups for pyridyl groups. Due to the more electronegative nature of nitrogen, one would expect triazine groups to be nearly non-basic. Thus, metal ions such as Cu(II) and Zn(II) that have a high affinity for N donor ligands[21] should be quite adversely affected by replacement of pyridyl groups by triazine groups, as in passing from DPP to DTphen. However, the triazine group is geometrically similar to a pyridyl group, so it should preserve the sterically derived preference of triazine-containing ligands for large metal ions. In addition, the absence of H-atoms on the nitrogens of triazine groups diminishes a problem suffered by polypyridyl groups, namely steric clashes between H-atoms at the 3-positions of the pyridyl groups, as summarized in scheme 3 for TPTZ vs. tpy complexes:[24]



Scheme 3. Complex stability of the Ca(II) complexes of tpy and TPTZ, showing the increased complex stability resulting from removal of sterically unfavorable non-bonded interactions.[24]

Studies we have performed[24] show that TPTZ is a weaker base ($pK_a = 3.3$) than tpy ($pK_a = 4.7$), because of the electron-withdrawing nature of the triazine group. Even so, TPTZ forms more stable complexes with large metal ions than does tpy. DFT calculations[25] we have performed[24] confirm that the triazine N donors of TPTZ are nearly non-basic (pK_a predicted by DFT to be ~ 0.3), but that this low basicity is compensated for by superior steric properties in TPTZ complexes, with the lack of steric clashes between H atoms in coordinated TPTZ, as are present in coordinated tpy.

In addition to the polypyridyl ligands and their triazine-substituted derivatives, we have studied the metal ion complexing properties of the phen derivatives PDA,[26] PDAM,[27,28] and PDALC.[29] The ligand PDA shows selectivity for larger metal ions that would be expected from its formation of five-membered chelate rings on complex formation. The carboxylate groups of PDA overcome a problem that polypyridyl donor ligands have, which is an inability to H-bond with the solvent and thereby stabilize the metal ion. This problem is more serious for metal ions of higher charge. The presence of carboxylate groups on PDA thus fulfils the role of removal of charge from the metal ion, and one sees complexes of unprecedented stability formed by metal ions such as La(III) with PDA as compared to their ability to complex with e.g. phen, as seen in Table 1:

Table 1. Log K_1 values[14,27-29] for phen, PDA, PDAM, and PDALC complexes of a selection of metal ions.

Metal ion:	Ca(II)	Pb(II)	La(III)	In(III)	Zn(II)	Cu(II)	Th(IV)
Ionic radius (Å):	1.00	1.19	1.03	0.80	0.72	0.57	0.94
log K_1(phen):	0.85	4.5	1.85	6.8	6.4	9.1	~2
log K_1(PDA):	8.2	11.4	13.5	19.7	11.0	12.8	25.7
log K_1(PDAM):	1.94	5.8	3.8	9.4	3.8	3.6	5.0
log K_1(PDALC):	3.7	7.3	5.3	9.1	6.6	7.6	8.6

The ligands PDAM[27,28] and PDALC[29] demonstrate the effect[21] of neutral oxygen donors on metal ion selectivity, which is to promote selectivity for metal ions with an anionic radius of close to 1.0 Å. One should compare log K_1 for PDA, PDAM, or PDALC with log K_1 for the phen complex to see the effect of the substituents on these ligands on complex stability and metal ion selectivity. Of particular interest is the fact that the electron-withdrawing amide groups of PDAM lower its pK_a to 0.6 as compared to 5.2 for phen itself.[14] This low basicity of the N donors of PDAM produces remarkable selectivity patterns,[27,28] with small metal ions of high N donor affinity such as Cu(II) showing very low affinity for PDAM, while large Ln(III) ions show unusually high affinity for PDAM.

An important remaining question is that of the factors that might control An(III)/Ln(III) selectivity. A factor that is emerging is that of metal ion size, insofar as it causes selectivity for many polypyridyl donor ligands to peak at about Sm(III), as seen in Figure 4. What is important is that Am(III) is closer in size to Sm(III) than to Gd(III), and much of the selectivity observed for Am(III) by extractants such as DTphen may derive from size-selectivity as much as from the covalency provided by the N donors of the ligand. DFT and MM (molecular mechanics) calculation suggest that the stability sequence from La(III) to Lu(III) is controlled by the fact that Ln(III)-ligand bond strength increases steadily from La(III) to Lu(III), but that the balance between this increase in strength and steric crowding causes a drop-off in log K_1 at some point along the series, with a flattening off in log K_1, as occurs for the polypyridyl ligands in Figure 4 with the Ln(III) ions after Sm(III).

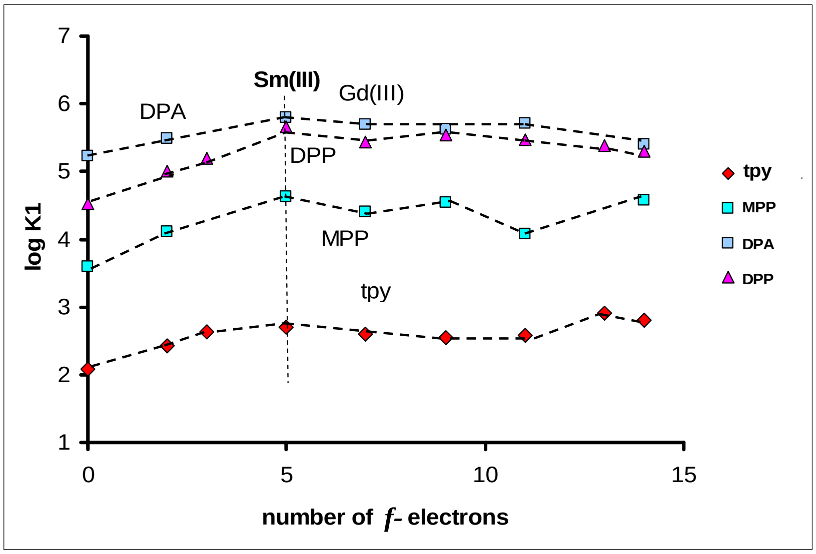


Figure 4. Variation in log K_1 for a variety of polypyridyl ligands[22,23,30-32] with Ln(III) ions, as a function of the number of *f*-electrons in the Ln(III) ion. Sm(III) is highlighted, as for larger Ln(III) ions log K1 increases from La(III) to Sm(III) with increasing Ln-N bond strength. After Sm(III), steric crowding leads to a flattening off in log K_1 as one approaches Lu(III).

In addition, the research has involved collaboration with other researchers at other Universities, including those who are part of the team on this project, as well as others:

Collaborators at other Universities: Dr. Kenneth L. Nash (WSU), Dr. Robert T. Paine (UNM), Dr. Randolph P. Thummel (U. Houston), Dr. J. H. Reibenspies (Texas A&M), Dr. D. G. VanderVeer (Clemson), Dr. I. V. Nikolayenko (U. Natal, S. Africa), Dr. S. B. Jones (UNCW).

References this Section.

1) Nash, K. L.; Madic, C.; Mathur, J. N.; Lacquement, J. in *The chemistry of the actinide and transactinide elements*, 3rd ed. Eds. Morss, L.R.; Edelstein, N.M.; Fuger, J. Springer: Netherlands, 2006, Vol. 4, p. 2622.
2) Diamond, R. M.; Street, K.; Seaborg, G. T. *J. Amer. Chem. Soc.*, **1954**, 76, 1461.
3) Musikas, C, Le Marois, G.; Fitoussi, R.; Cuillerdier, C. in *Actinide Separations,* Navratil, J. D.; Schulz, W. W. (eds.), ACS Symposium Series 117, American Chemical Society, Washington DC, 1980, pp. 131-45.
4) Petit, L.; Adamo, C.; Maldivi, P. *Inorg. Chem.* **2006**, *45*, 8517.
5) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B. Desreux, J. F.; Vidick, G.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T.-H.; Simonin, J. P. *J. Amer. Chem. Soc.*, **2011**, *133*, 13093.
6) Morss, L. R.; Rogers, R. D. *Inorg. Chim. Acta.* **1997**, *255*, 193.
7) Ensor, D. D.; Jarvinen, G. D.; Smith, B. F. *Solvent Extr. Ion Exch.***1988**, *6*, 439.
8) Musikas, C. *Inorg. Chim. Acta*, **1987**, *140*, 197.
9) Madic, C.; Hudson, M. J. Report EUR 18038 EN, 1998.
10) Hudson, M. J.; Boucher, C. E.; Braekers, D.; Desreux, J. F.; Drew, M. G. B.; Foreman, M. R. St. J.; Harwood, L. M.; Hill, C.; Madic, C.; Marken, F. *New J. Chem*. **2006**, *30*, 1171.
11) Foreman, M. R. S.; Hudson, M. J.; Drew, M. G. B.; Hill, C.; Madic, C. *Dalton Trans*. **2006**, 1645.
12) Drew, M. G. B.; Iveson, P. B.; Hudson, M. J.; Liljenzin, J. O.; Spjuth, L.; Cordier, P.-Y.; Enarsson, A.; Hill, C.; Madic, C. *Dalton Trans.* **2000**, 821.
13) Romanovskiy, V. N.; Babain, V. A.; Alyapyshev, M. Yu.; Smirnov, I. V.; Herbst, R. S.; Law, J. D.; Todd, T. A. *Sep. Sci. Technol*. **2006**, *41*, 2111.
14) Martell, A. E.; Smith, R. M. *Critical Stability Constant Database, 46*; National Institute of Science and Technology (NIST): Gaithersburg, MD, USA, 2003.
15) Hamilton, J. M.; Anhorn, M. J.; Oscarson, N. J.; El Ojaimi, M.; Thummel, R. P.; Hancock, R. D. *Inorg. Chem.* **2011**, *50*, 3785.
16) Ballance, D. G.; Hancock, R. D. to be published.
17) Billo, E. J. *EXCEL for Chemists*; Wiley-VCH: New York, 2001.
18) Cram, D. J.; Cram, J. M. *Acc. Chem. Res*. **1978**, *11*, 8.
19) Cockrell, G. M.; Zhang, G.; VanDerveer, D. G.; Thummel, R. P.; Hancock, R. D. *J. Amer. Chem. Soc*. **2008**, *130*, 1420.
20) Hancock, R. D.; Jackson, J.; Evers, A. *J. Chem. Soc., Dalton Trans.***1979**, 1384.
21) Hancock, R. D.; Martell, A. E. *Chem. Rev*. **1989**, *89*, 1875.
22) Carolan, A, N.; Mroz, A. E.; El Ojaimi, M.; VanDerveer, D. G.; Thummel, R. P.; Hancock, R. D. *Inorg. Chem.* submitted.

23) Hamilton, J. M.; Whitehead, J. R.; Williams, N. J.; El Ojaimi, M.; Thummel, R. P.; Hancock, R. D. *Inorg. Chem.* **2011**, *50*, 3785.
24) Littmann, G. C.; Nikolayenko, I. V.; Hancock, R. D. to be published.
25) Jaguar, version 7.8, Schrödinger, LLC, New York, NY, **2011**.
26) Williams, N. J.; Dean, N. E.; VanDerveer, D. G.; Luckay, R. C.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 7853.
27) Merrill, D.; Hancock, R. D. *Radiochim. Acta* **2011**, *99*, 161.
28) Merrill, D.; Harrington, J. M.; Lee, H.-S.; Hancock, R. D. *Inorg. Chem.* **2011**, *50*, 8348.
29) Gephart, R. T. III; Williams, N. J.; Reibenspies, J. H.; De Sousa, A. S.; Hancock, R. D. *Inorg. Chem.* **2009**, *48*, 8201.
30) Carolan, A. N.; Cockrell, G. M.; Williams, N. J.; Zhang, G.; VanDerveer, D. G.; Thummel, R. P.; Hancock, R. D., to be submitted.
31) Carolan, A. N.; Hancock, R. D., to be submitted.

Subtask 3. Structurally Hindered Aliphatic Amine Extractants

G. Patrick Meier, Washington State University

Background/Scope of Work: Earlier polyaza ligands were constructed on a series of functional backbone scaffolds generically related to ethylenediamine (piperazine, cyclohexane-1,2-diamine, benzene-1,2-diamine, and propylene-1,3-diamine). Though amide derivatives were initially synthesized, the methyl pyridine functionalized groups were found to be of greater interest. The initial target ligands combine selected features of TPEN, while introducing a limited rotation diamine backbone. Characterization of these ligands involved examination of both the thermodynamic and kinetic features of their interactions with Cu^{2+}, lanthanides and selected actinide cations. The utilization of aliphatic amines in the scaffold presents the free electrons of nitrogen to the metal ion(s) in a different geometry, net basicity and at a different angle from the aromatic nitrogens of the phen and bipy donors of **Subtask 2**. As noted above, complexants useful for actinide-lanthanide separations often combine hard and soft donor atoms. Introducing a variety of different peripheral functional groups allows the donicity of the polydentate ligand to be tuned to improve selectivity. Based on the earlier studies, the development of the synthesis of tetradentate piperazine analogs was proposed in which1) The chair/ boat conformational energy difference (corresponding to bidentate and tetradentate ligand coordination, respectively) is modified, while holding the pendant groups constant as 2-pyridylmethyls 2) the electronic character of the pendant ligands by substituting the 4-triazoylmethyl, bis(2-ethylhexyl)phosphine oxide, 2-ethylhexylphosphinic acid, and the N, N- di(2-ethylhexyl)carboxamidoyl moieties for the 2-pyridylmethyl group in the parent molecule, 3) the length of the tether between the pendent ligands described in Project 2 and the piperazine ring was to be varied.

