LA-UR- 11-03537

Title: Molecular Transuranic Coordination Chemistry

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Intended for: Rare Earth Research Conference

Increasing our understanding of the reactivity, structure, and bonding modes of the early to mid transuranic actinide ions can provide fundamental chemical knowledge to underpin developments in applications such as novel separations for Advanced Nuclear Fuel Cycles. Exploration of transuranic coordination chemistry under non-aqueous inert atmosphere conditions can inform, in depth, upon the basic bonding and reactivity principles of transuranic ions towards a wide range of donor types and ligand architectures. In turn, this information has the potential to be exploited in the applied arena, such as understanding and manipulating the behavior of actinide extractants. We will present the reaction chemistry of Pu(III), Pu(IV), Pu(VI), Np(VI), and Np(IV) towards a range of ligands including dithiophosphinates, phosphine oxides, and β-ketoiminates.

Molecular Transuranic Coordination Chemistry

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2011 Rare Earth Research Conference

21st June 2011, Santa Fe, New Mexico, USA

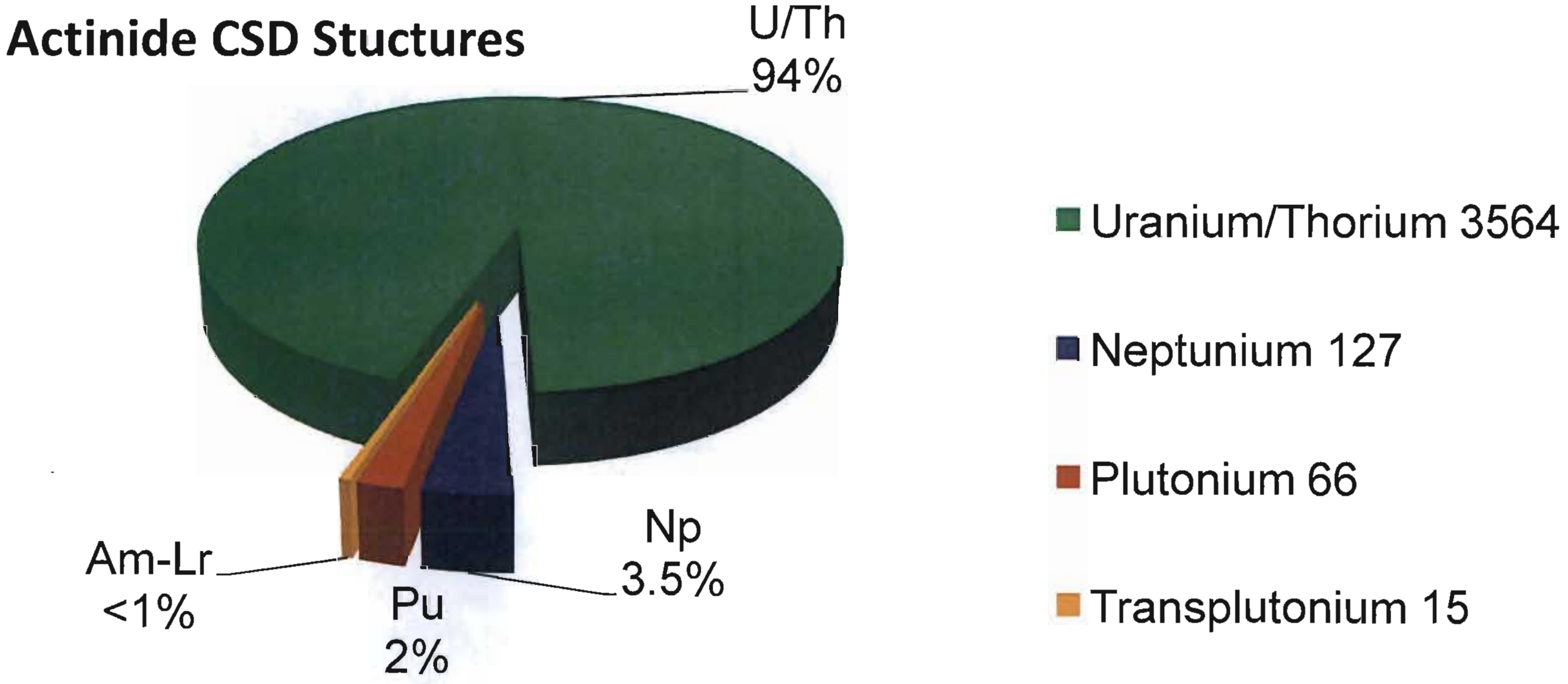
Los Alamos
NATIONAL LABORATORY

Overall Research Goals

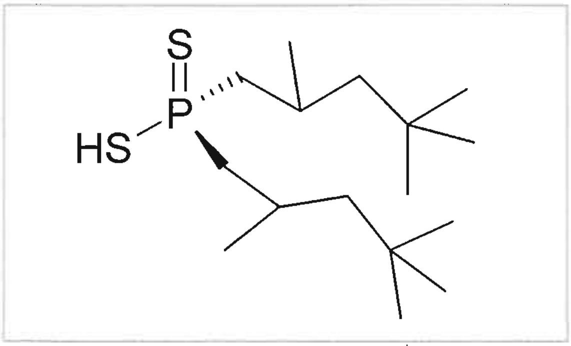
☐ Increase knowledge of transuranic coordination chemistry

- supports fuel cycle separation/waste process chemistry

- bonding properties least studied for transuranic ions even though they pose the most difficult waste/fuel cycle problems

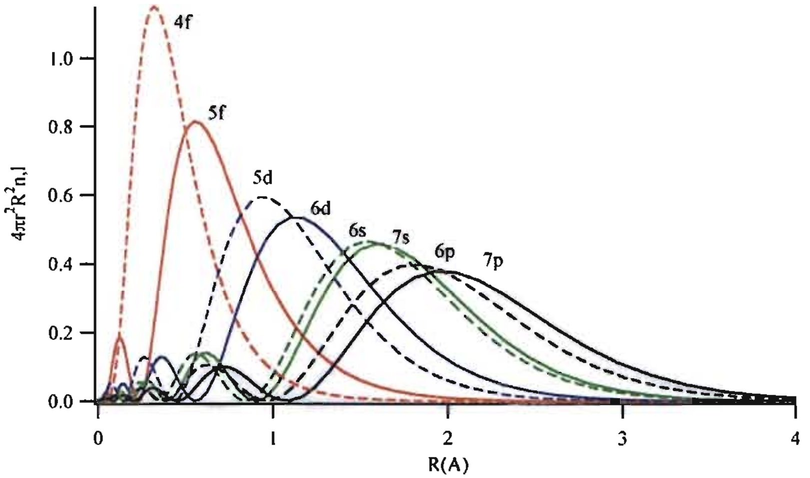


Chemical Bonding Relevance to Separations



Separation Factor An^{3+}/Ln^{3+}	Donor atoms
10	Cl^-
100 – 1000's	N (neutral – *e.g.* terpy)
up to 100,000	S^- (dithiophosphinates)

- ☐ Some soft donor extractants have a marked preference for An(III) over Ln(III)
- ☐ Radial extension, relative energies and symmetry of orbitals all important in bonding
- ☐ Can selectivity be explained by greater degree of **covalent** contribution to the bonding?



