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Title: f-Element Coordination Chemistry Related to Nuclear Fuel Cycle Separations

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f-Element Coordination Chemistry with Relevance to Nuclear Fuel Cycle Separation Challenges

Matthew B. Jones, Andrew J. Gaunt, Trevor W. Hayton, Nikolas Kaltsoyannis, Kelly A. Kluge, Cora E. MacBeth, Iain May, Sean D. Reilly, David D. Schnaars, Brian L. Scott

Research into ligand complexation reactions with f-element cations is motivated by both the desire to understand the electronic structure and bonding of these elements, as well as to further develop the use of their complexes in applications such as nuclear fuel cycles and radioactive waste remediation. Exploring the fundamental chemistry that underpins a range of actinide separation strategies is vital to facilitate development and implementation of fuel recycling and waste disposition/minimization options. For example, soft donor extractants have attracted a lot of attention due to their ability to selectively complex An(III) versus Ln(III) ions, a challenging separation as a result of the chemical similarity of these ions. In order to probe the role that covalency plays in effecting selectivity, we are studying structurally similar Ln(III) and An(III) complexes featuring N, O, S and Se donor ligands. Bonding comparisons across the An(IV) series are also considered. In particular, we incorporate transuranic molecules into our studies, of which far less is known compared to the chemistry of the lanthanides or thorium/uranium. The syntheses and characterization of these complexes, which include β-ketoiminates, diselenophosphinates, and tri(amidato)amine ligands, will be described. We will analyze for bonding differences that have implications for ligand design in actinide separation technology.

f-Element Coordination Chemistry Related to Nuclear Fuel Cycle Separations

Matthew B. Jones

Inorganic, Isotope and Actinide Chemistry (C-IIAC)

Chemistry Division

Los Alamos National Laboratory

A Career in Actinide Science: Tribute to Lester Morss
243rd National Meeting of the American Chemical Society
27th March 2012, San Diego, California

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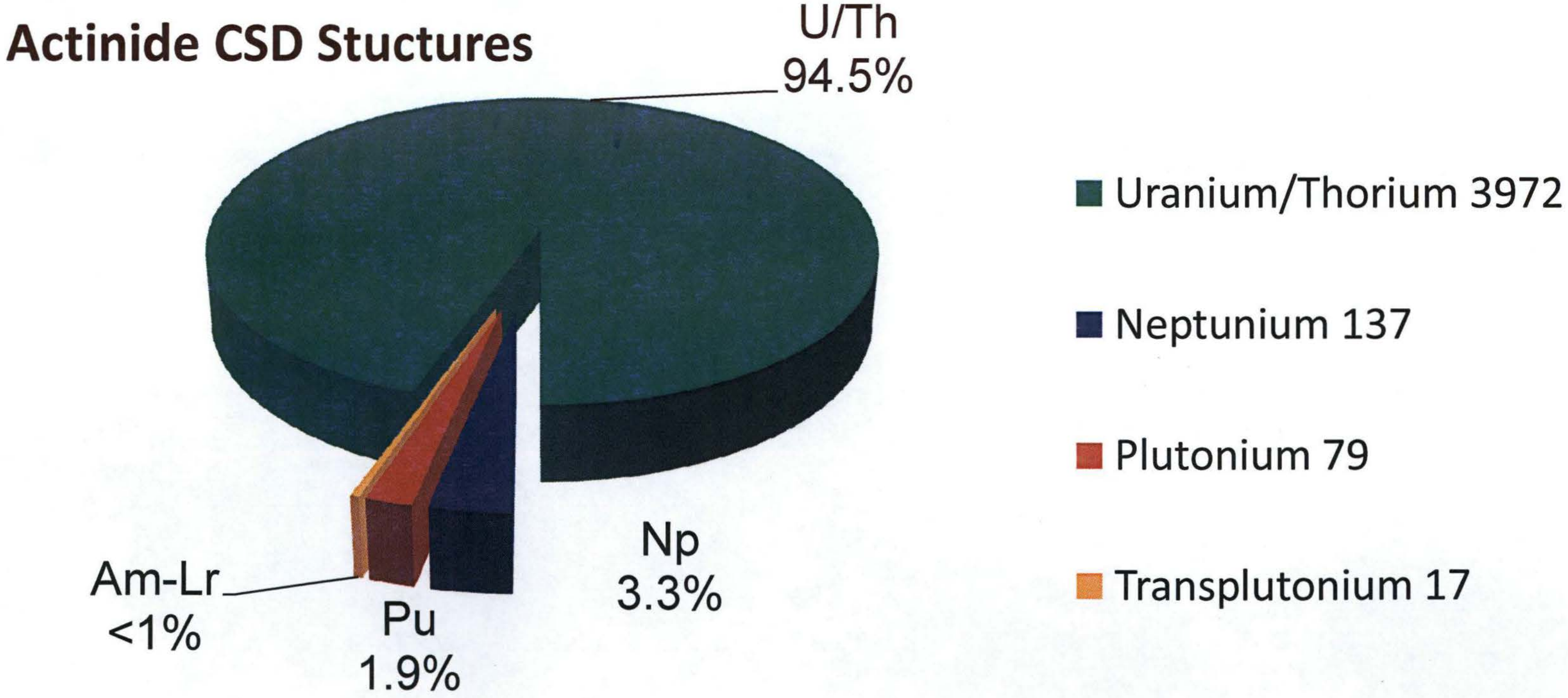
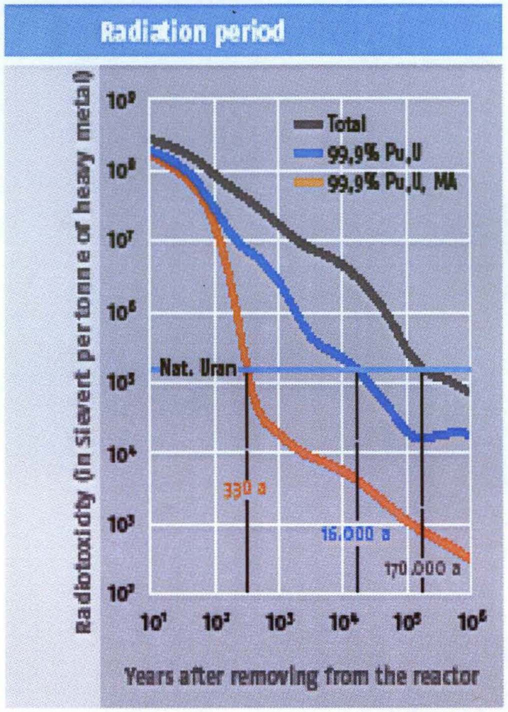
Overall Research Goals