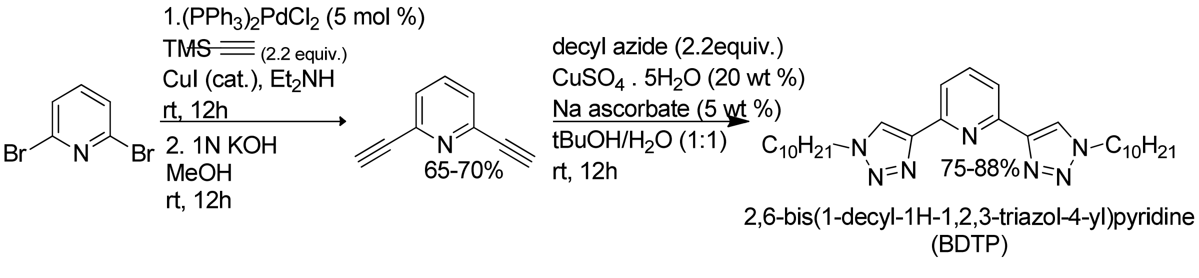
Though elegant syntheses were proposed, this thread of action was abandoned as the initial results of piperazine ligand development revealed that the energetic barrier of chair-boat configurations was not overcome by cation binding energy for this class of ligands binding to the cations of interest. With this realization, the project shifted toward examination of triazole functionalized pyridine/bipyridine complexants synthesized using Sharpless' "Click Chemistry". Examples of bidentate, tridentate and tetradentate complexants containing triazoles were prepared and subject to characterization studies

Subtask 3 Final Report. With recognition that the piperazine system offered substantial synthesis and metal complexation challenges, the shift of emphasis toward the development of extractant molecules based on the application of "click" chemistry to the synthesis of pyridine triazole ligands was immediately recognized as a valuable opportunity to modify the great success that the European program has enjoyed in creating triazine ligands based on pyridine and bipyridine. The stability of the triazole ring system offers a potential benefit in the creation of N3 and N4 extractant molecules, in that this arrangement could improve complexant stability and open additional ligand design options. The starting point for this investigation was the creation of representative bi- tri- and tetradentate triazole ligands to demonstrate both the viability/complexity of the organic synthesis and offr an opportunity to establish the comparative stability of these ligands. As the ultimate objective is separations applications, it was also important to provide metal ion interaction information. Because optimum lipophilicity was not achieved in the example compounds prepared, preliminary separations evaluations of the triazole ring remain uncertain Additional work will be needed to address this question. Synthesis is straight forward and in general yields are acceptable. Characterization of the derivatives prepared relies for the moment on structural characterization of transition metal complexes and ligand degradation studies being done using thermogravimetric analysis and infrared spectroscopy, which is not yet complete.

New tridentate polyaza- ligands expected to exhibit affinity for first-row transition metals, lanthanides and actinides have been designed and synthesized. As the intended primary application for these new compounds is radioactive waste management, both cation selectivity and radiolytic/hydrolytic stability are important evaluation criteria in assessing their utility. A library of 1,2,3-triazoles synthesized using Sharpless' "Click Chemistry" has been prepared and characterized. Variation of the backbone and substituents on the triazole ring allows for facile modification of the cation binding pocket and phase compatibility properties of the new compounds. Characterization of the new ligands has been done using conventional analytical methods. The primary tool for characterizing metal complexation is single-crystal X-ray diffraction. A crystal structure of a tridentate N, N, N donor ligand, 2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine and its complexes with Cu^{2+} ($CuLCl_2$), Cr^{3+} ($CrLCl_3$), and Fe^{3+} ($FeL_2Cl_2 \cdot Fe_2OCl_6$) are reported.

Synthesis of 2,6-bis(1-decyl-1H-1,2,3-triazol-4-yl)pyridine (BDTP). The BDTP ligand was synthesized and purified by modifying and combining the following procedures [1-4]. The decyl azide and 2,6-diethynylpyridine were made and purified separately. The 2,6-diethynylpyridine was synthesized via a Sonogashira coupling reaction with trimethylsilyl acetylene and bis-(triphenylphosphene) palladium dichloride as the Pd catalyst. The silyl groups were deprotected by reacting the product with 1N KOH in methanol. The click reaction was performed by adding a 1:2.2 ratio of the alkyne and azide to a solvent with a 1:1 ratio of tert-butanol/ water in the presence of copper sulfate (20 wt %) and sodium ascorbate (5 wt%), as seen in Scheme 1. The BDTP was recrystallized with diethylether to give a colorless powder. Yield 75-88%. L (**1**). Anal. Calc for $C_{29}H_{47}N_7$: C, 70.55; H, 9.59; N, 19.86. Found: C, 69.73%; H, 9.57%; N, 19.69%. FT-IR:(**1**): 3153, 2975, 2951, 2912, 2868, 1606, 1574, 1468, 1429, 992, 786, 785, 719, 651.

Scheme 1: Synthesis scheme of the BDTP ligand (**1**)



Synthesis of complexes $CuLCl_2$ (2), $CrLCl_3$ (3) and $FeL_2{\cdot}Fe_2OCl_6$ (4)

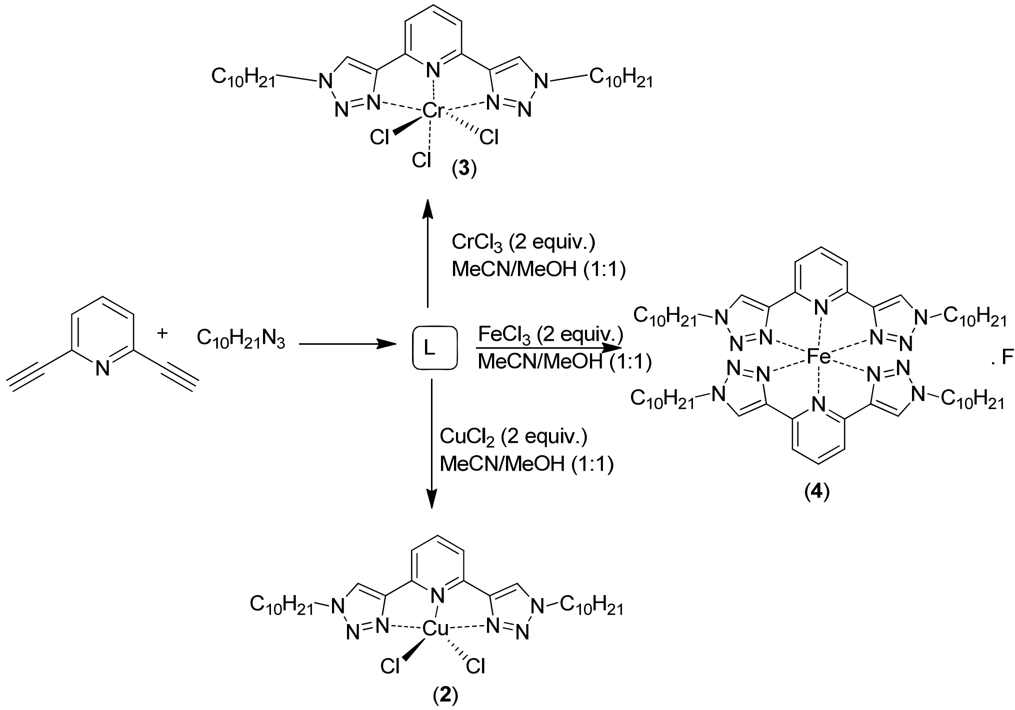
***General method*:** To prepare the metal-ligand complex, a 1:1 mole ratio of metal and ligand (0.025 g, 0.1 mmol) were dissolved in a 1:1 mixture of acetonitrile/methanol (2 mL of each). This solution was allowed to evaporate slowly until single crystals formed. They were isolated by filtration and washed with diethyl ether and then dried. The experimental conditions can be seen in Scheme 2.

$CuLCl_2$ (2): To prepare the copper(II)-BDTP complex, the general method was followed with a 1:1 ratio of copper(II)chloride and BDTP. Yield 63%. Anal. Calc for $C_{29}H_{47}Cl_2N_7Cu$: C, 55.45; H, 7.54; N, 15.61. FT-IR: 3070, 2915, 2854, 1589, 1465, 1357, 1265, 1203, 1110, 1084, 817, 725, 663, 555.

$CrLCl_3$ (3): To prepare the chromium(III)-BDTP complex, the general method was followed with a 1:1 ratio of chromium(III)chloride and BDTP. Yield 42%. Anal. Calc for $C_{29}H_{47}Cl_3N_7Cr$: C, 53.41; H, 7.26; N, 15.04. Found: C, 53.54%; H, 7.29%; N, 14.89%. FT-IR: 3317, 3085, 2915, 2854, 1587, 1465, 1280, 1126, 1064, 802, 709.

$FeL_2{\cdot}Fe_2OCl_6$ (4): To prepare the iron(III)-BDTP2 complex, the general method was followed with a 1:1 ratio of iron(III)chloride and BDTP. Yield 26%. $FeL_2{\cdot}Fe_2OCl_6$ (**4**). Anal. Calc for $C_{58}H_{94}Cl_6N_{14}O\ Fe_3$: C, 50.34; H, 6.85; N, 14.17. FT-IR: Complex 3 (**4**): 2915, 2854, 1575, 1450, 1434, 1373, 1203, 1049.

Scheme 2: Syntheses of the Metal-Ligand Complexes



It has been established that the BDTP ligand was synthesized and able to bind strongly to the first row transition metals of Cr(III), Fe(III) and Cu(II), in a manner analogous to other reported tridentate nitrogen containing ligands. These crystals were characterized by single crystal X-ray Diffraction, FT-IR and Elemental Analysis. From the data complied, the BDTP ligand was found to bind in a similar manner to three different metal centers with the lateral metal-N bonds being longer than the metal-N bond to the pyridine ring. It was also discovered that when the metal is bound to the ligand, the ligand puckers to bind and is no longer a planar molecule (Note:

accommodation of the smaller diameter of the first row transition metals suggests that complexation of the larger f-elements might not suffer this particular complication).

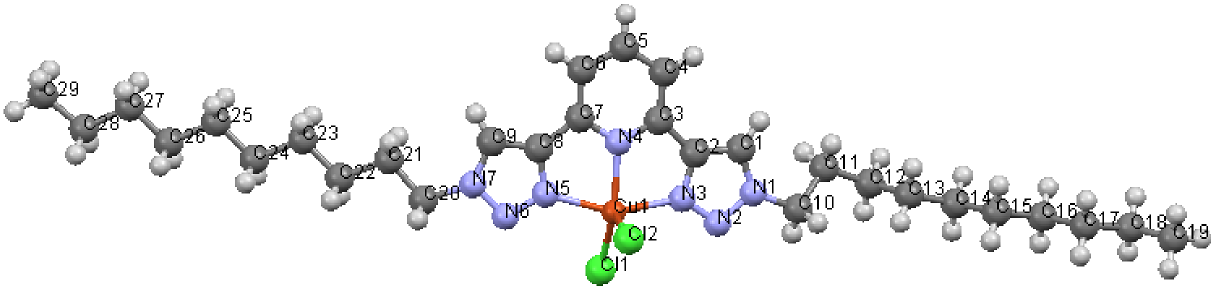
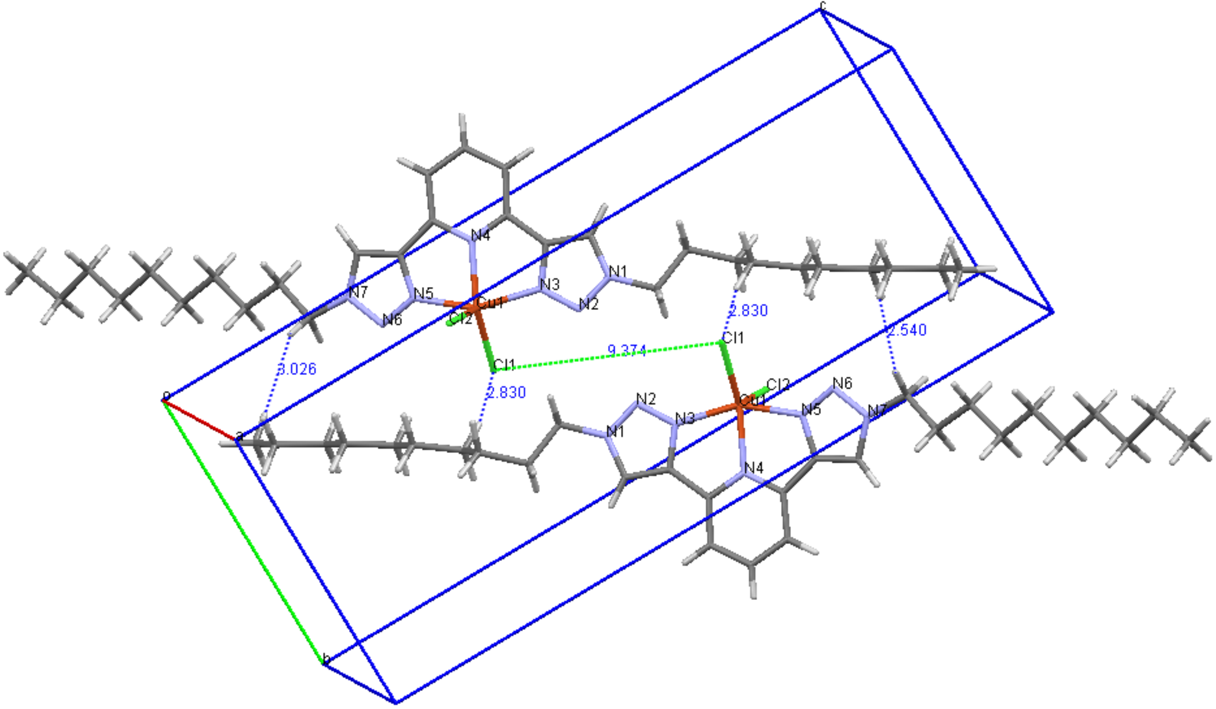


Figure 4: Packing of $CuLCl_2$ (**2**).