Orbital calculations performed by
P. Jeffrey Hay, LANL

Scientific Challenge: Better understand the role of covalency in actinide bonding with hard *vs* soft donor ligands

Experimental Approach

☐ Develop **synthetic access** to target complexes

- allow study of bonding modes across the An series, between oxidation states, and to Ln(III) for An/Ln separations relevance

☐ Isolate and characterize complexes with **hard and soft** donor ligands

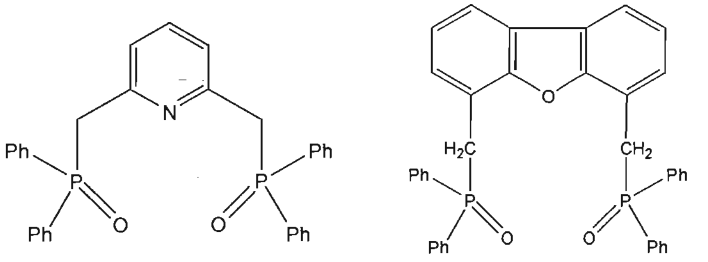
- compare structural data to uncover bonding trends

Perform in depth bonding analysis through collaborations:

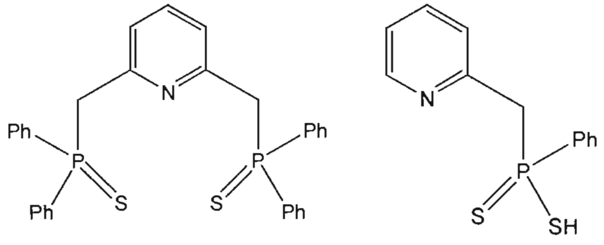
- model structures and orbital interactions through collaboration (Batista, Kaltsoyannis)
- ligand K-edge XAS to quantify orbital overlap (Kozimor, Shuh) and EXAFS spectroscopy
- relate knowledge from solid model complexes to solution separations

Long term goal: Uncover bonding differences that help explain/predict actinide selectivity behavior in separations and aid new improved ligand designs

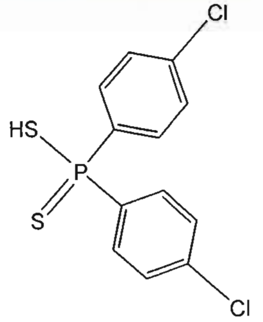
Ligand Classes



O-donor extractants (Paine, UNM)

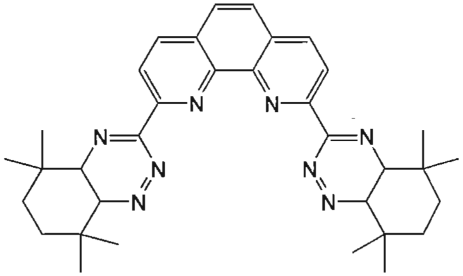


S-donor analogs



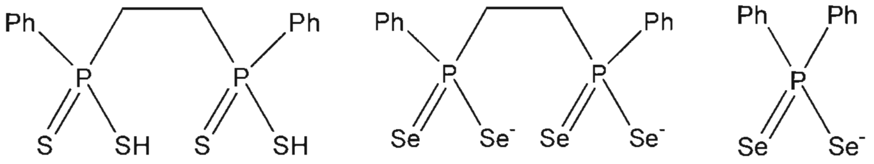
S-donor extractants

(Modolo, Germany)



N-donor extractants (Lewis, Reading)

(Sharrad, Manchester)

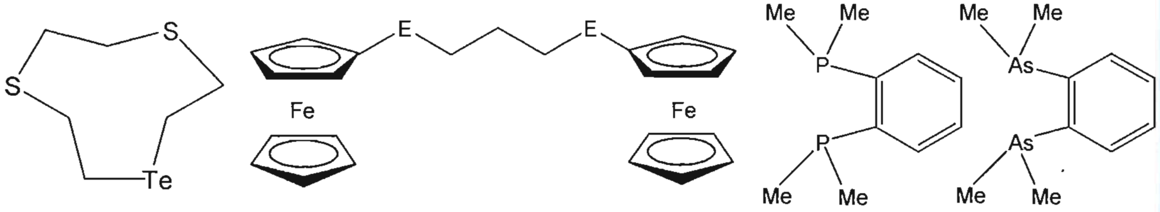


S-donor extractant derivatives and Se analogs

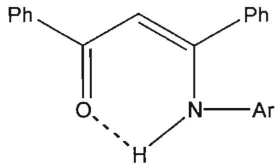
Davies, Imperial College

$^{-}S—SiR_3$ $^{-}Se—SiR_3$ $^{-}Te—SiR_3$

Electronically tunable chalcogenides



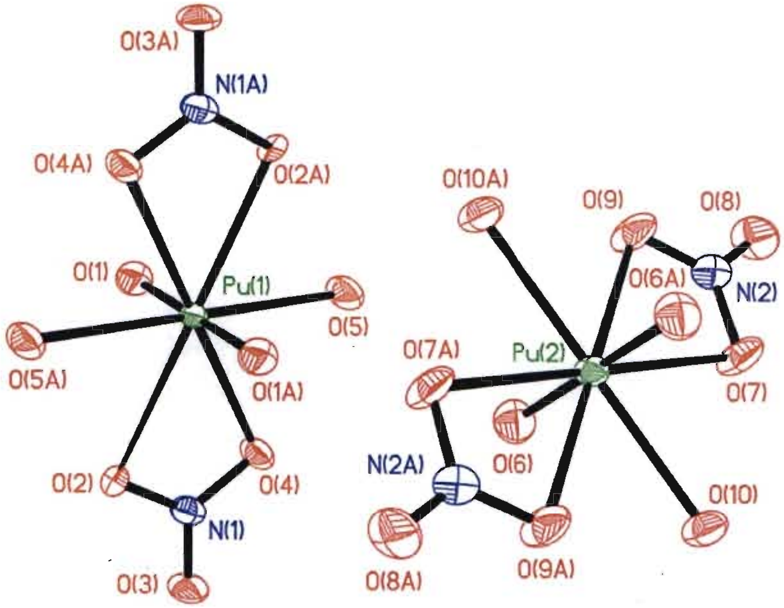
‘Ultra-soft’ neutral chalcogen and P/As donors



Mixed N,O-donors (Hayton, UCSB)

Plutonyl(VI) in Nitric Acid

- Pu speciation in nitric acid relevant to fuel cycle separations
- PuO_2^{2+} in HNO_3 is a precursor solution to starting materials for plutonyl chemistry