- 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



Chemistry of Nuclear Fuel Cycles



Spent Fuel Composition:

95 % U (less hazardous than U ore)

3 % Short lived FP's/Stable Isotopes

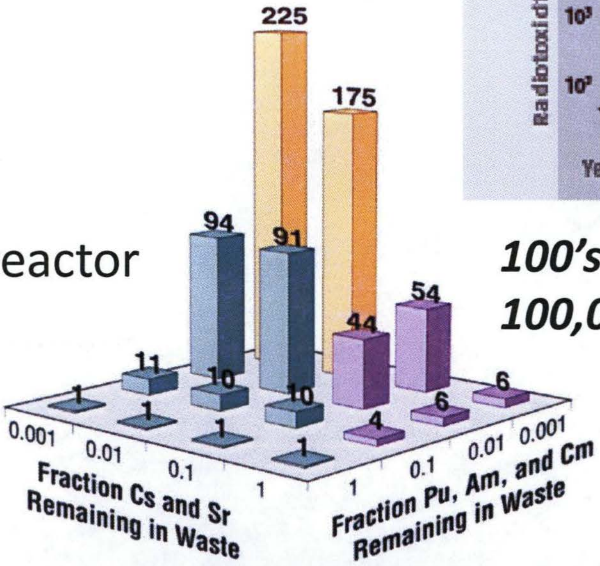
1% Transuranics (Pu, Np, Am, Cm)

Ln/An ratio > 10

Partitioning and Transmutation:

- Removes minor An from waste and recycles them by 'burning-up' in a reactor
- Vastly **reduces** waste **volume** and **time** needed for repository storage

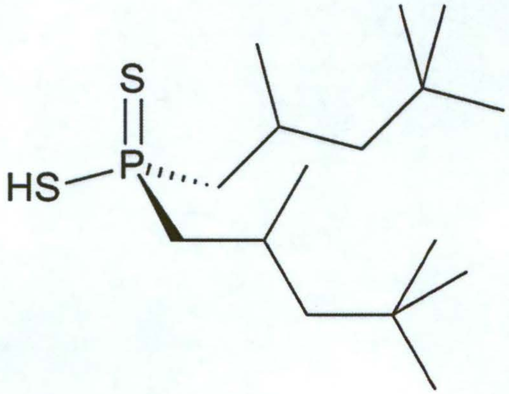
100's of years instead of 100,000's of years!



R.A. Wigeland et al., Nuclear Technology, ***2006****, 154, 95.*

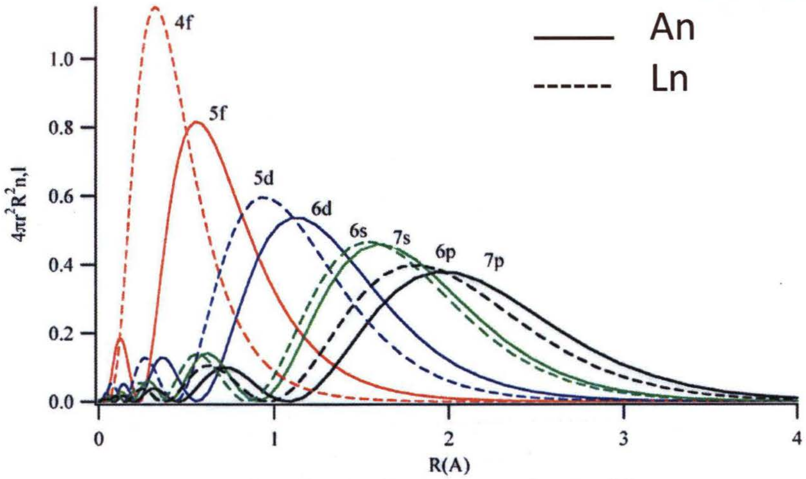
Challenge: An must first be separated from Ln in the spent fuel