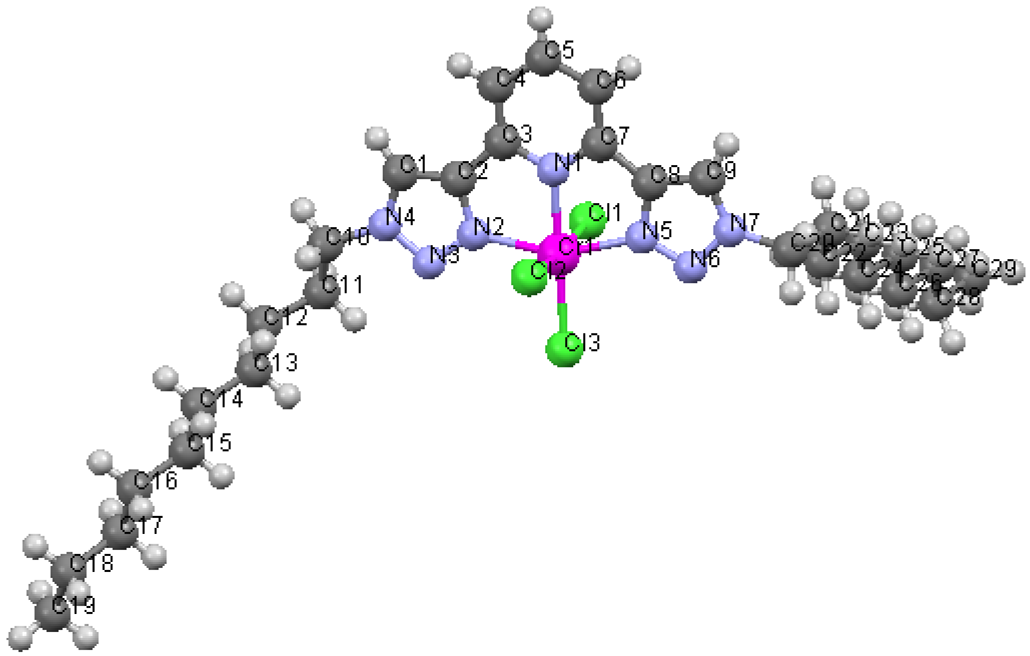


Figure 6: Packing of $CrLCl_3$ (**3**).

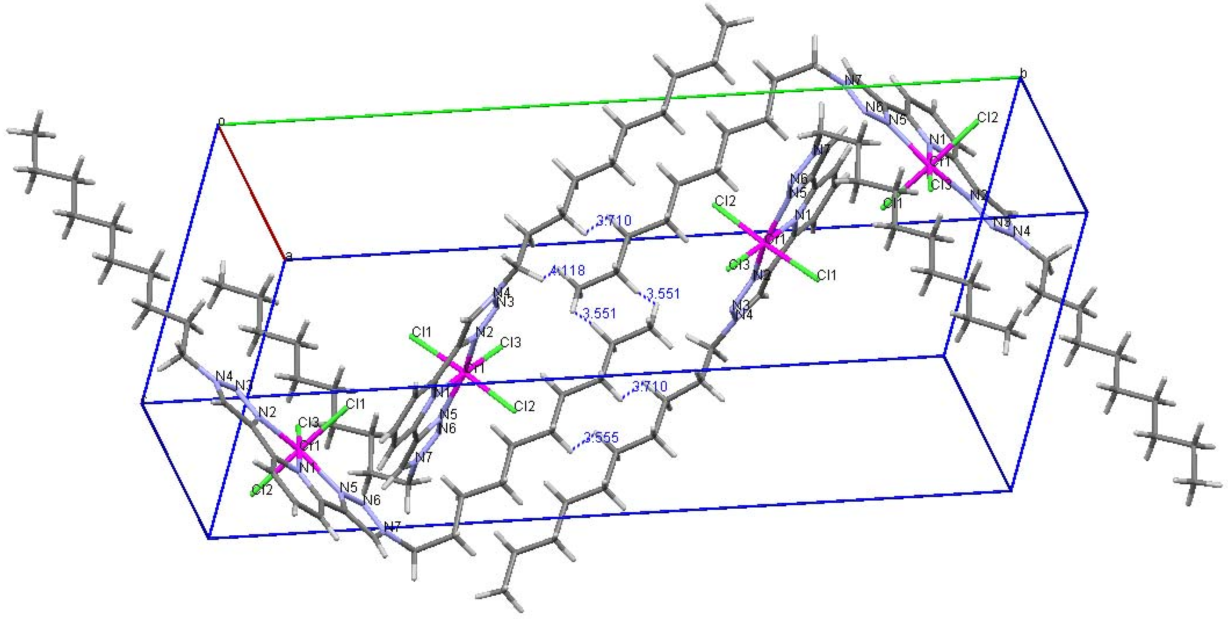


Figure 7: Crystal structure of *$FeL_2{\cdot}Fe_2OCl_6$* (***4***).

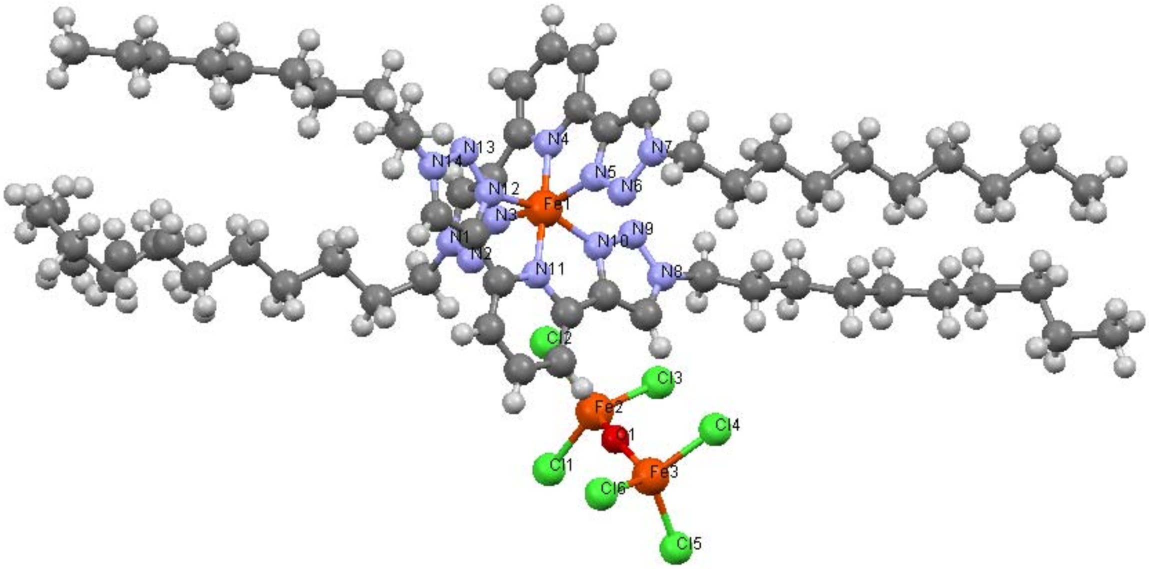
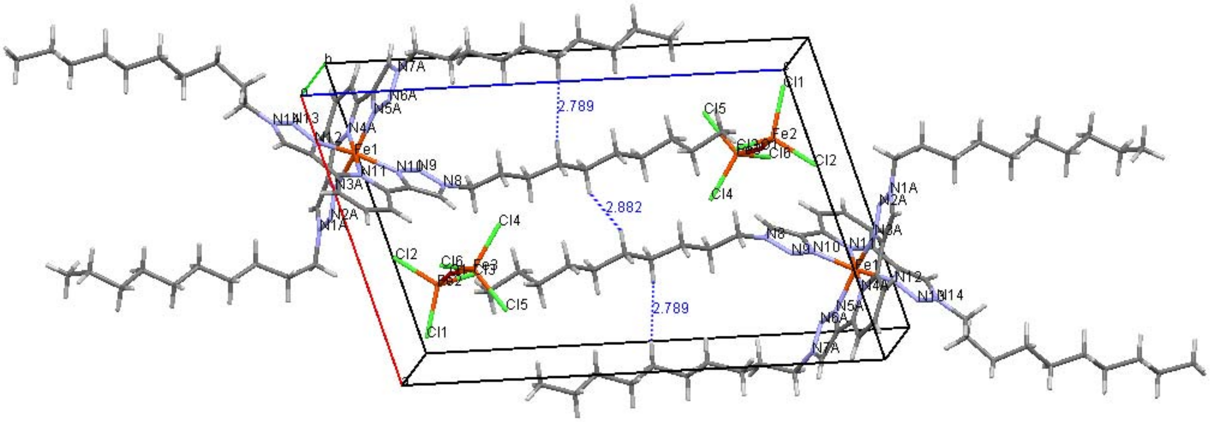


Figure 8: Packing of $FeL_2 \cdot Fe_2OCl_6$ ***(4)***.



References this section.

1) Li, Y., Huffman, J. C., Flood, A. H. Chem. Commun., 2007, 2692-2694.

2) Schulze, B., Friebe, C., Hager, M. D., Winter, A., Hoogenboom, R., Gorls, H., Schubert, U. S. Dalton Trans., 2009, 787-794.

3) Alvarez, S. G. and M. T. Alvarez. Synthesis. 1997, (4), 413-414.

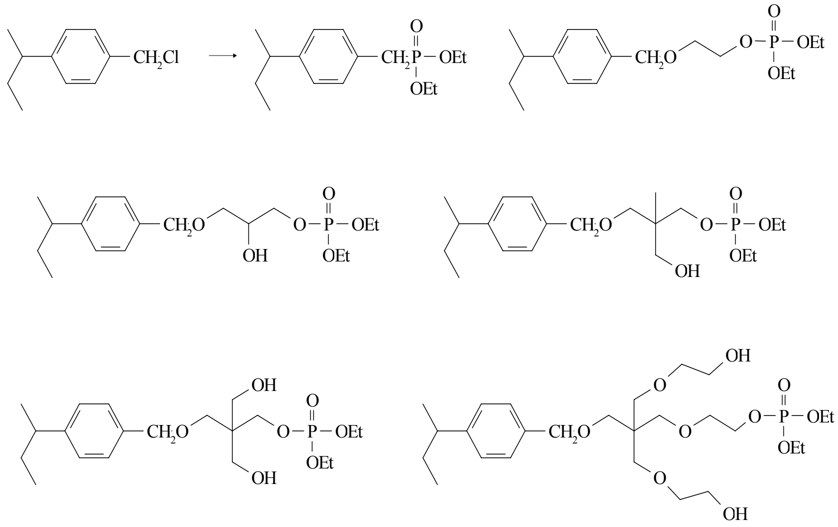
4) Sonogashira, K. J. Organomet. Chem. 2002, 653(1-2), 46-49.

Subtask 4. Functional Polymers for Actinide Partitioning

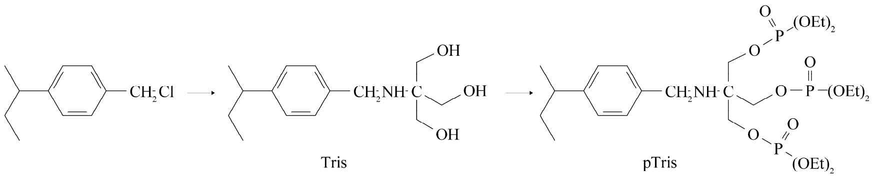
S.D. Alexandratos, Hunter College of the City University of New York

Background. The immobilization of ligands onto crosslinked polymer beads is an important methodology for metal ion separations. Immobilization of the complexants via covalent bonding onto polymer beads that are insoluble through crosslinking provides a route to making the separations process environmentally compatible. The separations can be carried out in a column as the aqueous phase passes through the beads and, after complexation, the polymer can be regenerated by elution with (oftentimes) an acid or base or can be treated as solid waste, depending on the value or toxicity of the metal ion. Besides operational simplicity: the polymer offers a unique microenvironment in which the electronic character of the ligands can be manipulated. This ‘microenvironmental effect’ has been observed when the beads are used as catalysts and in the complexation of the uranyl ion.

The polymers to be modified for actinide separations were prepared as beads by suspension polymerization of vinylbenzyl chloride (VBC) with a particle size of 250 – 400 µm to facilitate separations under continuous conditions. The microenvironment surrounding the tethered ligands can be varied to varying levels of polarity by preparing polymers with the VBC copolymerized with other monomers, including methyl methacrylate, methacrylic acid, and acrylamide. Polyethyleneimines will also be immobilized in a way that will give monosubstitution through one amine site and disubstitution through both $-NH_2$ sites on a given molecule to give a pseudo-macrocyclic ligand in the same way that pseudocrown ether have been formed $^{(87)}$. They will be further functionalized to give polyaminocarboxylates. Furthermore, recent theoretical calculations have shown that diamides have high actinide affinities $^{(89)}$ and these results will be extrapolated to the preparation of immobilized ligands based on tetramethylmalonamide.



A key electronic property that allows for the separation of actinides from lanthanides is the ionic polarizability. It has been shown that a phosphate diester ligand can be placed within different microenvironments formed by –OH groups through monophosphorylation of immobilized glycerol, tris(hydroxymethyl)ethane, pentaerythritol, and triethoxylated pentaerythritol on polyVBC beads (the phosphonate diester and phosphorylated ethylene glycol were included as controls (see scheme below)) and that this results in increasing polarizability of the phosphoryl oxygen which, in turn, gives it an increasing affinity for softer ions such as Pb(II). The mechanism that allows for the increased polarizability is hydrogen bonding between the –OH groups and P=O ligand.



Since the phosphorylated pentaerythritol has been found to have a high affinity for the uranyl ion, it will be studied in the present context. The –NH- group has also been found to significantly enhance the ionic affinities of the phosphate ligand by immobilizing tris(hydroxymethyl)aminomethane (Tris) onto polyVBC and then phosphorylating it to give the pTris polymer noted in the equation below. A variety of new polymer-supported reagents are possible.

Two ancillary issues that are addressed with the functionalized polymers are radiation stability and the rate of complexation. If a broader range of radiation stability is required, then the functionalization reactions will occur on silica gel. Modifications reactions on silica gel are well known for a wide variety of ligands. The binding of the ligands can occur directly on the surface silanol groups or through a triethoxysilane intermediate. The functionalization reactions will also enhance the stability of the silica gel over a wider pH range. The highly porous nature of the silica gel leads to rapid rates of complexation. The rate of complexation should be rapid with the organic polymers as well since the crosslink level will be maintained at 2% divinylbenzene, but rate enhancement, if needed, is achievable by synthesizing the support with an expanded gel structure by adding a diluent such as toluene to the polymerizing solution of co-monomers. The wide flexibility of options for the creation of ion exchange materials, including the option of incorporating any or all of the cation receptors being designed in this program offer a range of separations options that we will adapt to optimize out favored separations targets. Tetramethyl malonamide functionalized resins were also prepared and their lanthanide/actinide binding affinity evaluated. The metal uptake characterization activities of both the phosphate resins and the malonamides are described in **Subtask 5.**

Subtask 5. Lanthanide/Actinide Coordination Chemistry and Separation Science

K. L. Nash, S. B. Clark (WSU), D. D. Ensor (TTU)

Background: A useful separation system is one that selectively isolates the target species from the initial mixture leaving the undesirable components of the starting mixture in the counter phase. For analytical-scale separations, high efficiency of partitioning in one or only a few contacts is most desirable. Process scale separations are often run under conditions that favor less than quantitative partitioning of the target in each separation stage with many stages run to amplify the effect of lower single stage efficiency. A shift in conditions should return the target to a new phase for further purification (as necessary), and allow recycle of the separations agent for another round of separation. Favorable thermodynamics are essential, but displacement methods can often make a separation work against a free energy gradient. In most cases, rapid kinetics are also preferred, so that process throughput can be maximized. The ability to operate the separations process in a continuous fashion is also generally preferred, though not essential. Both solvent extraction and ion exchange separations are amenable to such operations, though continuous recycle (reflux) is easier in solvent extraction than in ion exchange or other solid-liquid techniques (e.g., precipitation).