$[PuO_2(NO_3)_2(H_2O)_2]\cdot H_2O$

CN = 8

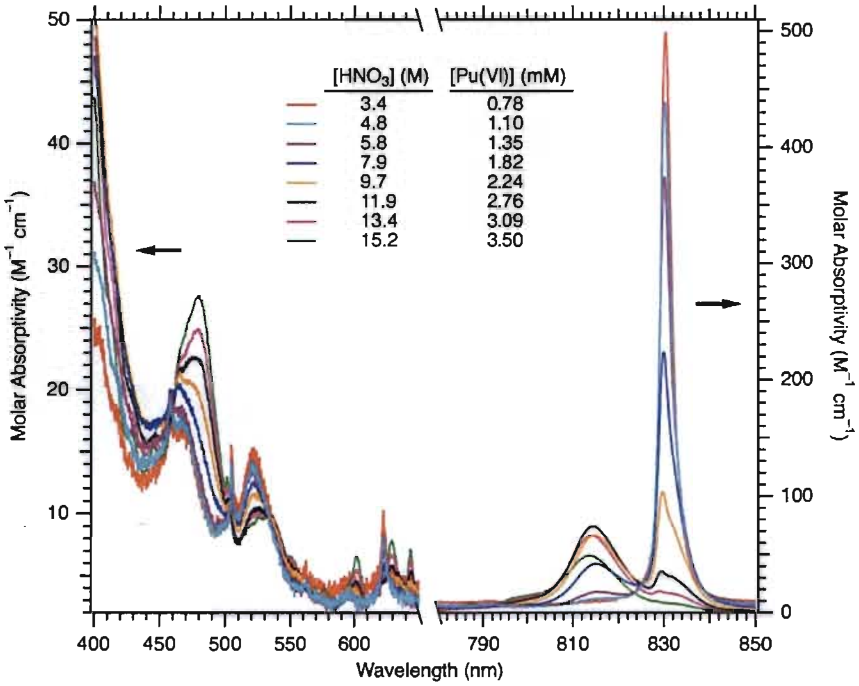
Distorted Hexagonal-Bipyramid

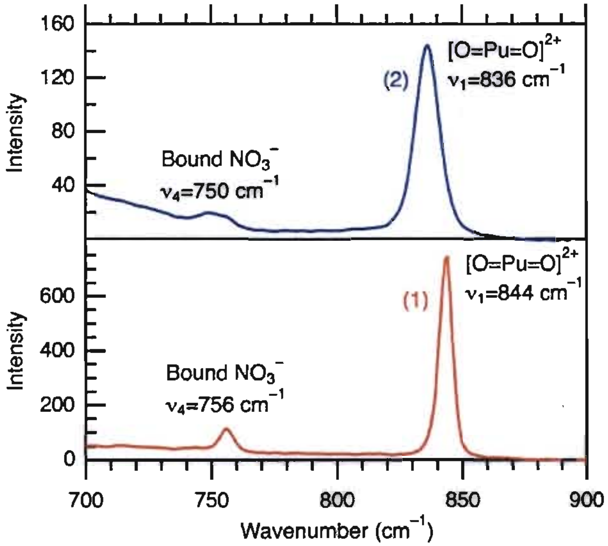
Avg. **Pu-O$_{(yl)}$**	1.728(7) Å
Avg. **Pu-O$_{(nitrate)}$**	2.497(11) Å
Avg. **Pu-O$_{(water)}$**	2.432(9) Å

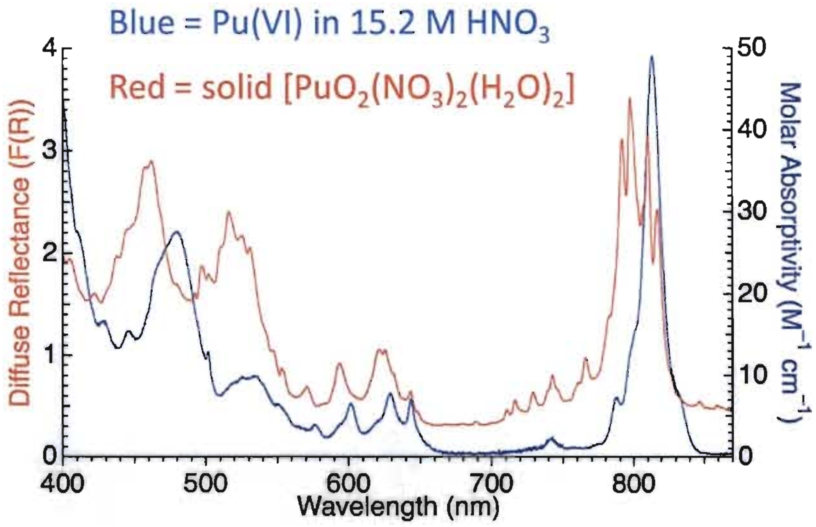
- Literature conflicting – Is the Pu(VI) dinitrate a relevant solution species or not?
- The structure affords a first chance to establish the dinitrate spectroscopic signatures

Plutonyl(VI) in Nitric Acid

- ☐ At 1 and 3 M HNO_3, no observable nitrate coordination, only 830 nm ‘aquo’ band
- ☐ At 5.8 M and above, **815 nm** band grows in for the **$PuO_2(NO_3)^+$** mono-nitrate species
- ☐ 11.9 - 15 M, **815 nm band still dominates**







Blue = Pu(VI) in 15.2 M HNO_3

Red = solid $[PuO_2(NO_3)_2(H_2O)_2]$

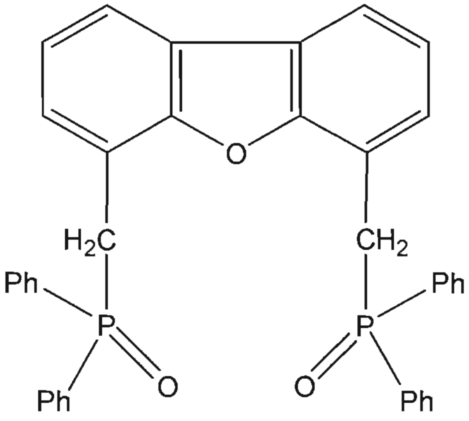
- ☐ Comparison of **solid $PuO_2(NO_3)_2$** vis/nIR and Raman spectra to Pu(VI) in 15.2 M HNO_3

➔ No appreciable **$PuO_2(NO_3)_2$** in HNO_3 solution

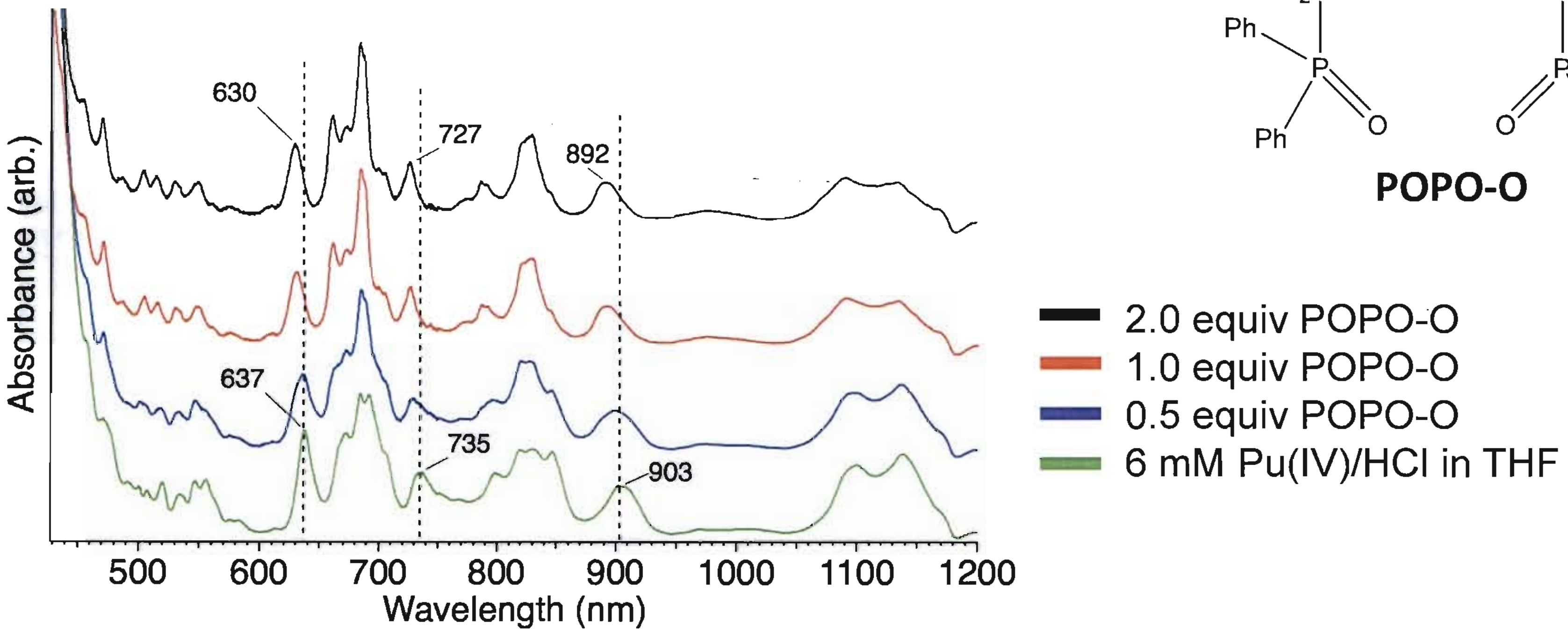
*Gaunt, et al, Inorg. Chem., **2011**, asap article.*