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)

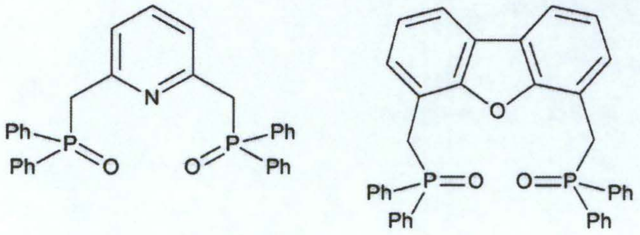
- Some soft donor extractants have a marked preference for An(III) over Ln(III)
- Radial extension, relative energies and symmetry of orbitals all important in bonding
- Can selectivity be explained by greater degree of **covalent** contribution to the bonding?



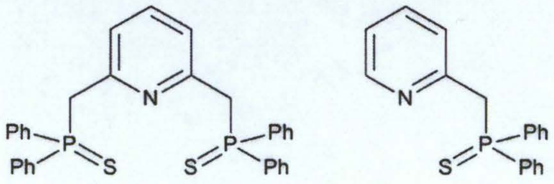
Orbital calculations performed by P. Jeffrey Hay, LANL

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

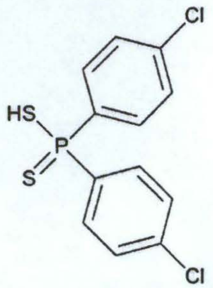
Ligand Classes



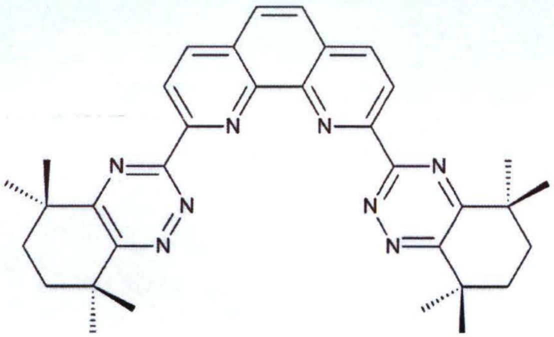
O-donor extractants (Paine, UNM)



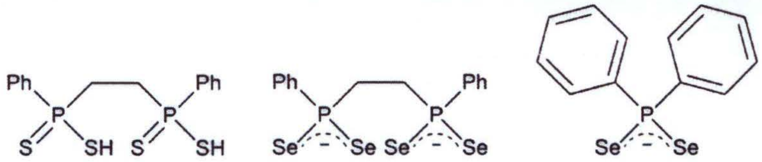
S-donor analogs



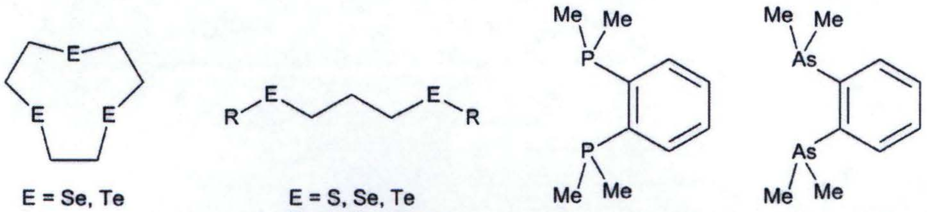
S-donor extractants
(Modolo, Germany)



N-donor extractants (Lewis, Reading)
(Sharrad, Manchester)



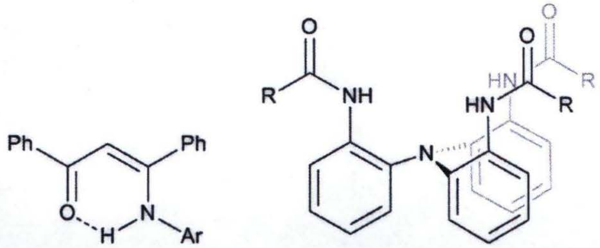
S-donor extractant derivatives and Se analogs
(Davies, Imperial College)