In the design of chelating agents and the development of processes separating radioactive materials, it is critical that the following four factors not be ignored: *1) relative complex stability, 2) phase compatibility, 3) radiolytic/hydrolytic stability and 4) rapid ligand exchange/phase transfer kinetics*. *Relative complex stability* will determine the affinity of the material for the target ion and its ability to reject the contaminants. *Phase compatibility* considers whether the complexant will be water miscible, lipophilic, insoluble in everything or in need of immobilization in a polymeric matrix. *Radiolytic and hydrolytic stability* must be determined by direct consideration of the stability of the material and will require its intentional damage and analysis of the products of decomposition. *Rapid kinetics* is almost always desirable, but it is possible to develop separation strategies based on differences in rates. Examination of relative complex stability of the material for the target ion and the species to be rejected is the first essential test that must be passed for any material to prove useful. Therefore, the characterization of new materials will always start with an evaluation of the relative stability of actinide and lanthanide complexes. It is wise to employ oxidation state/structural analogs where needed (for example, because of redox instability) and important to always consider cross series trends in the lanthanides. Standard and radioanalytical methods of analysis should be used liberally. Previous experience indicates that studies of the stability of Cu^{2+} of amine complexes represents a useful rapid analysis tool for actinide-lanthanide separation ligand evaluations. All other factors are considered only after the new material passes this first test. Many of the same techniques will still apply for the secondary characterization. In this portion of the program, the emphasis is placed on study of the basic thermodynamics and kinetics of metal-ligand interactions in the primary screening of the systems.

Conduct of the Complexant Evaluation Process: As has been done in earlier work, the evaluation of new materials and the ultimate development of new separations systems will grow out of a process of discovery of the basic features of the interactions of the target metal ions with the new materials. The partners in this program with specific responsibilities for preparing new materials are well versed in the art and science of ligand design. The target compounds are based at least to some degree on ligand architectures and functional groups that have been considered in some variation previously. Because the energetic differences supporting a successful separation are so small, quantum leap changes in ligand designs are not needed to develop successful separations procedures. In fact, one of the greatest utilities of solvent extraction is the ability to manipulate so many features of the separation system. A successful separation is often derived from the cumulative effect of a summation of small variations in relative interaction strength between the separations media and the target metal ions. Minimizing the impact of enthalpy-entropy compensation effects is often central to a successful separation.

The process of evaluation of the separation potential for the new complexants and polymeric materials being synthesized in Subtasks 1-4 demanded a significant amount of effort in both fundamental coordination chemistry of f-element complexes (and relevant analog systems, as in the aforementioned Cu^{2+} studies), and “applied” evaluations of the separations performance of the new species. The coordination chemistry evaluations followed the patterns that have been employed for decades, combining radiotracer studies with macro-scale spectroscopic and other evaluations of cation-ligand-solvent interactions. Where appropriate, structural studies have been conducted. However, as the most relevant information is based on the behavior of these metal ions and complexes in fluid phases, to a significant degree both the coordination chemistry and separations science of the systems relies on fundamental thermodynamics and kinetics of metal-ligand-solvent interactions in fluid phases. Studies of analog systems also provide useful guidance. Our suite of analytical methods that are routinely conducted in ligand design activities include (in addition to various radioanalytical techniques) potentiometry, electrochemistry, calorimetry, UV-visible-NIR spectrophotometry, stopped-flow spectrophotometry (fast reaction kinetics), multinuclear NMR spectrometry, FTIR, ICP-AES and ICP-MS. Similar facilities are available at each of our National Lab partner institutions with the addition of selected other facilities (e.g., laser induced fluorescence).

WSU Clark Group investigations. The major work done in this project is to evaluate the following ligands for their potential usage in solvent extraction for separation of trivalent lanthanides and actinides. All these ligands are soft donors (N), which should provide for discrimination between the trivalent lanthanides and actinides. With significant responsibility for evaluating the separations performance of polyaza complexing agents, progress in this area was hindered by the pace of preparation of new complexing agents. Some effort was diverted to the characterization of uranyl gluconate complexation and stability, resulting in a publication that complemented other work done on metal complex characterization in this program . The gluconate results are not described here.

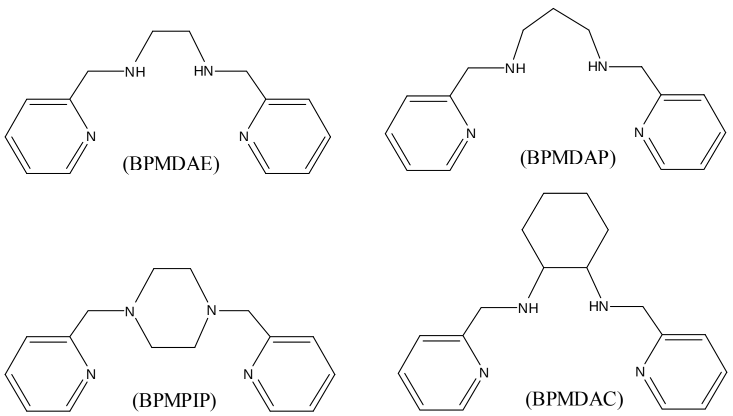
1. Aliphatic amine derivative ligands

Scheme I shows structures of amine derivative ligands synthesized previously. For those ligands, the following work was conducted:

1.1 Evaluation for solvent extraction application

- Studies of distribution ratios of ligands: Organic phase: n-octanol/cyclohexane (volume 20/80); aqueous phase: acidic nitrate solutions. Distribution ratios of all ligands are near zero. (Figure 1)
- Tests of solubility: All ligands have good solubility in both organic and aqueous phases (> 20 mM). Unfortunately, they are too soluble in the aqueous phase. (see Figure 1)
- Suggestions: The ligands need to be modified to increase their affinity to organic phase to allow their use in solvent extraction.

Scheme I



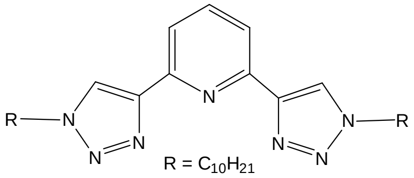
1.2 Coordination with lanthanides

- These ligands appear to weakly bind to tri-valance lanthanides in slightly acidic aqueous solutions. Any binding that occurs appears to form outer-sphere complexes because no shift of the hypersensitive band of Nd(III) was observed when the ligand was added to Nd(III) solution.(see Figure 2)

2. Bis-Triazolyl Pyridine

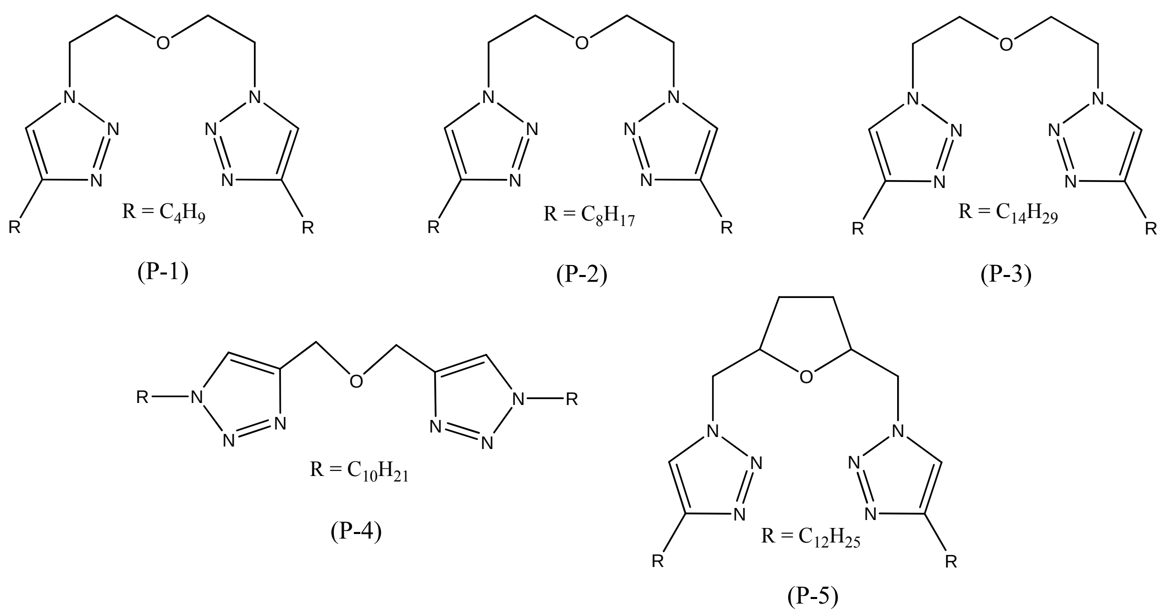
Scheme II is a structure of bis-triazolyl pyridine ligand. It was synthesized in Subtask 3. Ligand solubility was tested. The ligand has good solubility in n-octanol/cyclohexane, and is nearly immiscible in water. Therefore, it shows promise as a separation agent for solvent extraction. However, when the ligand was in contact with the organic phase for any significant length of time, it precipitated. This suggests that this ligand is not stable in the solvent extraction system that was used. As a result, no further evaluation was conducted for this ligand.

Scheme II



(C-1)

Scheme III



3. Bis-triazolyl ethers

Scheme III shows structures of bis-triazolyl ether ligands synthesized by Prof. Patrick Meier. In this series of ligands, length of alkyl groups on a triazolyl group was varied, which affects the ligand’s affinity for the organic phase. The following work was conducted or planned.

Solubility tests

The solubility of those ligands was tested in various media, including water, nitrate solutions, 20% octonol / 80% cyclohexane (v/v), decane and toluene. The results were listed in Table 1. It is evident that the P-2 ligand (C8-BTEE (bid-triazolylethyl ether)) is a good candidate for the further investigation because of its strong affinity to organic solvents. Also, toluene appeared to be a good choice as an organic phase for the solvent extraction work.

Determination of separation factor of C8-BTEE for Eu(III) and Am(III)

The experimental determination of distribution ratios of Eu(III) and Am(III) with C8-BTEE as an extractant was planned but was not completed. HTTA is proposed as a synergistic ligand in the planned solvent extraction work.

Table 1. Solubility of bis-triazolyl ether ligands in various media (unit: mM)

Ligand ID	**Water**	**Nitric acid (0.5M)**	**20%Octanol/ 80%Cyclohexane**	**Decane**	**Toluene**
P-1	2.5-5.0		>20	<5	>20
P-2	.<1	<1	10 - 20	<5	>20
P-3	<1		<5	<5	5-10
P-4	<1		~5	<5	~10
P-5	<1		<5	<5	<10 (~5)

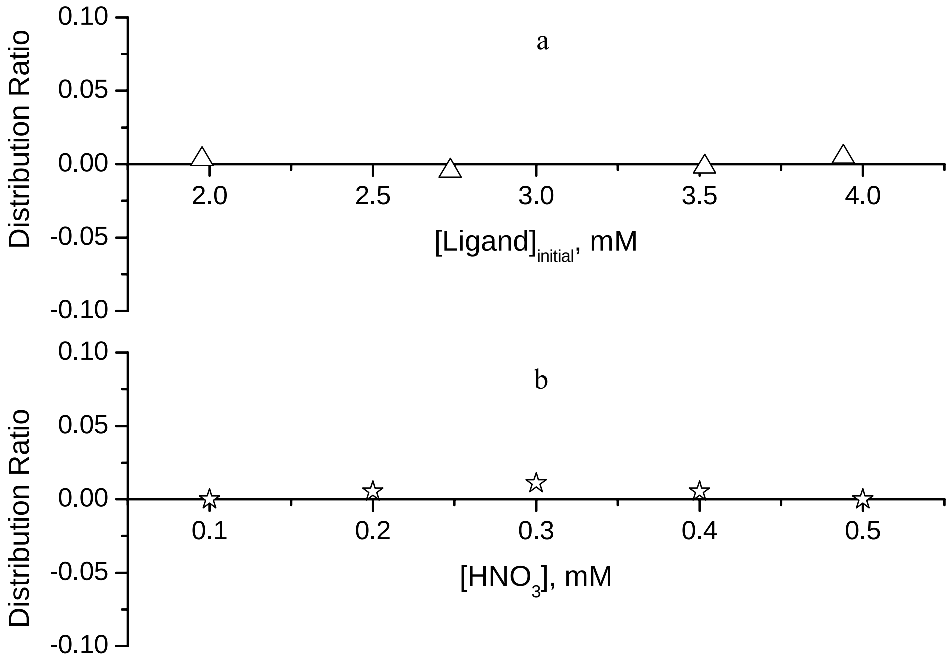


Figure 1. Distribution ratios of ligand BPMDAE. (a) varied ligand concentrations with 0.1 M nitric acid, $[\text{Nitrate}]_{\text{total}}$ = 0.5 M; (b) varied nitric acid concentrations with 3.0 mM ligand, $[\text{Nitrate}]_{\text{total}}$ = 0.5 M.