Pu(IV) O-Donor Extractant Studies

- ☐ Collaboration with Prof. Paine (UNM) who designs ligands as potential extractants
- ☐ Phosphine oxide POPO derivative with furan ring in backbone
- ☐ Aim is to study and compare Pu(III), Pu(IV), Ln(III) complexes



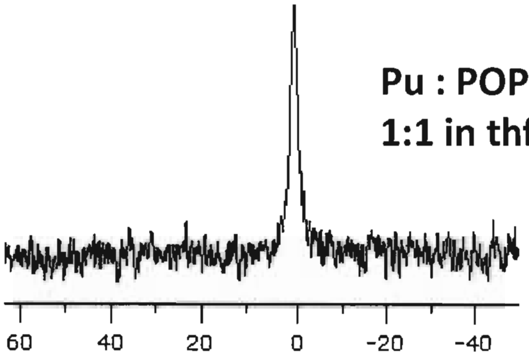
POPO-O



- ☐ UV/vis/nIR spectroscopy indicates formation of a 1:1 complex only

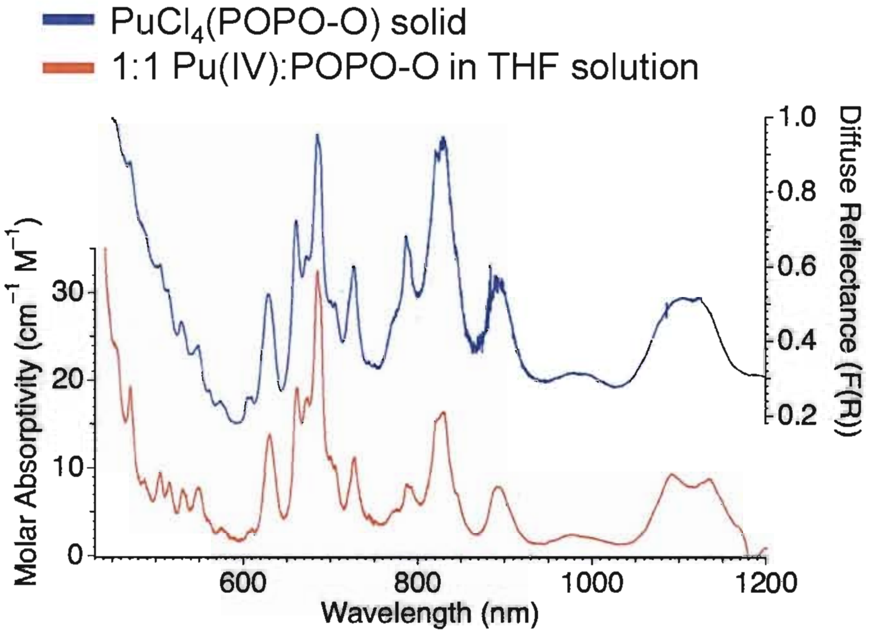
Pu(IV) O-Donor Extractant Studies

☐ ^{31}P NMR shows single complex in solution, paramagnetic broad peak at -0.58 ppm

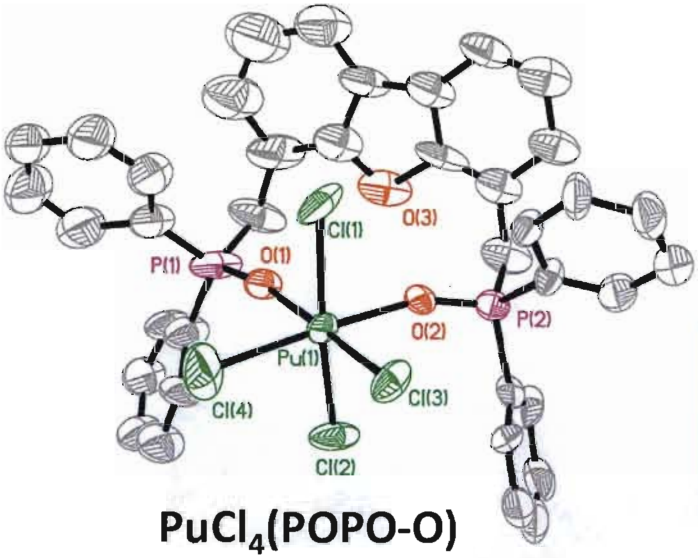


Pu : POPO-O ratio
1:1 in thf-d_8

The solution and solid state UV/vis/nIR spectra show excellent correlation



☐ The 1:1 complex was crystallized from THF/MeOH



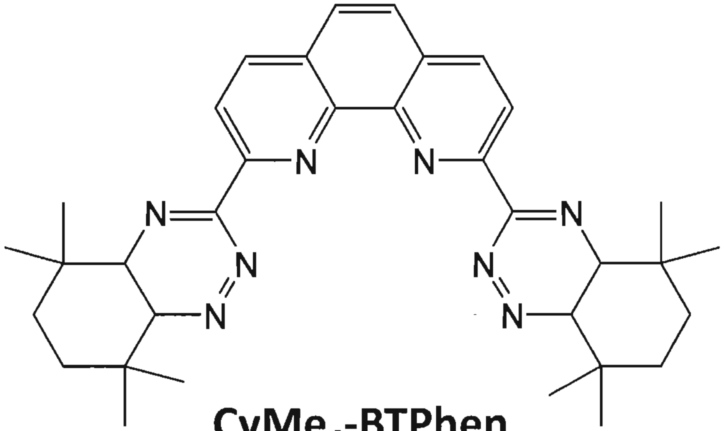
$PuCl_4$(POPO-O)

Pu-$O_{(POPO-O(1))}$	2.243(11) Å
Pu-$O_{(POPO-O(2))}$	2.202(11) Å
Avg. **Pu-Cl**	2.564(10) Å