E = Se, Te

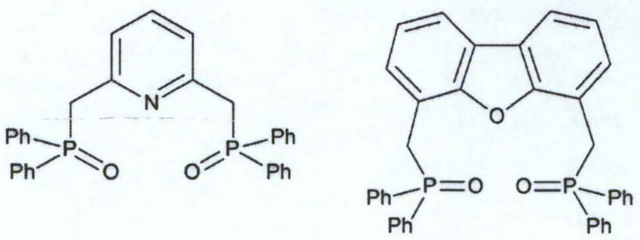
E = S, Se, Te
R = bulky group

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

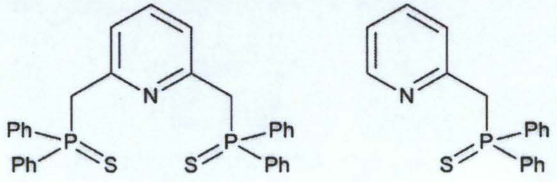


Mixed N,O-donors (Hayton, UCSB)
(MacBeth, Emory)

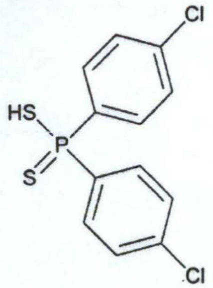
Ligand Classes



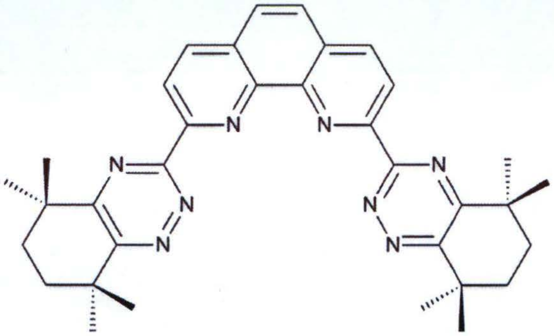
O-donor extractants (Paine, UNM)



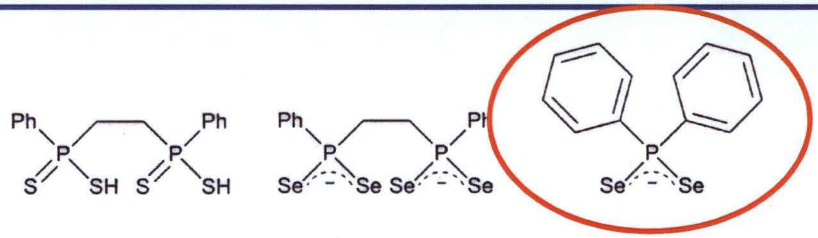
S-donor analogs



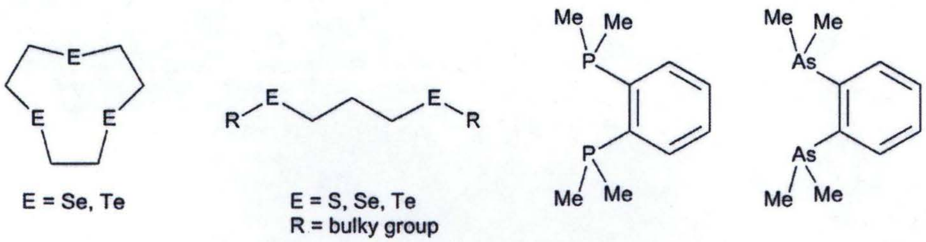
S-donor extractants
(Modolo, Germany)



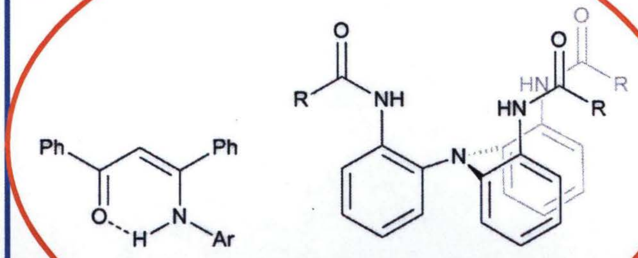
N-donor extractants (Lewis, Reading)
(Sharrad, Manchester)



S-donor extractant derivatives and Se analogs
(Davies, Imperial College)



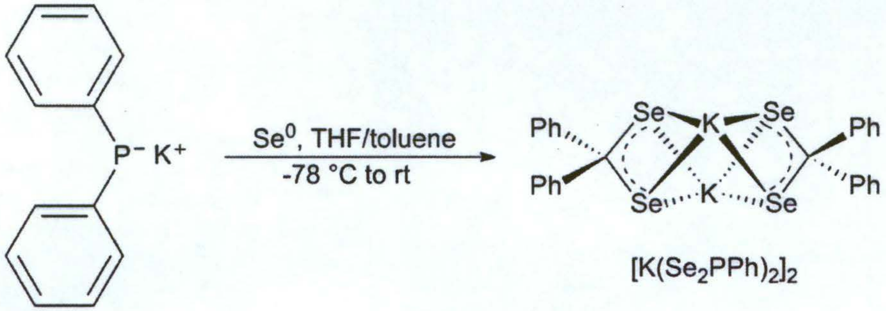
'Ultra-soft' neutral chalcogen and P/As donors



Mixed N,O-donors (Hayton, UCSB)
(MacBeth, Emory)