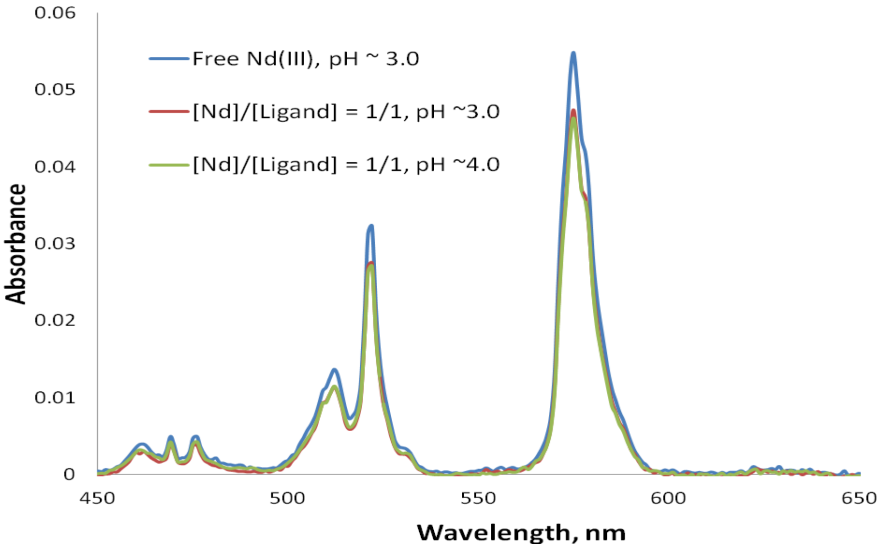


Figure 2. Absorbance spectra of ligand BPMDAE with Nd(III) in weakly acidic solutions. To a free Nd(III) solution, an aqueous solution of ligand A and 1 M NaOH solution were added, separately, to reach the desired metal/ligand ratio and pH. Upon each addition, an absorbance spectrum was taken.

WSU Nash Group Complex/materials characterization. Metal complex, complexant, separations performance evaluations were accomplished using a variety of complementary observation techniques, many involving radioanalytical chemistry methods. In some areas the availability of new materials became rate a limiting step and characterization of existing systems was extended. TALSPEAK studies are reported here.

Complexation of Am(III) and Nd(III) by 1,10-Phenanthroline-2,9-dicarboxylic acid

Mark D. Ogden, Serguei I. Sinkov, Mikael Nilson, Gregg J. Lumetta, Robert D. Hancock and Kenneth L. Nash

The complexant 1,10-phenanthroline-2,9-dicarboxylic acid (PDA) is a planar tetradentate ligand that is more preorganized for metal complexation than its unconstrained analogue ethylendiiminodiacetic acid (EDDA). Furthermore, the backbone nitrogen atoms of PDA are aromatic, hence are softer than the aliphatic amines of EDDA It has been hypothesized that PDA will selectively bond to trivalent actinides over lanthanides. In this report, the results of spectrophotometric studies of the complexation of Nd(III) and Am(III) by PDA were reported. Because the complexes are moderately stable, it was necessary to conduct these titrations using competitive equilibrium methods, competitive cation complexing between PDA and diethylenetriamine-N,N,N’,N”,N”-pentaacetic acid (DTPA) and competition between ligand protonation and complex formation in PDA-metal solutions. Stability constants and ligand protonation constants were determined at 0.1 M ionic strength and at 0.5 M ionic strength nitrate media at 21±1 ºC. Metal complex species indicated in the data fitting include $M(PDA)^+$ and $M(PDA)_2^-$ as the dominant metal complex species. $Am(PDA)_2^-$ is seen in the PDA neutralization experiments to be about 40 times stronger than the corresponding $Nd(PDA)_2^-$ complex. Discrepancies between the fitting of the spectrophotometric data by the two techniques ultimately left concerns about the accuracy/completeness of the metal DTPA complexes in the existing literature.

The derived stability constants are lower than those predicted from first principles and speciation calculations indicate that Am^{3+} selectivity over Nd^{3+} is less than that exhibited by 1,10 phenanthroline. The spectrophotometric studies were conducted at the Pacific Northwest National Laboratory. Spectra for Nd(PDA) and Am(PDA) complexes are shown in Figures 1 and 2.

In general, the fitting of values to PDA complexation and protonation constants is challenging due to limitations of the amount and reliability of data available in the literature for not only PDA but also for some limitations in DTPA information. A more precise determination of the Nd/Am PDA interaction parameters would be obtained if it were possible to accurately account for Na^{+}-association with both ligands. However, estimates can be made to give more likely values, i.e. values that match well with previous observed trends in thermodynamic data from the literature. The values for protonation of the free PDA ligand at 0.5 $mol \cdot L^{-1}$ $NaNO_3$ and stability constants for Am^{3+} and Nd^{3+} in solution at 0.1 M and 0.5 $mol \cdot L^{-1}$ are report in a manuscript that is in press in the Journal of Solution Chemistry.

Even though the complexation values are high, the selectivity of PDA for Am^{3+} over Nd^{3+} is lower than expected perhaps because of the effect the electron withdrawing carboxylate groups have upon the phenanthroline backbone nitrogen atoms. Considering the comparison of $\log_{10} K_{101}$ Am(III) with $\log_{10} K_{101}$ Nd(III) (Figure 3) the selectivity of PDA falls on the same line as other polyaminocarboxylates at 0.1 and 0.5 $mol \cdot L^{-1}$ ionic strength. This Linear Free Energy Relationship demonstrated an actinide selectivity increase of approximately 7% relative to the purely ionic carboxylate complexant model, as has been reported previously by Choppin and coworkers.

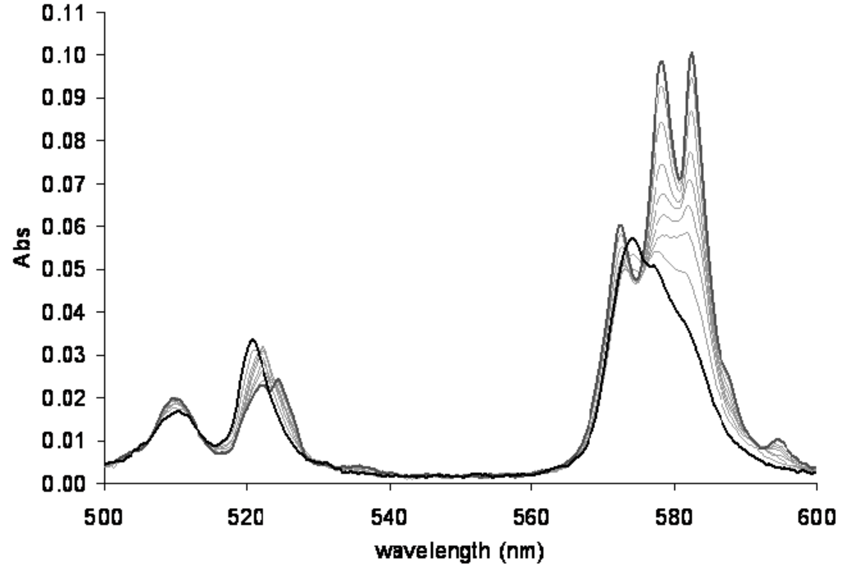


Figure 1. Spectra of Nd^{3+} (2.00×10^{-5} $mol \cdot L^{-1}$) and PDA (7.00×10^{-5} $mol \cdot L^{-1}$) as a function of pH at high acidity (pH 0.30 to 2.55) and 0.5 $mol \cdot L^{-1}$ ionic strength. The black line is the start point (pH 0.30) and the grey line the end point (pH 2.55).

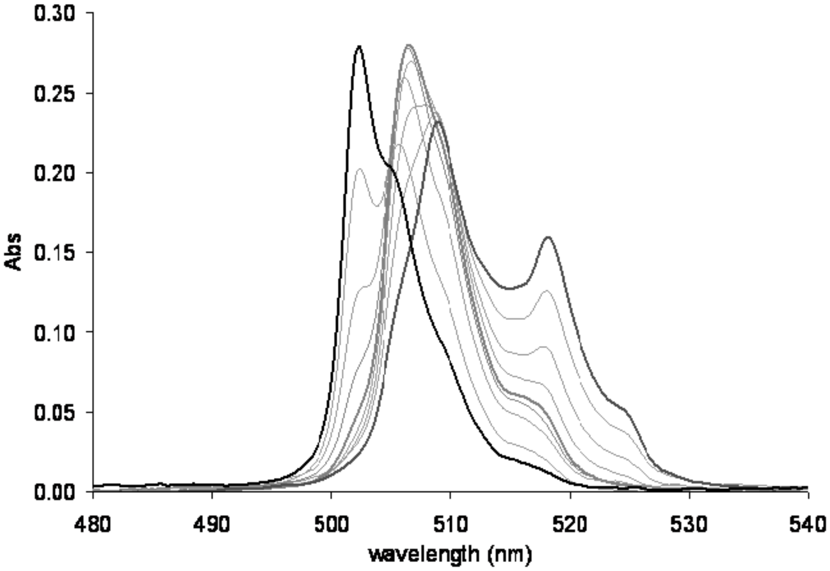


Figure 2. Spectra of Am^{3+} (2.00×10^{-6} mol·L^{-1}) and PDA (7.00×10^{-6} mol·L^{-1}) as a function of pH at high acidity (pH 0.30 to 2.55) and 0.5 mol·L^{-1} ionic strength. The black line is the start point (pH 0.30) and the grey line the end point (pH 2.55). The 1:1 Am(III)PDA species is highlighted by the thick light grey line.

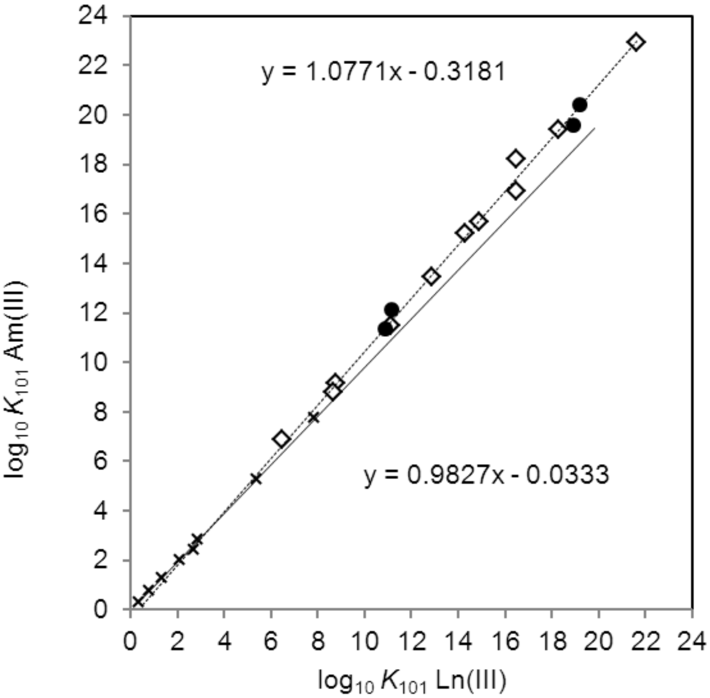


Figure 3. Plot of $\log_{10} K_{101}$ for Nd^{3+} versus Am^{3+} of selected polyaminocarboxylates (◇); ● = PDA values for ML^+ and ML_2^- complexes at 0.1 and 0.5 mol·L^{-1} ionic strength; and × = carboxylic acids. Values for selected carboxylates and polyaminocarboxylates with Am^{3+} and Ln^{3+} are taken at 0.1 mol·L^{-1} ionic strength and 25 ºC.

Even though PDA shows promise for a wide variety of applications, its utility is hindered by its low solubility in aqueous solutions (~10^{-4} mol·L^{-1} in alkaline solution, less in acidic media). To date, attempts at derivatization to improve lipophilicity of this moiety (as conducted by the Hancock group) has not produced a candidate reagent with adequate solubility in an organic solvent that would enable its use as an extractant. Almost certainly, the solubility limitation of this class of reagents is a result of the ease with which the extended aromatic network packs in the solid state. Functionalization in the aromatic backbone will almost certainly be required to improve the solubility of PDA derivatives in either aqueous or organic media. Alternatively, if the phenanthroline backbone of PDA could be sulfonated, the aqueous solubility of the ligand could be increased. Sulfonation is likely to alter the basicity of the metal complexing atoms, so tany sulfonated compounds would have to be reassessed as complexants. Similarly, the introduction of aliphatic substituents in the aromatic ring system at some combination of the 4, 5, 6, and 7 ring positions would potentially provide a surfactant-like configuration that would result in a reagent more useful for solvent extraction applications. The potentially less daunting option of immobilizing PDA in a polymeric matrix was considered, but a suitable linker was not identified. A concept that was not explored in this investigation, but potentially which is worthy of consideration would be to attempt such functionalization with the objective of making the reagent compatible with unconventional media like room temperature ionic liquids, supercritical CO_2 or the fluorinated diluents favored in separation systems developed in Russia.

It must be noted that it is unclear how the addition of a strong electron withdrawing sulfonate group (or some groups that might improve lipophilicity) to the backbone would affect the electron density of the phenanthroline backbone nitrogen atoms and hence the selectivity of the ligand. PDA could also potentially be made compatible with organic diluent either by addition of alkyl chains to the phenanthroline backbone or by conversion of the carboxylate groups to alkylated amides. The selectivity of PDA for Am^{3+} over Nd^{3+} could then be used to effectively separate one from the other using solvent extraction methods. Although this report attempts to investigate the presumed selectivity of PDA for An(III) over Ln(III), a more thorough and systematic study of lanthanide complexation is required to ascertain the lanthanide trend and the overall compensation effect of PDA binding. This needs to be complemented by Na^+ complexation studies of DTPA and PDA at relevant ionic strengths. However, these development pursuits will not produce reagents useful for hydrometallurgical separations applications without significant increases in reagent and complex solubility.