☐ Follow up by studying similar (P=S) phosphine sulfide ligand systems

Pu N-Donor Extractant Studies

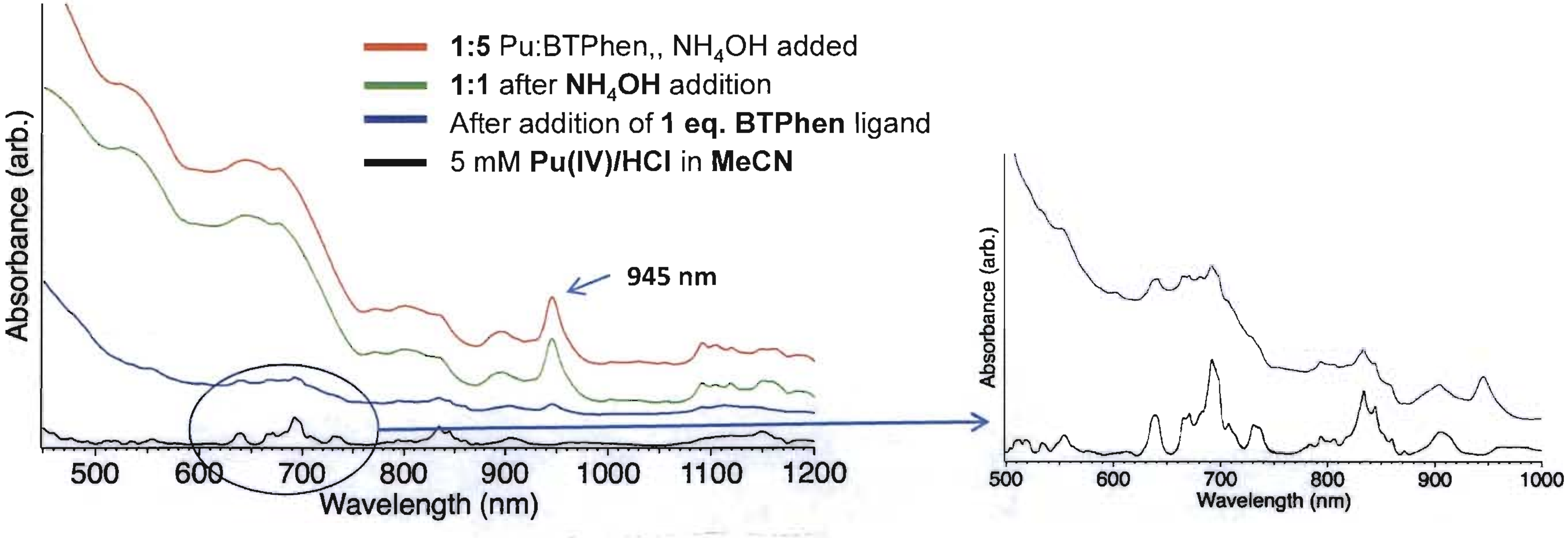
- ☐ Collaboration with Dr. Lewis (Reading) for ligand design and Dr. Sharrad (Manchester) for the uranium and thorium comparisons



$CyMe_4$-BTPhen

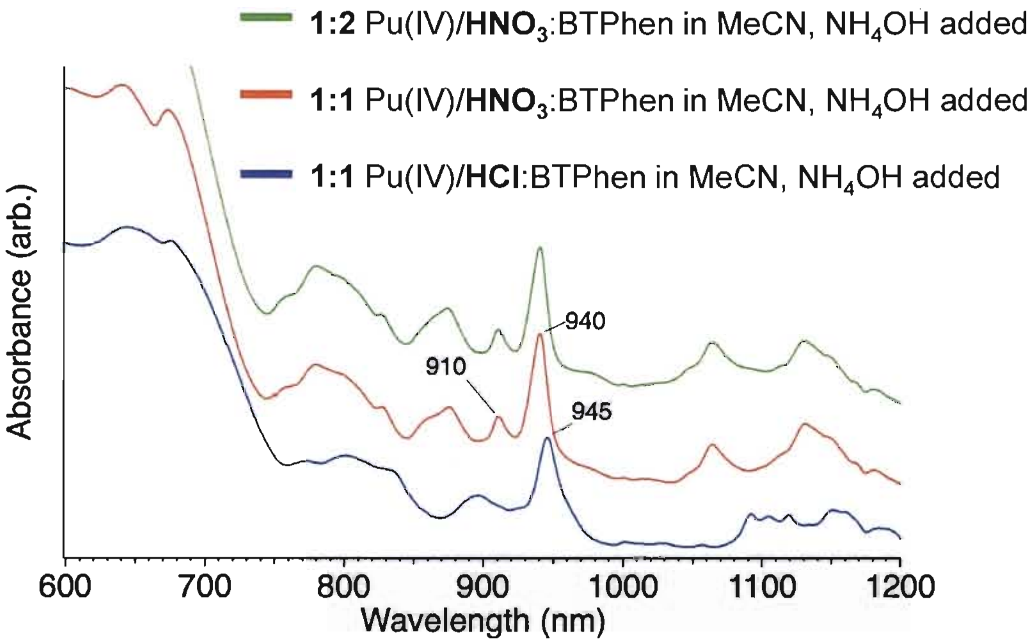
Polydentate **neutral N donor** ligands that display **high An/Ln selectivity**

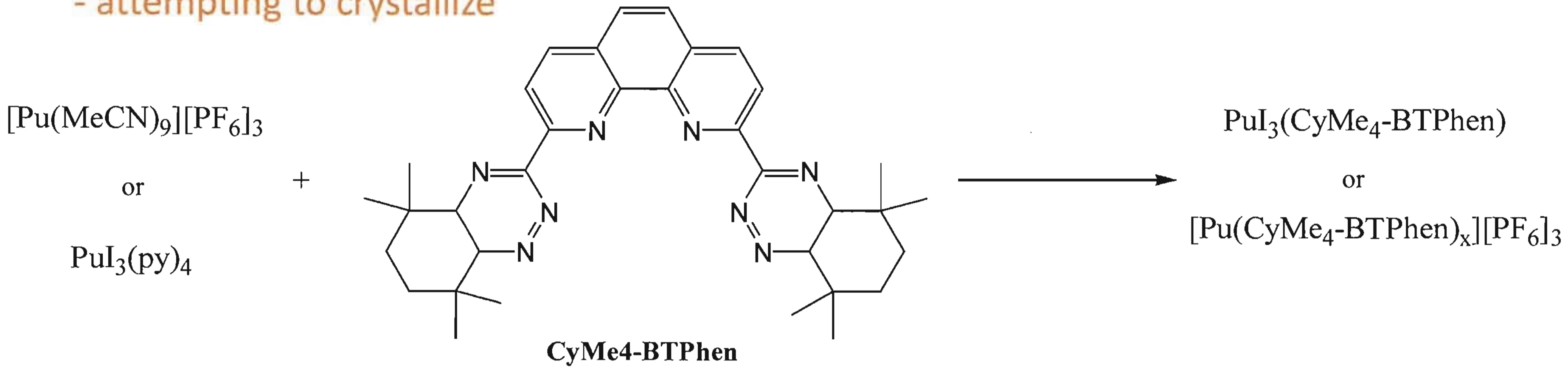
Aim to compare bonding between Pu(IV), U(IV), Np(IV), Pu(III), Ln(III) and Np(VI), and U(VI) complexes