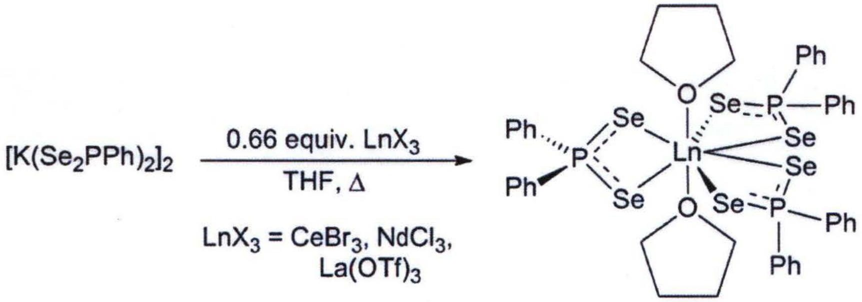
Diselenophosphinate Ligand

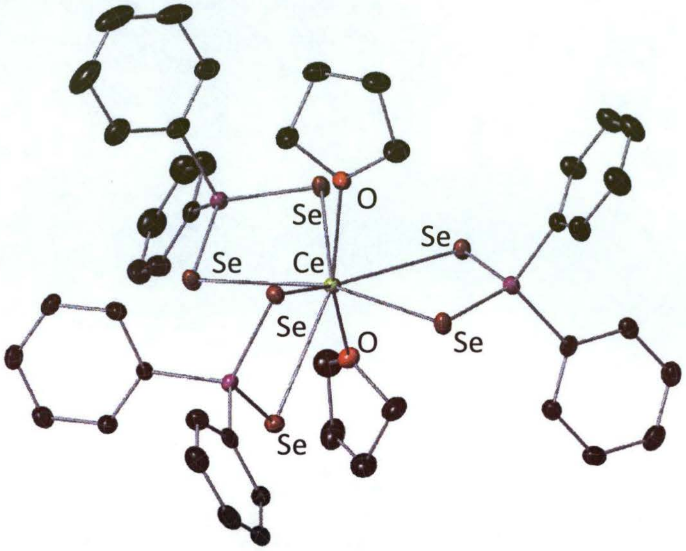
- Softer analog of known dithiophosphinate, no reported f-block complexes