Optical Spectroscopy Study of Lanthanide Organic Phase Complexes in the TALSPEAK Separations Process

Travis S. Grimes, Guoxin Tian, Linfeng Rao, Kenneth L. Nash

Time-Resolved Fluorescence Spectroscopy (TRFS) and FT-IR spectroscopy were applied to characterize the coordination environment of lipophilic complexes of Eu^{3+} with di-(2-ethylhexyl)phosphoric acid (HDEHP) and 2-ethylhexyl phosphonic acid, mono-2-ethylhexyl ester (HEH[EHP]). The focus of the study was on understanding the role of lactate in lanthanide partitioning into 1,4-diisopropylbenzene solutions of HDEHP or HEH[EHP] as it is employed in the TALSPEAK process for lanthanide/trivalent actinide separations. It is known that both lactate and lanthanides are extracted in this milieu. Reports from the prior literature have proposed a direct interaction between lanthanide cations, lactate and the extractant molecules in these organic solutions. The application of spectroscopic methods is seen as a means of characterizing the nature of this interaction. Samples prepared by quantitative partitioning of 1.0 mM Eu^{3+} from 0.01-2.0 M lactate buffer media (pH. 3.6) demonstrate no significant fluorescence emission intensity changes in the $^5D_0 \rightarrow {}^7F_1$ transition (590-600 nm) or the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ (615-620 nm) in the HDEHP systems, despite an increase in the organic phase lactate concentration as the aqueous lactate concentration increases. This observation establishes that there is no interaction between organic phase lactate and extracted Eu^{3+} under these conditions. As the total lanthanide concentration is increased (by the addition of up to 0.037 M La^{3+}), the $^5D_0 \rightarrow {}^7F_1$ transition singlet is seen to split into a doublet with a large increase in intensity observed for both the $^5D_0 \rightarrow {}^7F_1$ and the $^5D_0 \rightarrow {}^7F_2$ electronic transitions. The increased multiplicity in the emission spectra indicates the existence of multiple Eu^{3+} coordination environments. The increased emission intensity of the 618 nm band implies an overall reduction in symmetry of the extracted Eu^{3+} complex in the presence of macroscopic La^{3+}. Fluorescence lifetime measurements indicate that the extracted complexes are all anhydrous. IR spectroscopy results confirm a direct Ln^{3+}-lactate interaction at high concentrations of lanthanide and lactate in the extractant phase. These observations are interpreted to indicate that at high concentrations of metal ions, a mixed complex of stoichiometry $Ln(Lac)(AHA)_2$ may dominate the speciation of lanthanide complexes in TALSPEAK extractant phases. This work has been submitted for publication in Inorganic Chemistry.

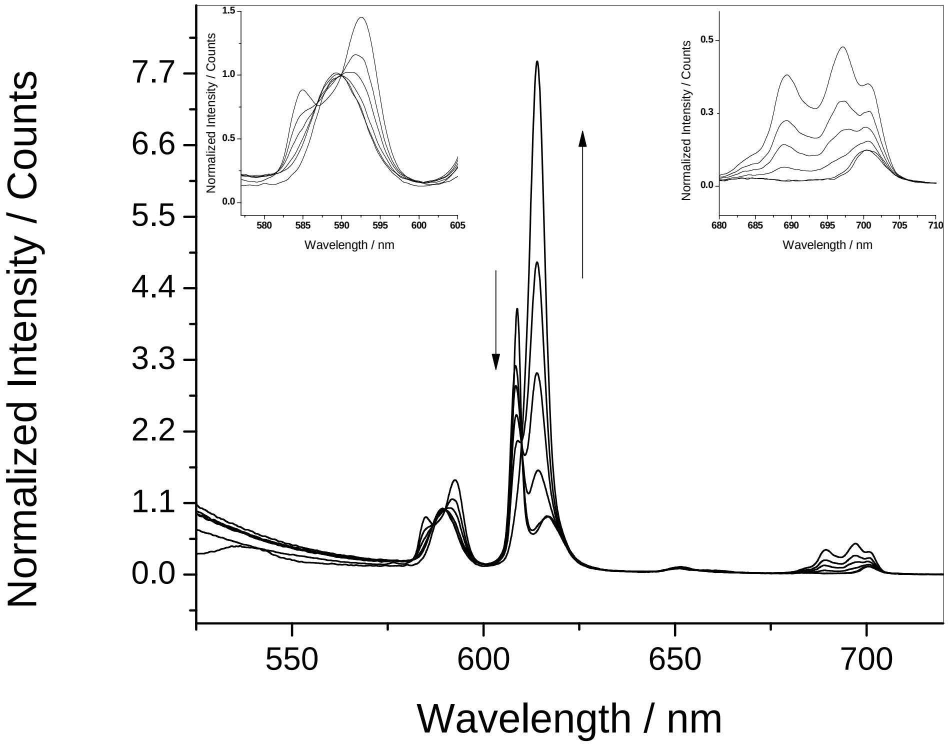


Figure 1. Emission spectra for extracted Eu^{3+} complexes under loading conditions. La^{3+} was used to load the organic phase with a 0.001 M Eu^{3+} spike to promote fluorescence. The excitation wavelength for these experiments was 464 nm. The aqueous conditions are as previously described. The La^{3+} concentrations for metal loading were, 0.001M, 0.003 M, 0.010 M, 0.017 M, 0.025 M, and 0.037 M.

Spectroscopic measurements of organic extractant solutions relevant to the TALSPEAK process have revealed that all extracted complexes are, as expected, completely dehydrated. This result would seem to eliminate the possibility of reverse micelles or microemulsions as important species in such organic phases. Lactic acid partitioning experiments have established a terminal 3:1 HDEHP:HL ratio, suggesting a possible direct interaction between the two molecules. More experiments are needed to confirm this possible interaction.

Under most conditions, the dominant extracted species is the well-known 1:6 complex $Ln(AHA)_3$ in which the Ln^{3+} ion is coordinated with three HDEHP (or HEH[EHP]) dimers. As the lactate concentration increases, the fluorescence emission reveals that no large changes are occurring in the inner coordination sphere of the complex, suggesting the dominant extracted species at low Ln^{3+} concentration is present in the organic phase as previously described. When the ratio of extractant to Ln^{3+} drops below the conventional stoichiometric limit of 6:1, it appears the lactate becomes directly involved in the extracted complex. The previous ^{31}P NMR/ESI-MS study has identified a bimetallic complex species, $La_2(Lac)_2(DEHP)_4$, as the dominant species in HDEHP samples created from high lactate media and containing high lanthanide concentrations. The present results are consistent with the earlier reported speciation. As this change in stoichiometry occurs only at high metal loading, the development of thermodynamic models to explain anomalous features of lanthanide extraction in TALSPEAK has been directed toward more complete profiling of the role of interactions of the extractant HDEHP with both Na^+ and lactic acid extraction in conventional TALSPEAK separations. This result has also spurred interest in identifying new combinations of cation exchanging extractants and aminopolycarboxylate complexants.

Acid Dissociation and Rare Earth Stability Constants for DTPA

Travis S. Grimes and Kenneth L. Nash

To support more accurate modeling of the thermodynamics that govern TALSPEAK separations, the acid dissociation constants and stability constants for rare earth complexes with diethylenetriamine-N,N,N',N",N"-pentaacetic acid (DTPA) have been determined in 2.0 M ionic strength ($NaClO_4$) media. The acid dissociation constants for DTPA and the stability constant for $Eu{\cdot}DTPA^{2-}$ were also determined in sodium trifluoromethanesulfonate (established as a thermodynamic analog for lactate ion as a supporting electrolyte) at 2.0 M ionic strength to assess the potential impact of changing the nature of the electrolyte. Speciation plots show the details of $Ln{\cdot}DTPA^{2-}$ complexation and free DTPA ligand species using experimentally determined thermodynamic parameters at 2.0 M ionic strength ($NaClO_4$ and sodium triflate). These results have been compared to 0.1 M literature values (KNO_3). The available free energy data in the literature for $Ln{\cdot}DTPA^{2-}$ complexation was compiled and compared with the results of this study. Analysis of the trends in the compilation of data is reported. Thermodynamic parameters are used to construct speciation plots to predict $Ln{\cdot}DTPA^{2-}$ complexation during a titration of a metal/lactate solution with DTPA in TALSPEAK media (1.0 M lactate, pH 3.6).

Potentiometric titrations have been conducted to determine protonation constants and stability constants for DTPA and corresponding rare earth metal complexes at 2.0 M ionic strength. Ionic strength was adjusted with two different background electrolytes, $NaClO_4$ and sodium triflate. Stability constants β_{101} and β_{111} have been determined and both were compared to 0.1 M ionic strength data. Experimental data shows the $Ln{\cdot}DTPA^{2-}$ and $Ln{\cdot}HDTPA^-$ complex stabilities increase from La^{3+} to Gd^{3+} then, remain constant from Dy^{3+} through Lu^{3+}. This is consistent with previous studies at different ionic strength media. Both the pK_a and log β values are smaller in 2.0 M ionic strength media than the 0.1 M systems. The pK_a values are smaller in sodium triflate media, but all pK_a values determined in this study (regardless of background electrolyte) are on the same order of magnitude.

Speciation calculations were conducted to compare the relative stability of the $Eu{\cdot}DTPA^{2-}$, $Eu{\cdot}HDTPA^{-}$, and free DTPA ligand in 0.1 M KNO_3, 2.0 M $NaClO_4$ and 2.0 M NaO_3SCF_3. The speciation differences are slight and application of this internally consistent data set to the speciation in TALSPEAK system gives results as expected. Additional speciation calculations were conducted in a simulated titration to determine the stability of $Ln{\cdot}DTPA^{2-}$ complexation in the presence of concentrated lactate media. The calculations determined the stability of the $Ln{\cdot}DTPA^{2-}$ complexes in concentrated lactate medium are identical across the lanthanide series. Titration results using thermodynamic parameters determined in 2.0 M sodium triflate matched the results observed in the $NaClO_4$ media. It appears from the Na triflate data that a concentrated lactate medium should have little effect on the log β_{101} for the $Eu{\cdot}DTPA^{2-}$ complex under traditional TALSPEAK conditions. These results have been employed as the launching point for the determination of complexation enthalpies and entropies using calorimetry. Ultimately, these investigations target the development of procedures for the conduct of "entropy titrations" that in principle will enable the determination of a complete suite of thermodynamic parameters describing lanthanide speciation in complex media like the concentrated lactate buffer background electrolyte of TALSPEAK.

Table 1. Acid dissociation constants in 2.0 M $NaClO_4$ and sodium triflate (this work). The data from NIST Database [1], Gritmon et al. [2], Tian and Rao [3], and Thakur et al. [4] are a selection of known pK_a values for DTPA at various ionic strengths.

			Ionic Strength			
	0.1 M[a]	0.5 M[b]	1.0 M[c]	2.0 M[c]	2.0 M[c]	2.0 M[d]
	NIST Database[1]	Gritmon et. al.[2]	Tian and Rao[3]	Thakur et. al[4]	This	Work
Species	log K_a	log K_a	log K_a	log K_a	log K_a	log K_a
HL	10.48	9.86	9.43	9.46	9.50 ± 0.01	9.20 ± 0.01
H_2L	8.60	8.32	8.26	8.28	8.31 ± 0.01	8.06 ± 0.01
H_3L	4.28	4.12	4.23	4.13	4.38 ± 0.01	4.25 ± 0.01
H_4L	2.60	2.85	2.56	2.64	2.53 ± 0.03	2.68 ± 0.01
H_5L	2.00	1.95	2.37	2.12	2.41 ± 0.01	2.03 ± 0.03
H_6L	1.6					1.96 ± 0.02
H_7L	0.7					
H_8L	-0.1					

[a] K^+ salt used as background electrolyte.
[b] KNO_3 used as background electrolyte.
[c] $NaClO_4$ used as background electrolyte.
[d] Sodium triflate used as background electrolyte.

Table 2. Free energy and stability constants for Ln·DTPA^{2-} complexes in $NaClO_4$ and sodium triflate at 25 °C. The stability constants at 0.1 M ionic strength are from Moeller and Thompson [18].

		Ionic	Strength		
	[a]0.1 M[18]	[a]2.0 M	[a]2.0 M	[a]2.0 M	[b]0.1 M[18]
Metal	log β_{101}	log β_{101}	log β_{111}	log K_{111}	log K_{111}
Y	22.05	20.13 ± 0.02	21.87 ± 0.04	1.74 ± 0.03	1.91
La	19.48	18.02 ± 0.02	20.38 ± 0.03	2.36 ± 0.03	2.60
Ce	20.50	19.06 ± 0.01	20.77 ± 0.02	1.72 ± 0.02	—
Pr	21.07	19.64 ± 0.01	21.34 ± 0.02	1.71 ± 0.02	2.38
Nd	21.60	20.23 ± 0.01	21.57 ± 0.05	1.34 ± 0.04	2.39
Sm	22.34	20.79 ± 0.01	22.39 ± 0.02	1.59 ± 0.02	2.20
Eu	22.39	21.03 ± 0.01	22.56 ± 0.03	1.54 ± 0.02	2.15
Gd	22.46	21.15 ± 0.02	22.38 ± 0.02	1.23 ± 0.02	2.39
Tb	22.71	21.15 ± 0.01	22.77 ± 0.02	1.61 ± 0.02	2.14
Dy	22.82	21.23 ± 0.01	22.81 ± 0.02	1.58 ± 0.02	2.19
Ho	22.78	21.43 ± 0.02	22.76 ± 0.05	1.33 ± 0.05	2.25
Er	22.74	21.41 ± 0.02	22.66 ± 0.05	1.25 ± 0.05	2.00
Tm	22.72	21.10 ± 0.02	22.45 ± 0.05	1.35 ± 0.04	1.90
Yb	22.62	20.96 ± 0.01	22.53 ± 0.02	1.57 ± 0.02	2.30
Lu	22.44	21.14 ± 0.01	22.21 ± 0.05	1.07 ± 0.05	2.18
		2.0 M NaTriflate			
Eu		20.74 ± 0.01	22.48 ± 0.02	1.74 ± 0.02	

[a] KNO_3 used as background electrolyte.

[b] $NaClO_4$ used as background electrolyte.

References this section.

1) A.E. Martell, R.M. Smith, NIST Critically selected stability constants of metalcomplexes database, Version 8.0, 2004.
2) T.F. Gritmon, M.P. Goedken, G.R. Choppin, The complexation of lanthanides by aminocarboxylate ligands—I: Stability Constants, J. Inorg. Nucl. Chem. 39 (1977) 2021-2023.
3) G. Tian, L. Rao, Effect of temperature on the protonation of the TALSPEAK ligands: Lactic acid and diethylenetrinitropentaacetic acids, Sep. Sci. Technol. 45 (2010) 1718-1724.
4) P. Thakur, J.N. Mathur, R.C. Moore, G.R. Choppin, Thermodynamics and dissociation constants of carboxylic acids at high ionic strength and temperature, Inorg.Chim. Acta. 360 (2007) 3671-3680.