Pu N-Donor Extractant Studies

- ☐ Switched to Pu(IV) nitrate stock solution
  - relevant to processing conditions
  - 1:2 known for Ln(III) nitrates
- ☐ Electronic absorption spectra similar
  - consistent with a 1:1 complex
  - no change in spectrum for 1:2
  - $Pu(NO_3)_4(CyMe_4\text{-}BTPhen)$ formed
- ☐ Pu(III) reactions proceed readily
  - attempting to crystallize





$[Pu(MeCN)_9][PF_6]_3$

or

$PuI_3(py)_4$

+

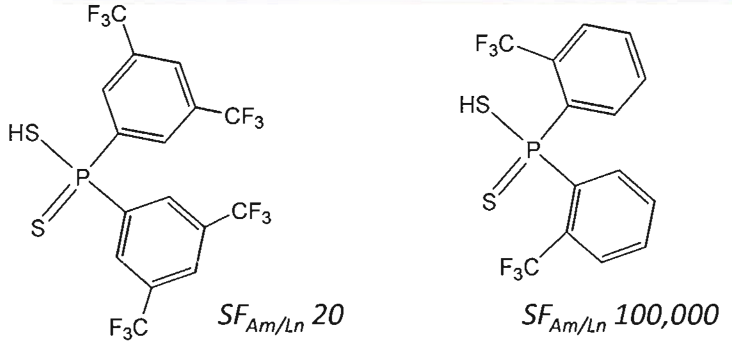
CyMe4-BTPhen

$PuI_3(CyMe_4\text{-}BTPhen)$

or

$[Pu(CyMe_4\text{-}BTPhen)_x][PF_6]_3$

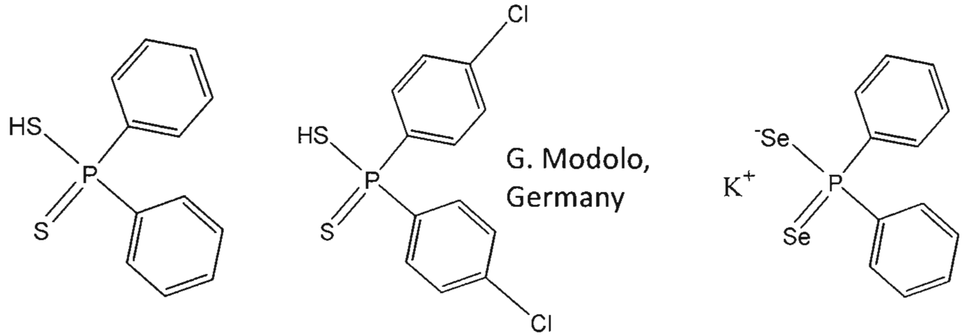
S Donor Extractant Derivatives



$SF_{Am/Ln}$ 20

$SF_{Am/Ln}$ 100,000

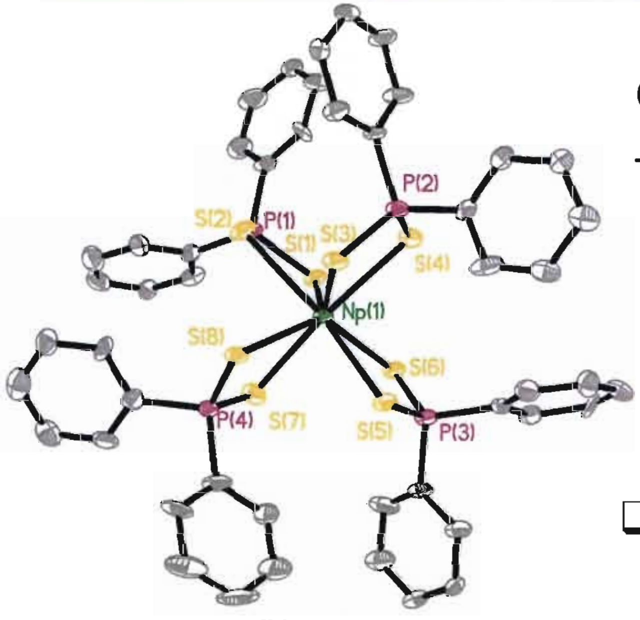
DOE-NE, Peterman (INL), Ln(III), Pu(III) XAS comparison



G. Modolo, Germany

- Fundamental study of wider range of $^{-}EPR_2$ anions across oxidation states and elements

$$[PPh_4]_2[NpCl_6] \ + \ 4\ KS_2PPh_2 \xrightarrow{THF} Np(S_2PPh_2)_4 \ + \ 4\ KCl \ + \ 2\ PPh_4Cl$$



$Np^{IV}(S_2PPh_2)_4$

CN = 8

Triangular dodecahedral geometry

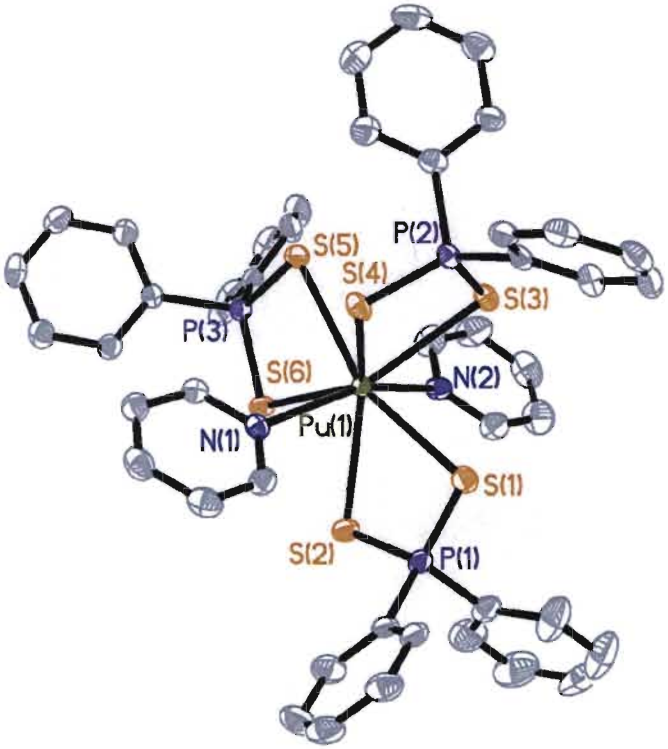
	$Np(S_2PPh_2)_4$	$U(S_2PPh_2)_4$	$U(Se_2PPh_2)_4$
Avg U-E length (Å)	2.832(10)	2.844(3)	2.970(1)

- Repeating with *para*-Cl derivative for Pu(III/IV) and Ln(III)
  - progress to softer Se analogs and other derivatives
  - acquire S/Se K-edge XAS data (Kozimor, LANL)