[$K(Se_2PPh)_2]_2$

Davies, et al. Inorg. Chem., ***2004****, 43, 4802.*



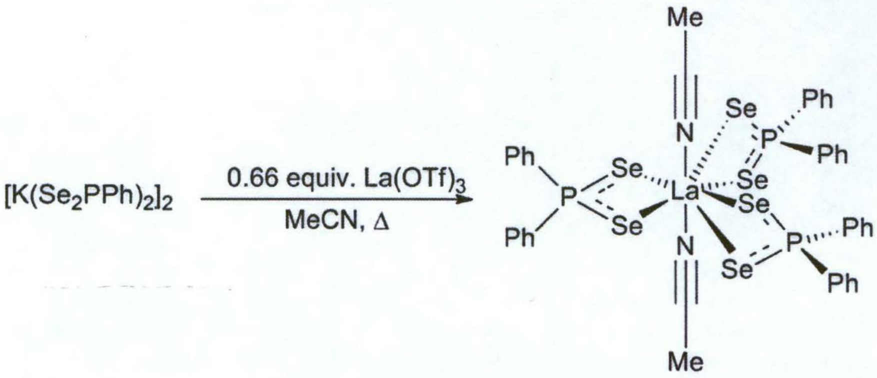


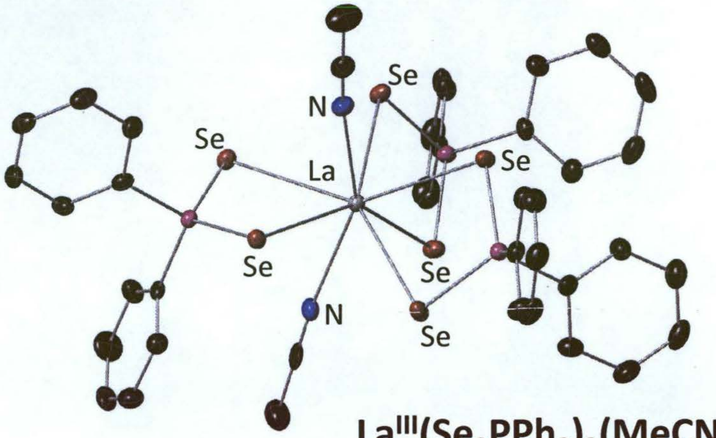
$Ce^{III}(Se_2PPh_2)_3(THF)_2$

6-coordinate
triangular dodecahedral

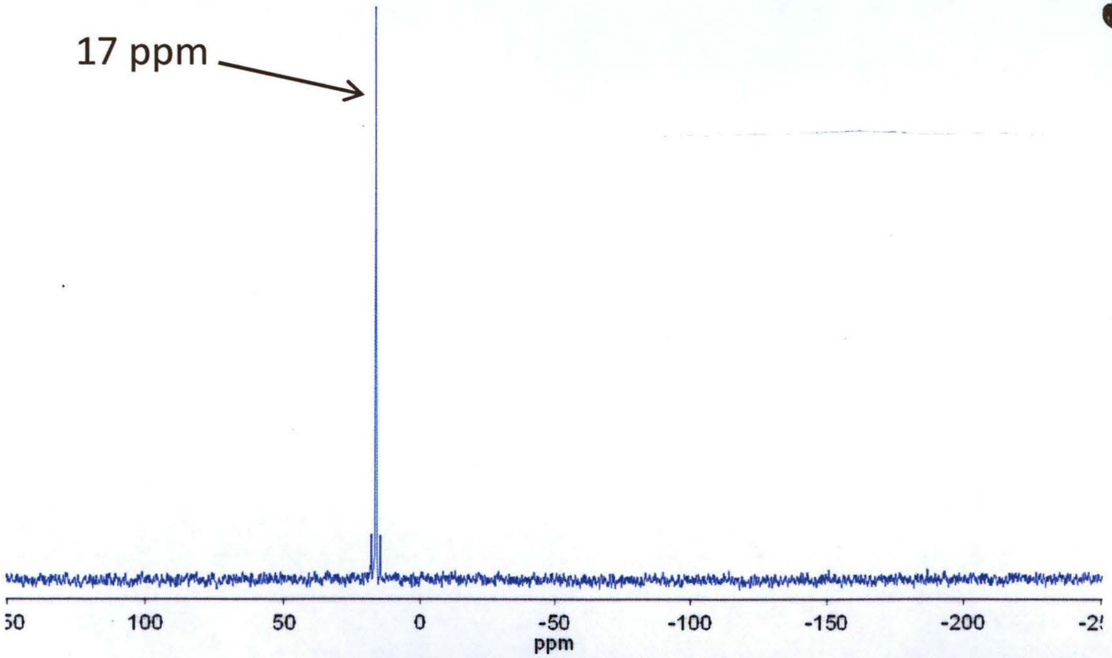
- 3 bidentate **Se donors** and 2 coordinated **solvent** molecules
- 2 selenophosphinate moieties approximately in plane, the third is perpendicular

Changing Coordinated Solvents





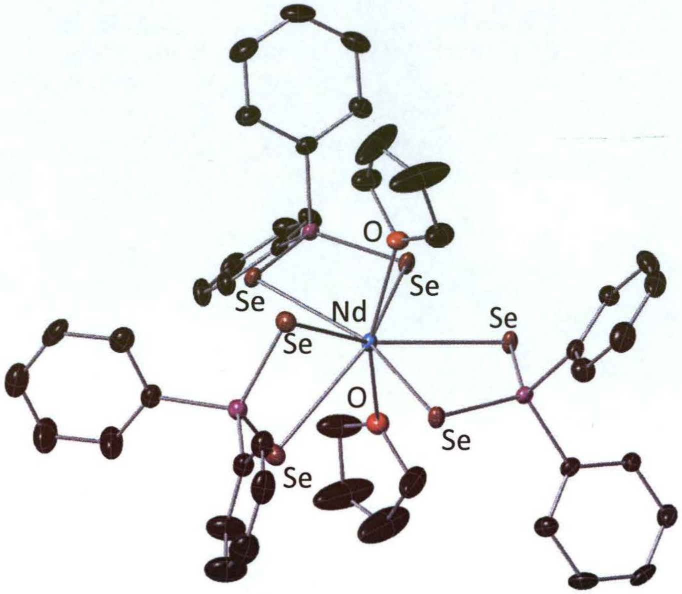
La^{III}(Se$_2$PPh$_2$)$_3$(MeCN)$_2$


17 ppm

- 8- coordinate, triangular dodecahedral geometry
- Switching from THF to MeCN causes 90 degree flip of ligands
- Symmetry in solution gives complexes one unique ^{31}P peak

	[K(Se$_2$PPh$_2$)]$_2$	La^{III}(Se$_2$PPh$_2$)$_3$(THF)$_2$	Ce^{III}(Se$_2$PPh$_2$)$_3$(THF)$_2$	Nd^{III}(Se$_2$PPh$_2$)$_3$(THF)$_2$
^{31}P	25 ppm	17 ppm	-58 ppm	-279 ppm