Explorations of TALSPEAK chemistry in extraction chromatography: Comparisons of TTHA with DTPA and HDEHP with [HEH]EHP

Jenifer C. Braley, Daniel McAlister, E. Philip Horwitz, Kenneth Nash Submitted for publication, Solvent Extraction and Ion Exchange

An advanced nuclear fuel cycle that supports transmutation includes a reprocessing stage for the group separation of the lanthanides from the trivalent actinides. The TALSPEAK (Trivalent Actinide - Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) solvent extraction process provides the An^{3+}/Ln^{3+} separation through the use of an organic lanthanide extractant (bis-2-ethyl(hexyl) phosphoric acid, HDEHP) and an aqueous actinide-selective holdback reagent (diethylenetriamine-N,N,N’,N’’,N’’-pentaacetic acid, DTPA). Organic phase interactions in TALSPEAK have proven sufficiently complex that, even with substantial research effort, a completely successful descriptive thermodynamic model has yet to be developed. If one were to consider an extraction chromatographic (EXC) version of TALSPEAK, the presence of concentrated extractant on the resin surface should augment the multifaceted organic phase chemistry. This study examines the previously unexplored impact of each aqueous phase TALSPEAK component (holdback reagent, carboxylic acid buffer, and pH) on the chemistry of the EXC system. The presence of alternative reagents, 2-ethyl(hexyl) phosphonic acid mono-2-ethyl(hexyl) ester acid (HEH[EHP]) and triethylenetetramine-N,N,N’,N’’,N’’’,N’’’-hexaacetic acid (TTHA) are also considered. Results indicate the concentrated extractant appears to enhance solid-phase reactions that most likely involve water, lactate and sodium. The presumed water, lactate and sodium partitioning consumes resin capacity sufficiently that the weaker hold-back reagent under TALSPEAK aqueous conditions (pH ~ 3.6), TTHA, provides preferential Am^{3+}/Ln^{3+} separations performance. If a TALSPEAK-EXC process were to be developed, a resin with solvent diluted extractant or covalently bound functional groups may be preferential to reduce the complexity of the solid-phase chemistry.

A fundamental examination of a solid-liquid application of TALSPEAK chemistry has been completed. The substitution of TTHA for DTPA in some experiments displayed the potential for improved Am/Eu separations. However, the associated increased retention of the light lanthanides will be undesirable in most circumstances. Since comparable lactate and pH dependences were observed using DTPA or TTHA (which saturates the coordination sphere of any lanthanide), the possibility of ternary complex formation, $M(Lac)(DTPA)^{-}$, in the aqueous phase seems unlikely. High concentrations of lactate (>1.0 M) seem to decrease metal extraction by changing the composition of the organic phase, not by retaining lanthanides in the aqueous phase through the $M(Lac)_4^{-}$ species. Both of these findings are in agreement with the recent literature. Fundamental differences in extraction trends were observed when HEH[EHP] was used in place HDEHP as the TALSPEAK organic extractant. The differences in extraction trends suggest complicating reactions involving lactate, sodium and water are more prevalent in the LN1 (HDEHP-based) resin. To improve the chemistry of the EXC system, the use of a resin with solvent diluted extractant or covalently bound functional groups may be preferential to minimize the effects of complex solid-phase chemistry.

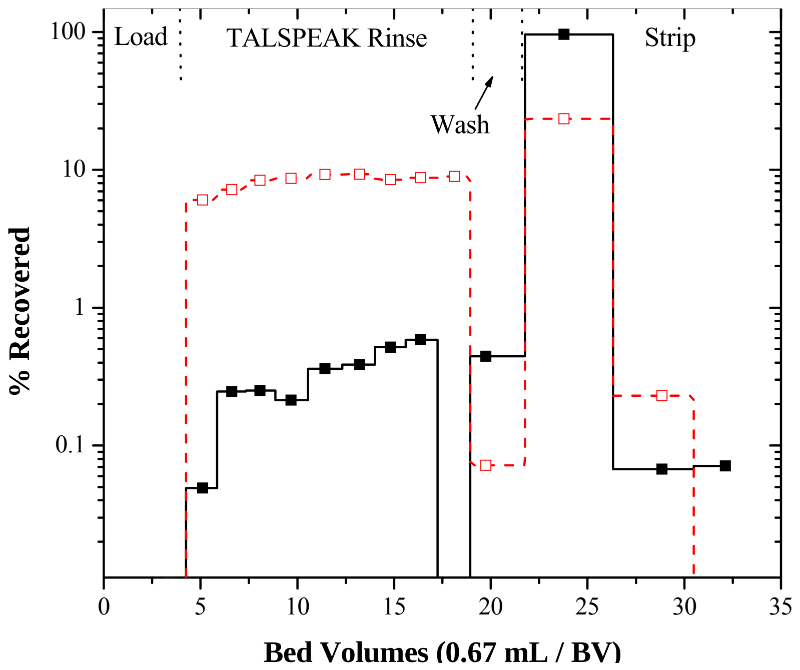


Figure 1. Optimized Lanthanide elution curve for Am^{3+} from the least extracted lanthanide (La^{3+}) during a simulated liquid waste separation using LN (HDEHP) S-grade (50-100 µm) Amberchrom GC71 resin. Flow rate: 1 mL / min. Column rinse volume: 20 mL. Column strip volume: 10 mL *Load:* 1 M Lactate, pH 3.3, Simulated Waste Concentrations of Lanthanides *TALSPEAK Rinse*: 2.5 mM TTHA, 1 M NO_3^-, pH 3.5 *Wash*: 0.001 M HNO_3 *Strip*: 1 M HNO_3
Lanthanide concentrations defined in Table 2.

Table 1. Optimized Lanthanide elution curve separation for all lanthanides using LN (HDEHP) S-grade (50-100 µm) Amberchrom GC71 resin. Flow rate: 1 mL / min. Column rinse volume: 20 mL. Column strip volume: 10 mL **Load***:* 1 M Lactate, pH 3.3, Simulated Waste Concentrations of Lanthanides **TALSPEAK Rinse**: 2.5 mM TTHA, 1 M NO_3^-, pH 3.5 **Wash**: 0.001 M HNO_3 **Strip**: 1 M HNO_3

Fission Product	Observation Wavelength (nm)	[Ln], mM	TALSPEAK Rinse %	Elution %	Total Recovery %
La		0.63	3.4	96.1	99.5
Ce		1.2	2.6	97.2	99.8
Pr		0.58	2.1	97.6	99.7
Nd		2.0	2.6	97.1	99.7
Pm		Trace	1.4	98.6	100
Sm		0.41	1.6	98.3	99.9
Eu		0.077	0.15	99.6	99.9
Gd		0.012	0.59	99.2	99.8
Tb		.0038	0.25	99.7	99.9
Dy		.0025	0.10	99.9	100
Y		1.7	>0.01	99.8	99.8
Am		Trace	75	25	100

INVESTIGATIONS INTO THE PROPERTIES OF NOVEL PHOSPHORYL BASED SOLVATING EXTRACTION RESINS

J. C. Shafer, S.D. Alexandratos, K. L. Nash

Characterization of the pPenta, pTris and pTris-Mono resins (Figure 1) produced by Dr. Alexandratos has been completed. Infrared spectra and NaOH titrations and IR spectra performed initially after synthesis have shown the resin to be absent of ion exchanging groups, however extraction results continue to show evidence that can be interpreted to indicate the presence of exchangeable protons on the resin. This discussion reports new evidence for the degradation of the phosphate esters in the pPenta, pTris and pTris-Mono resins to phosphate acids, which can undergo cation exchange behavior, which will produce a quite different pattern of cation uptake as a function of pH. Significant insights were derived from the application of techniques designed to ”saturate” the resin samples with non-radioactive, but strongly sorbed metal ions like Fe^{3+} and Zr^{4+}. Metal ion uptake studies provide evidence for notable changes in the performance of the phosphate resins when contacted with acidic nitrate media.

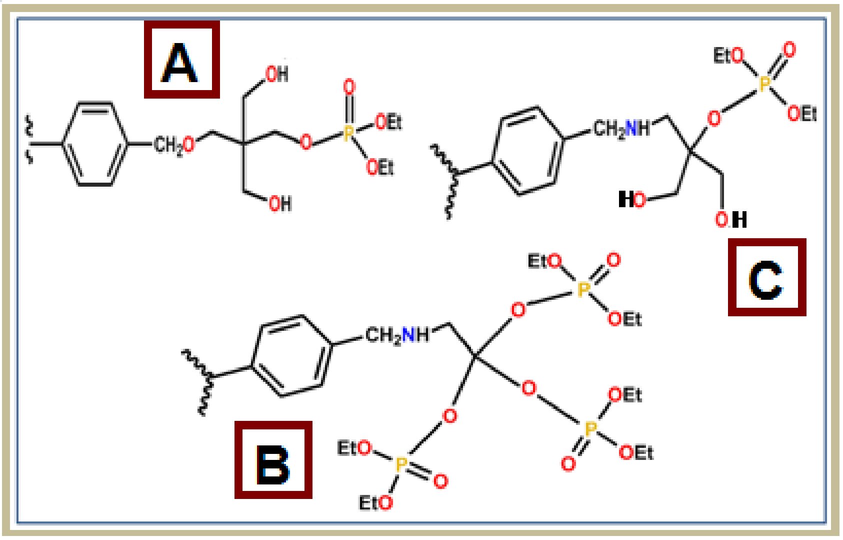


Figure 1. Structures of immobilized: a) pentaerythritol triethoxylate (**pPenta**) b) tris(hydroxymethyl)amino methane (**pTris**) c) mono-tris(hydroxymethyl)amino methane (**pTris-Mono**)

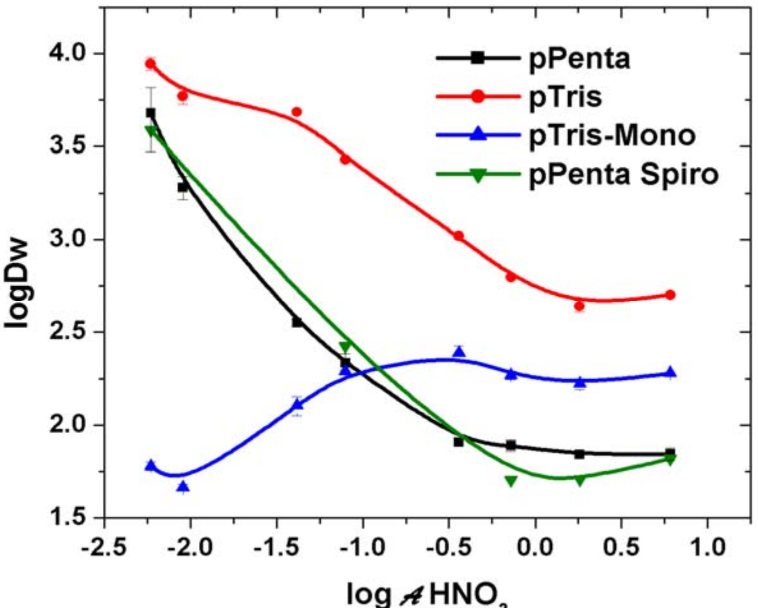


Figure 2. Extraction of UO_2^{2+} as a function of the activity of nitric acid from 6.4 X 10^{-3} M to 4 M HNO_3. The green data displays the UO_2^{2+} extraction reported in Dr. Alexandratos's lab

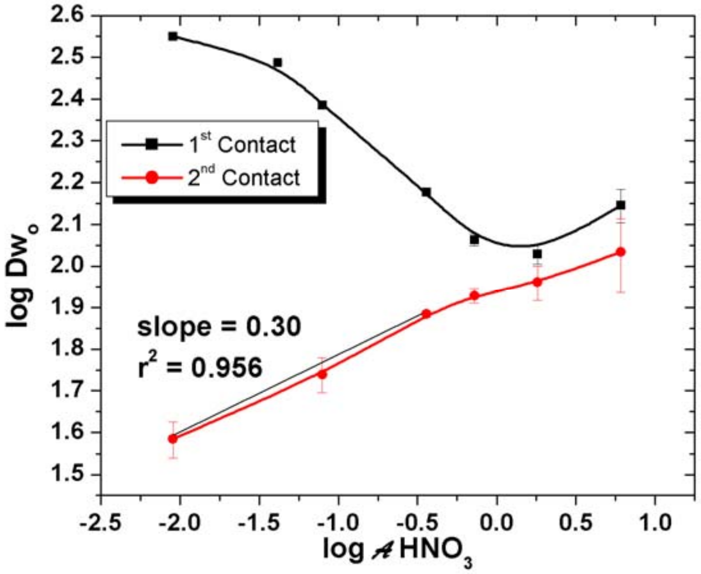


Figure 3. The nitric acid dependence of uranium uptake using 0.05 meq of the pTris resin. The 1st contact indicates the uptake of uranium from resin that has not been used for uranium extraction before. The 2nd contact indicates the use of that same resin after an attempted reconditioning has been performed.

This work focused on evaluation of the actinide sorption properties of a polystyrene resin functionalized with neutral organophosphorus extractacts covalently bonded of the backbone These extractants are analogous to the tri-n-butyl phosphate extractant used for the decontamination of Al leachates in previous work. To encourage sufficient partitioning of the aqueous phase to a more hydrophobic resin, hydrophilic alcohol groups were placed in several of the developed resins. Some preliminary studies have been published examining uranium, lanthanide and transition metal uptake by the resins from nitric acid media. This work initially sought to expand these opening investigations with investigations examining transuranic metal partitioning from varied nitrate media.