Pu(III) Dithiophosphinate Complex

$PuI_3(py)_4$ + 3 equiv HS_2PPh_2 + 3 equiv $Na[N(SiMe_3)_2]$

$$\xrightarrow[\text{(ii) Toluene/hexanes}]{\text{(i) THF}}$$



$Pu^{III}(S_2PPh_2)_3(py)_2$

Coordination number = 8

Triangular dodecahedron geometry

Average **Pu-S** length is **2.931(3) Å**

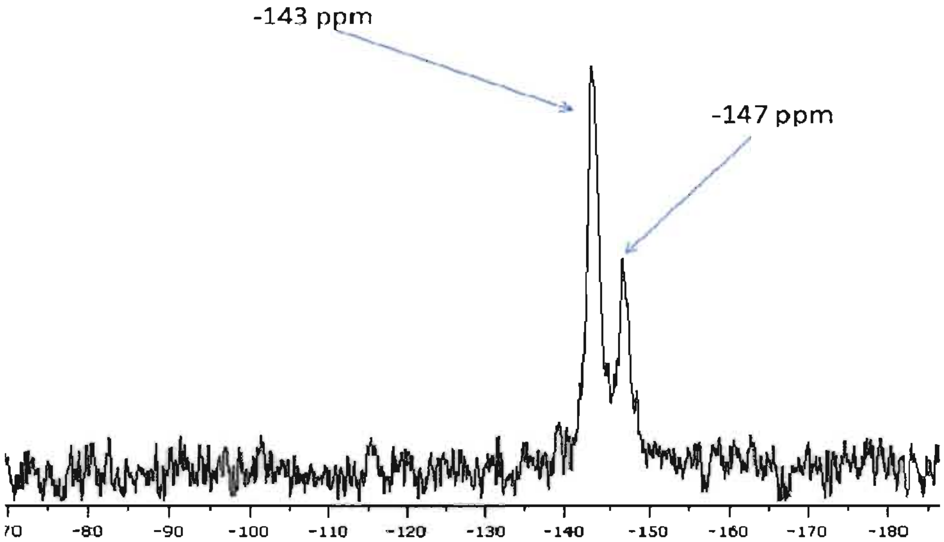
Average **Pu-N** length is **2.617(4) Å**

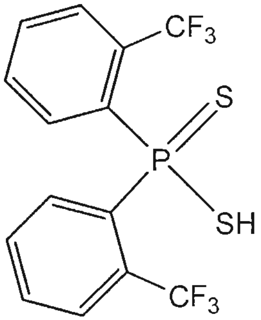
❑ 3 bidentate **S donors** and 2 coordinated **pyridine** molecules

❑ ^{31}P NMR signal at -107 ppm in Toluene-d_8 but 3 other peaks as well

Pu(III) Reactions Followed by ^{31}P NMR

$Pu[N(SiMe_3)_2]_3$ + 3 equiv $HS_2P[(o\text{-}CF_3)Ph]_2$ in thf-d_8

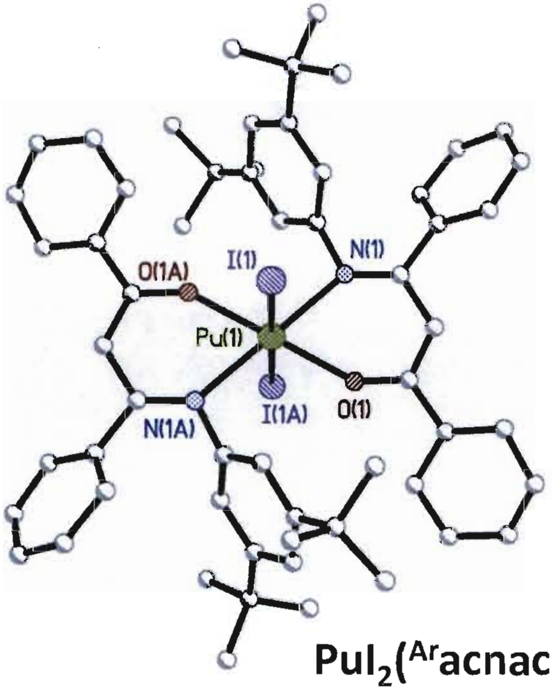




- ☐ Ligand provided by Dean Peterman and co-workers (INL)
- ☐ Two Pu(III) resonances in ^{31}P NMR – either 2 species or 2 ligand binding modes
- ☐ Next step is to perform XAS measurements and DFT calculations on these molecules

β-ketoimininate N,O Donor Complexes

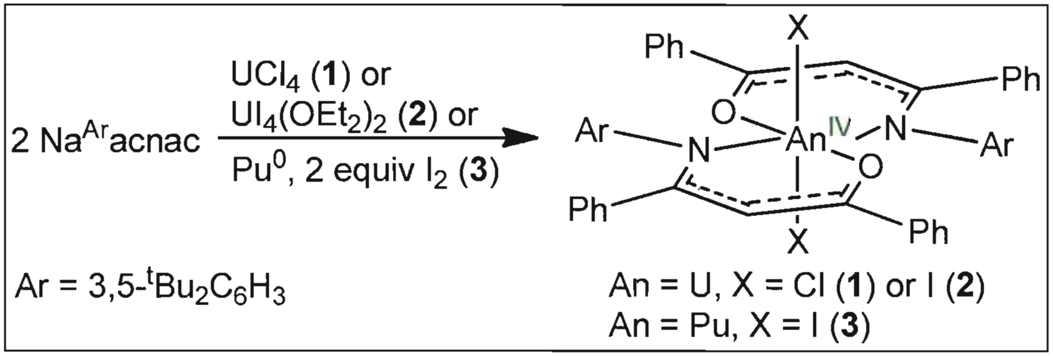
- ☐ Collaboration with Prof. T. Hayton, D. Schnaars (UCSB)
- ☐ Provided access to a very rare U(IV) *vs* Pu(IV) isostructural molecular comparison



$PuI_2(^{Ar}acnac)_2$

Coordination number = 6

Distorted octahedral geometry


$2\ Na^{Ar}acnac \xrightarrow[Pu^0,\ 2\ equiv\ I_2\ (\mathbf{3})]{UCl_4\ (\mathbf{1})\ or\ UI_4(OEt_2)_2\ (\mathbf{2})\ or}$

Ar = $3,5\text{-}^tBu_2C_6H_3$

An = U, X = Cl (**1**) or I (**2**)
An = Pu, X = I (**3**)

$Pu^{IV}I_2(^{Ar}acnac)_2$		$U^{IV}I_2(^{Ar}acnac)_2$		ΔM-L
Pu-I	2.9859(3)	**U-I**	3.0288(5)	+0.043 Å
Pu-O$_{(acnac)}$	2.1727(17)	**U-O$_{(acnac)}$**	2.163(4)	-0.010 Å
Pu-N$_{(acnac)}$	2.3635(19)	**U-N$_{(acnac)}$**	2.409(5)	+0.046 Å

- ☐ U-O *vs* Pu-O and U-N *vs* Pu-N changes not explained well by ionic bonding alone

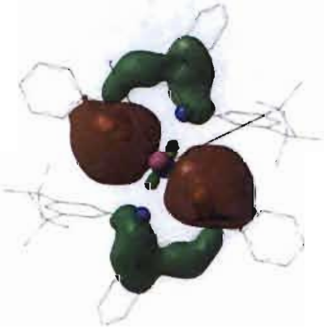
β-ketoiminate N,O Donor Complexes

☐ Turned to DFT modeling to look for any 5f or 6d orbital interaction differences
-(Batista, LANL)