Ln(III) Metrical Parameters

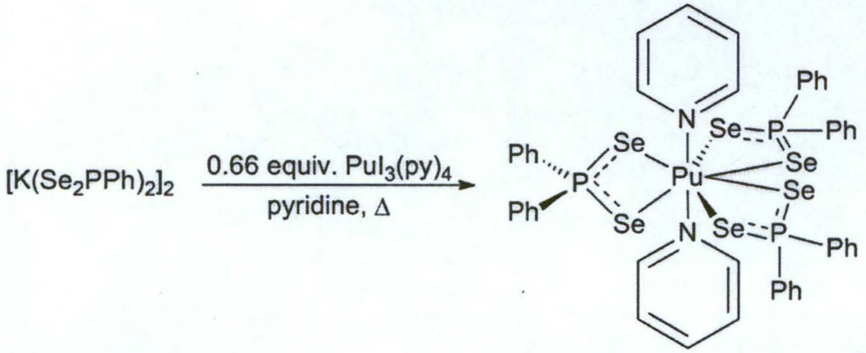


$Nd^{III}(Se_2PPh_2)_3(THF)_2$

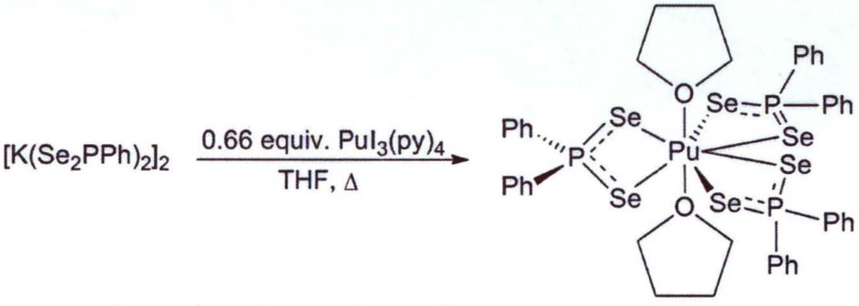
- MeCN complex results in shorter M—Se bonds
- Bond distances don't appear to follow expected trend, but are within error (3σ)

	$La^{III}(Se_2PPh_2)_3(MeCN)_2$	$La^{III}(Se_2PPh_2)_3(THF)_2$	$Ce^{III}(Se_2PPh_2)_3(THF)_2$	$Nd^{III}(Se_2PPh_2)_3(THF)_2$
M—Se (Å)	3.0932(5)	3.110(1)	3.1127(3)	3.0636(2)
Δ	+ 0.0168	+ 0.0027		- 0.0491

Pu(III) Complex

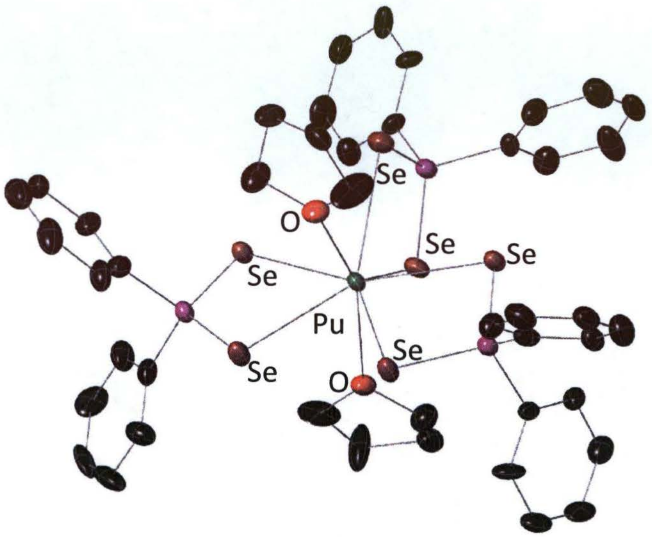


- ^{31}P NMR: -184 ppm
- difficult to obtain quality crystals



minor product

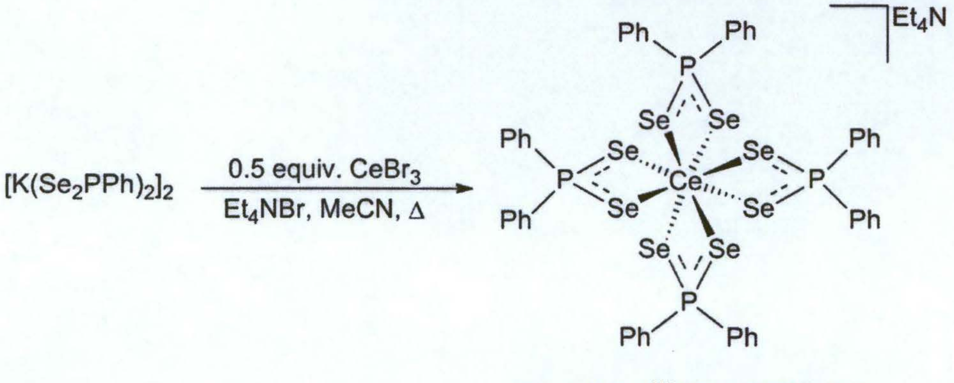
- 2 unique molecules in unit cell
- ^{31}P shift appears identical to py adduct
- ionic radii (+3, 6-coord): Ce, 1.01; Pu, 1.00