The original plan quickly changed course as metal partitioning patterns indicated the ethoxy groups of the organophosphorus extractant were hydrolyzing. Hydrolysis of phosphate esters leads to the formation of an acidic organophosphorus extractant, which would partition metals using a cation-exchange mechanism. To confirm the presence of ion-exchange groups, several studies were performed. Iron generally has a higher affinity for cation-exchange materials than uranium. Examining uranium uptake in the presence of iron at lower pH's did show some circumstantial evidence for the presence of ion exchange groups on the resin. Infra-red spectra of the resins, before and after acid contact, were obtained. Peaks were observed in areas consistent with phosphoric acid wags at ~2300 cm^{-1}; however, the asymmetric stretch of CO_2 is also present in this region (and spectra were taken in air). Since the IR was not purged with N_2 before spectra were obtained, the definitive observation of the phosphoryl wag was not possible. The overall conclusion to this study was that the use of phosphate ester functionalized polymeric materials should probably be restricted to contact with neutral pH solutions, e.g.,

Studies on the extraction properties of Eu, Th, U and Am with tetramethylmalonamide resin and column chromatographic separation

Asako Shimada, Jana Sulakova, Kenneth L Nash, Yijia Yang, and Spiro Alexandratos

Tetramethylmalonamide-immobilized resin (TMMA resin) have been developed in the Alexandratos lab and evaluated for their applicability to the separation of trivalent, tetravalent, and hexavalent actinide elements. As a fundamental study of the extraction mechanism and to design a chromatographic separation scheme, distribution coefficients (K_d) for Eu(III), Th(IV), U(VI), and Am(III) in HNO_3, $NaNO_3$, HCl and NaCl solutions with TMMA resin were determined, in addition to the K_d for HNO_3. The order of the K_d values was Th(IV) > U(VI) > Am(III), Eu(III) in all tested solutions. The competition between metal extraction and HNO_3 extraction was confirmed by the extraction data and FT-IR spectra. The loading capacities of $Eu(NO_3)_3$ and $UO_2(NO_3)_2$ at 3 M HNO_3, determined by a dynamic method with TMMA resin (TMMA in the resin was 2.05 mmol/g), were 0.83 mmol/g and 1.6 mmol/g, respectively, implying that the metal:functional group stoichiometry was 1:2 for Eu and 1:1 for U. Because the K_d values for Th and U were over 100 in all solutions tested, the influence of organic acids on the K_d values of Th and U from 3 M and 0.01 M HNO_3 solutions was studied to survey potential stripping agents. The effects of the major components that presumably constitute low-level radioactive waste, Na, Al, K, Ca, Cr, Ni, and Fe, on the K_d values of Am were also studied. Although the Am K_d values decreased with ≥0.01 M Fe(III), the influence of the other ions was negligible. Based on these fundamental experimental results, an extractive chromatographic scheme was designed and operated.

From the extraction data and FT-IR spectra, HNO_3 extraction was found to compete with metal-ion extraction on TMMA resin. Proton transfer from HNO_3 to the TMMA resin was thought to play an important role in the mechanism of HNO_3 extraction; 2 or 3 mol of HNO_3 were extracted by 1 mol TMMA in ≥ 5 M HNO_3 solutions. The TMMA resin strongly extracted actinide elements in the order Th(IV) > U(VI) > Am(III), Eu(III), not only from HNO_3 and HCl solutions, but also from $NaNO_3$ and NaCl solutions. Compared to other malonamide-derived resins under similar conditions, TMMA resin had higher K_d values for Th(IV), U(VI), and Am(III), and a higher loading U(VI) capacity. The higher K_d values for Am were advantageous: Am was difficult to extract on other malonamide-derived resins. However, the Am extraction kinetics with TMMA resin (Figure 1) were slow, similar to the slow kinetics of Eu, and a slow flow rate would be required for the chromatographic extraction of Am onto TMMA resin. In contrast, TMMA resin strongly extracted Th and U from NaCl solution, and these loading capacities are expected to be high. Therefore, TMMA resin may be suitable for the recovery of Th and U from sea water.

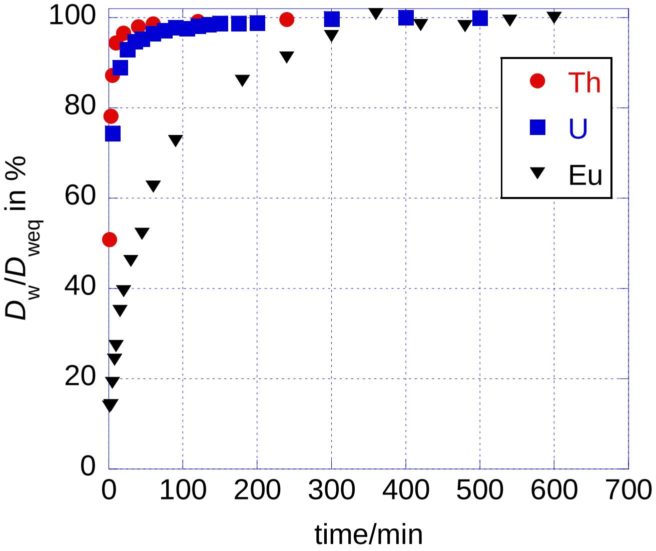


Fig. 1 Kinetics for the sorption of Eu(III), Th(IV) and U(VI) ions on TMMA resin at 3 M HNO_3.

Extraction of Lanthanide and Actinide Nitrate and Thiocyanate Salts by 2,6-Bis[(bis(2-n-octyl)phosphino)methyl]pyridine N,P,P`-trioxide in Toluene

J. Sulakova, R.T. Paine, M. Chakravarty, K.L. Nash submitted for publication Separation Science & Technology

Organophosphorus reagents for solvent extraction have played a particularly important role in actinide science and technology. A wide variety of compounds of varying basicity, denticity and geometric arrangement of donor groups have been reported during the past 50-60 years. In earlier reports, some features of the extraction of actinides by 2,6-bis[(bis(2-ethylhexyl) phosphino)methyl]pyridine N,P,P`-trioxide, TEH(NOPOPO), have been reported. The presence of a chiral center at the ethylhexyl groups makes purification difficult, though its solubility is improved by the presence of four chiral centers. In contrast, the structurally-related extractant 2,6-bis[(bis(2-n-octyl)phosphino)methyl] pyridine N,P,P`-trioxide, TO(NOPOPO), can be purified by crystallization (at the price of lower solubility limits relative to TEH(NOPOPO)). This work reports new results describing the extraction of Am(III), Th(IV), Pu(IV), Np(V), and U(VI) from acidic nitrate and thiocyanate media by the trifunctional organophosphorus ligand TO(NOPOPO) in toluene. Trans–lanthanide trends for extraction are also explored. TO(NOPOPO) behaves as a classic solvating extractant reagent, wherein extraction preference increases as the effective charge of actinide metal cation increases. The corresponding lanthanide extraction patterns are either flat (nitrate) or tending to discriminate between light and heavy lanthanides (thiocyanate). The extractant stoichiometry of the phase transfer reaction of the actinides into TO(NOPOPO) in toluene varies between 1 and 2 for the suite of metal nitrates and thiocyanates investigated. The back extraction of trivalent ions and Np(V) can be accomplished with a shift to less acidic media, but stripping of hexavalent and tetravalent ions requires a complexant. Results indicate that TO(NOPOPO) in toluene is a strong extractant for actinide nitrates in all oxidation states and potentially a suitable platform to explore for trivalent actinide-lanthanide separations from thiocyanate media.

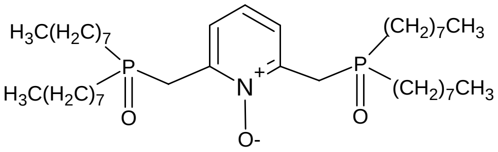


Figure1 Structure of TO(NOPOPO).

The result of actinide and Eu^{3+} extraction studies from nitric acid media are shown in Figure 2. It can bee noted that Th^{4+} is strongly extracted by TONOPO from 0.02 to 4.0 M. UO_2^{2+} extraction shows a similar comparative independence of cation extraction with changing acidity, though about 10 times weaker extraction than that for Th^{4+}. The reduced extraction strength differs from the pattern seen in CMPO extraction from nitric acid media, perhaps reflecting issues related to the positioning of donor atoms in the NOPOPO extractant. The spherically symmetrical trivalent Am^{3+} and Eu^{3+} ions demonstrate nitric acid extraction patterns completely consistent with those seen in the analogous CMPO extraction system. The extraction of NpO_2^+ is greater than that reported for CMPO, under the conditions of these experiments approaching that of Am^{3+} in dilute acid media. The slight increases seen in Np extraction at higher concentrations of HNO_3 could indicate the partial oxidation of NpO_2^+ to NpO_2^{2+} under these conditions. The pattern seen for Pu extraction would appear, relying on the oxidation state analog principle, to indicate a predominance of Pu^{3+} in dilute acid, Pu^{4+} becoming increasingly important at higher nitric acid concentrations. The reduced extraction of Pu that is seen at low [HNO_3] could also indicate the effect of partial hydrolysis, though there were no indications of lost accountability of Pu

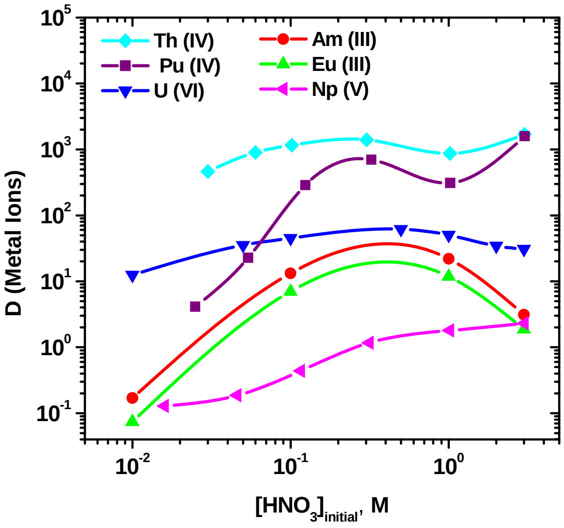
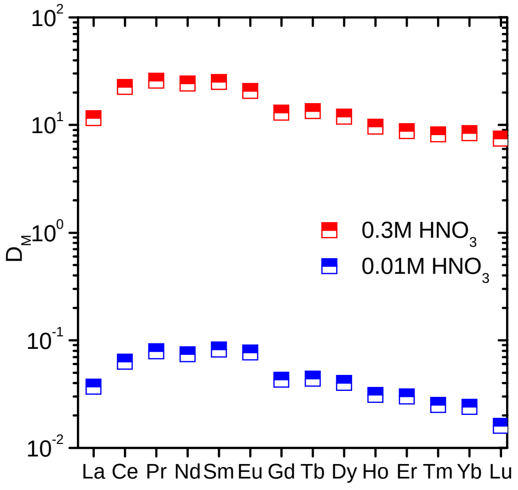


Figure 2 Dependence of distribution ratios D of Th, Pu, U, Am, Eu, and Np on [HNO_3] using TO(NOPOPO) in toluene as organic phase at 21±1 ºC. For extraction of the metal ions the [TO(NOPOPO)] = 0.03 M in toluene except for Th, for which [TO(NOPOPO)] = 0.01 M.

radioactivity in the radiotracer experiments in dilute acid media. No attempt was made in these experiments to control the oxidation state of either Np or Pu. Trans-lanthanide extraction trends are also often diagnostic of extractant behavior. The results of studies of lanthanide extraction from nitric acid (Figure 4) and HCl/NH_4SCN (Figure 5) are also reported. In each system, the highest extraction is seen to occur of the lanthanide ions between Ce and Gd, more or less coinciding with the distribution of fission product lanthanides in used fuel. Not unexpectedly, NOPOPO also extracts HNO_3 and HSCN strongly.



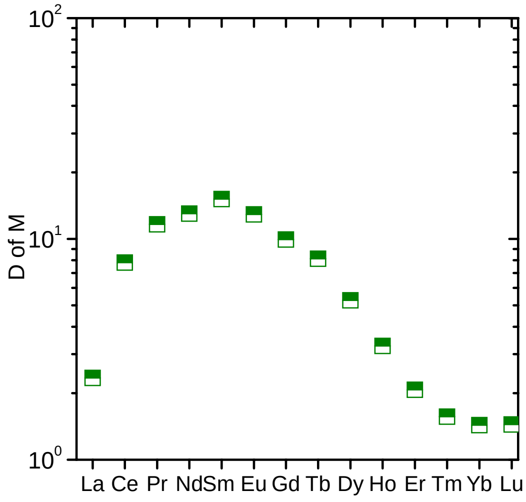


Figure 4 (left) Extraction trends across the lanthanide series using 0.03 M TO(NOPOPO) in toluene as organic phase. The aqueous phases used were 0.1 M and 0.3 M HNO_3.

Figure 5 (right) Extraction trends across the lanthanide series using 0.0003 M TO(NOPOPO) in toluene as organic phase. The aqueous phases used were 0.01 M NH_4SCN in 0.001 M HCl.

The trifunctional phosphine oxide extractant 2,6-bis[(bis(2-n-octyl)phosphino)methyl] pyridine N,P,P`-trioxide (TO(NOPOPO) has been shown to effectively extract tri-, tetra-, penta-, and hexavalent actinide ions from nitric acid media. In contact with dilute acid ammonium thiocyanate media, this extractant also exhibits measureable preference for extraction of Am^{3+} over Eu^{3+}. Despite the competing extraction of mineral acids (HNO_3, HSCN), the affinity of this extractant for actinide nitrates is sufficient to support simultaneous extraction of actinides in any oxidation state from moderately concentrated nitric acid solutions. Back extraction of trivalent actinides and NpO_2^+ appears to be feasible using a shift to lower concentrations of HNO_3, while the results suggest that reductive stripping of Pu^{4+} might also be easily accomplished. Application of either oxalic acid or sodium carbonate appears necessary to complete back extraction of Th^{4+} and UO_2^{2+}. As has been noted in a previous report, this performance is similar to that seen for application of the TRUEX extractant octyl(phenyl)N,N-diisobutylcarbamoyl(methyl) phosphine oxide (CMPO). Similarities between the extraction performance of TO(NOPOPO) and the well-established CMPO suggests that some continued research into the potential application of this class of ligands for actinide separations is merited.

National Lab Participation

In this program the cooperation with investigators at PNNL (Lumetta) LBNL (Rao) and INL (Herbst) have served several important purposes. The integration of National Lab scientists into this program serves three important functions: 1) Each of the investigators and their colleagues are proven mentors of young talent, as well as being highly capable experts in actinide chemistry and separation science; 2) Inclusion of National Lab facilities enables experiments that are either quite challenging or impossible in university facilities, specifically, at each institution academic scientists (graduate students and postdocs) have the opportunity to conduct research on samples containing multi-milligram quantities of TRU elements; 3) Posting of students to the National Labs for the conduct of portions of their research has the dual benefit of allowing the students to examine the National Lab work environment and consider whether this is a location they might like to spend a career, while simultaneously the National Lab scientists have an opportunity to judge whether these particular graduate students or postdocs might be suitable employees. These National Lab scientists have been full partners in this project. As funding becomes available in the future, opportunities to further expand connections between academic researchers and the National Lab community will become increasingly important.