Bond	Orbital Interactions
U-N	33 kcal/mol
Pu-N	28 kcal/mol
ΔE	**5 kcal/mol**

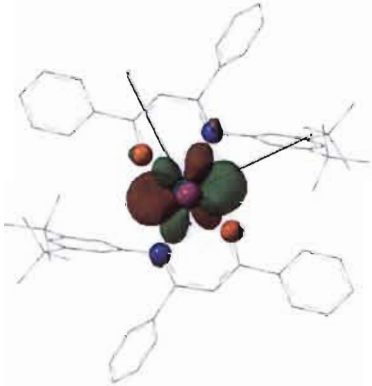
Bond	Orbital Interactions
U-O	65.5 kcal/mol
Pu-O	49 kcal/mol
ΔE	**16.5 kcal/mol**

☐ Similar U-N *vs* Pu-N orbital interaction strength and type
- shorter Pu-N bond due to actinide contraction/increased electrostatic interaction



strongest U-O couple
23 kcal/mol

70% **6d**,
30 % **7s** metal character



strongest Pu-O couple
16.5 kcal/mol

100% **6d**,
metal character

☐ Stronger U-O *vs* Pu-O orbital interactions lead to shorter U-O bond
- the O atom carries 17% greater charge than the N atom in the ^{Ar}acnac ligand
- it is the 'hard' O donor rather than the 'softer' N donor that exhibits 'covalency' differences!

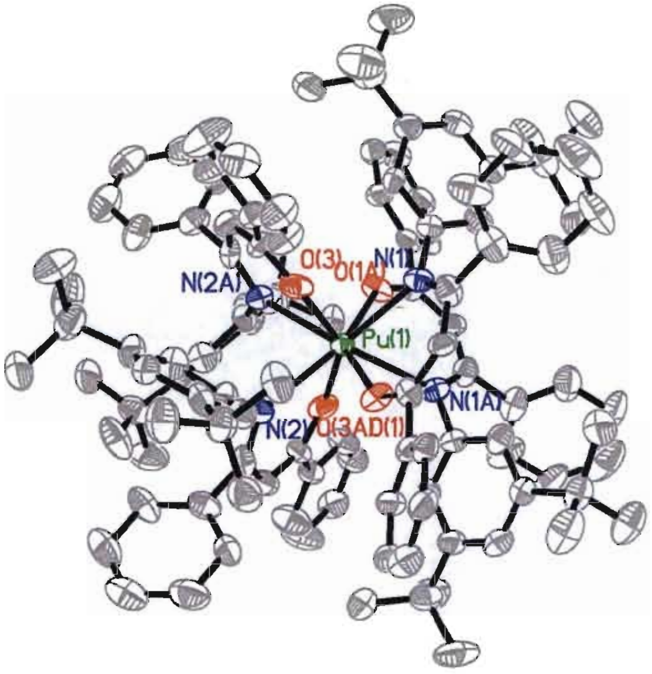
Gaunt, Hayton, Schnaars, Batista, et al, Chem. Commun., ***2011****, submitted*

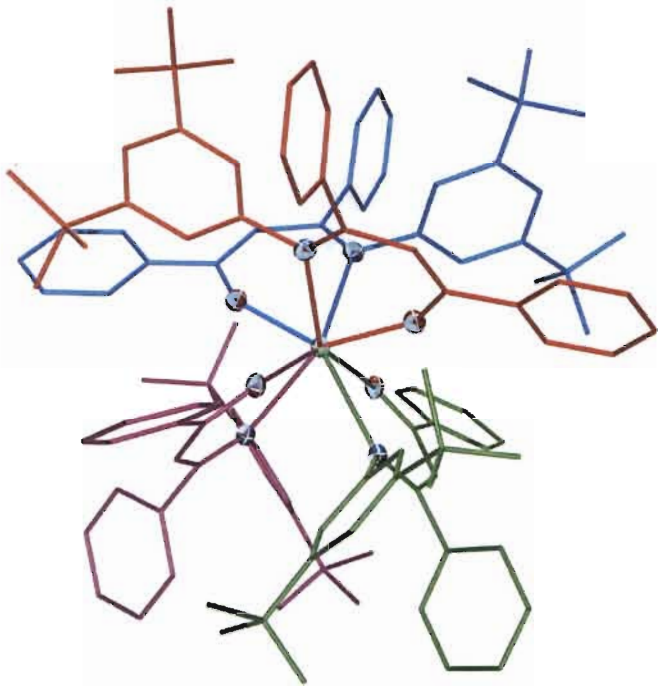
β-ketoiminate N,O Donor Complexes

☐ Attempts to synthesize the Cl analog, $PuCl_2(^{Ar}acnac)_2$, gave surprising result

$$[PPh_4]_2[PuCl_6] \quad + \quad 2\ Na^{Ar}acnac \xrightarrow{\times} Pu^{IV}Cl_2(^{Ar}acnac)_2$$

$$[PPh_4]_2[PuCl_6] \quad + \quad 2\ Na^{Ar}acnac \longrightarrow \mathbf{Pu^{IV}(^{Ar}acnac)_4}$$





$Pu(^{Ar}acnac)_4$

☐ Th(IV) and U(IV) analogs prepared at UCSB, trying to isolate the Np(IV) complex

☐ Rare chance for structural comparison across Th(IV), U(IV), Np(IV), Pu(IV) series

Future Directions

☐ For the ligands shown, complete characterization across Pu(III), Pu(IV), Np(IV) and Ln(III) ions

- draw comparisons and establish bonding trends and differences
- integrate all of the structural data with DFT modeling (Batista, Kaltsoyannis)
- identify candidates for first S, Se, N, O K-edge XAS measurements

☐ Progress to new ligand sets including 'very-soft' donors

- electronically tuneable thiolates and selenolates
- electronically tuneable N,O donor frameworks (MacBeth)
- neutral chalcogen ethers, phosphines (may require organometallic scaffolds)

☐ Relate to separations to the extent possible

- solution measurements (K-edge XAS, EXAFS)
- solution metal-ligand competition reactions
- effect of hydration upon the coordination sphere

Funding

U.S. Department of Energy – Office of Science, Early Career Program
(ARRA Stimulus Activity)
-Started April 2010

University of California Lab Fees Program
-U β-ketoiminate chemistry at UCSB (Hayton), and TRU actinyl studies led to the pursuit of Pu(IV) presented here

DOE-NE, Fuel Cycle R&D, Separations
-dithiophoshinate chemistry and K-edge

G. T. Seaborg Institute at LANL for summer student program *(D. Schnaars)*

People

Sean D. Reilly, Matthew B. Jones
-early career project

Scott Daly, Kozimor, Batista, May, Jarvinen
-DOE-NE, FC R&D project

R. T. Paine (UNM)
-phosphine oxides/sulfides

T. W. Hayton, D. Schnaars (UCSB)
-β-ketoiminates

F. Lewis (Reading), C. Sharrad (Manchester)
-polydentate N donor extractants

C. MacBeth (Emory)
-tripodal N,O donor ligands

I. May (LANL), M. Neu (LANL, now DOE-EM)
-LANL BES program, scientific discussions

E. Batista (LANL), N. Kaltsoyannis (UCL)
-theoretical calculations

S. Kozimor (LANL), D. Shuh (LBL)
-ligand K-edge XAS, and KS_2PPh_2 (Kozimor)