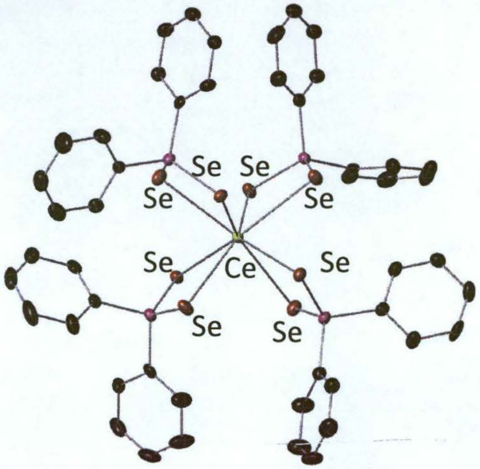
$Pu^{III}(Se_2PPh_2)_3(THF)_2$

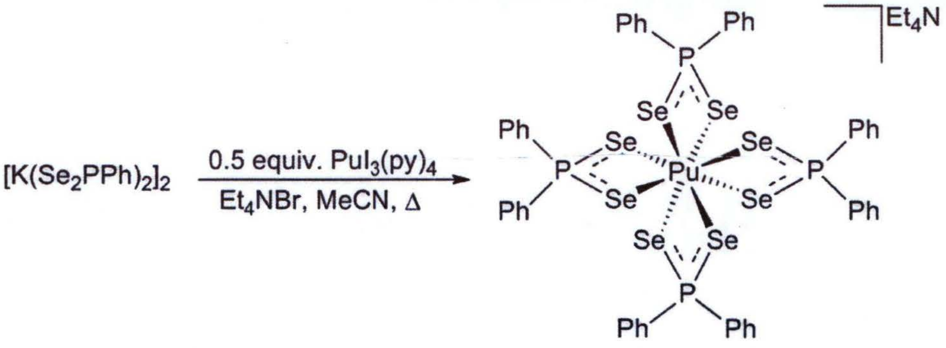
Bonds (Å)	$Pu^{III}(Se_2PPh_2)_3(THF)_2$	$Ce^{III}(Se_2PPh_2)_3(THF)_2$	ΔM-L
M—Se	**3.0803(7)**	3.1127(3)	+ 0.0324
M—O	**2.4999(6)**	2.4876(3)	- 0.0123

4:1 Complexes

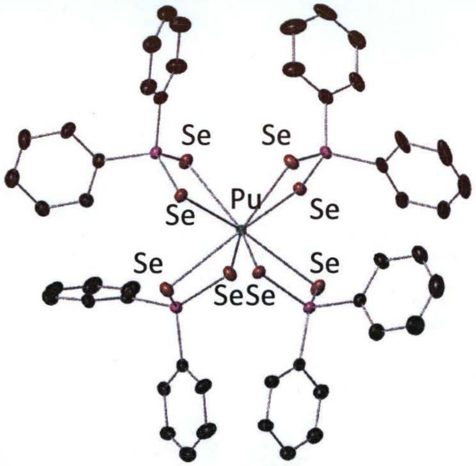


$Et_4N[Ce^{III}(Se_2PPh_2)_4]$





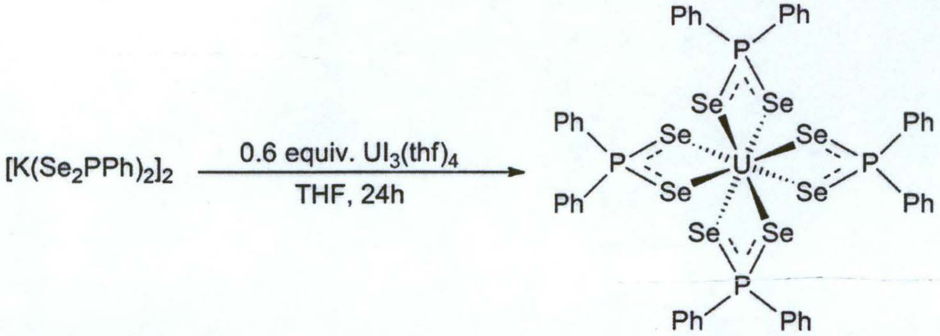
$Et_4N[Pu^{III}(Se_2PPh_2)_4]$



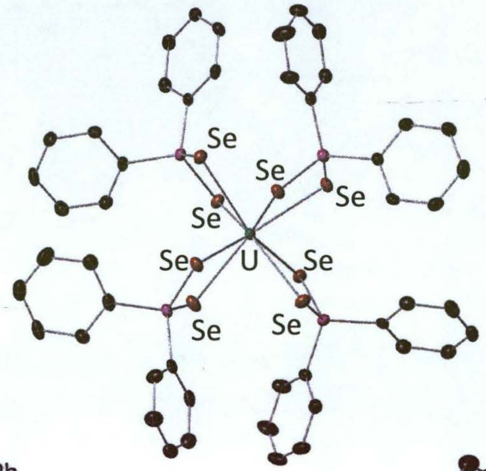
- both complexes are C_4-symmetric in solution
- ^{31}P NMR: -68 ppm (Ce), -170 ppm (Pu)

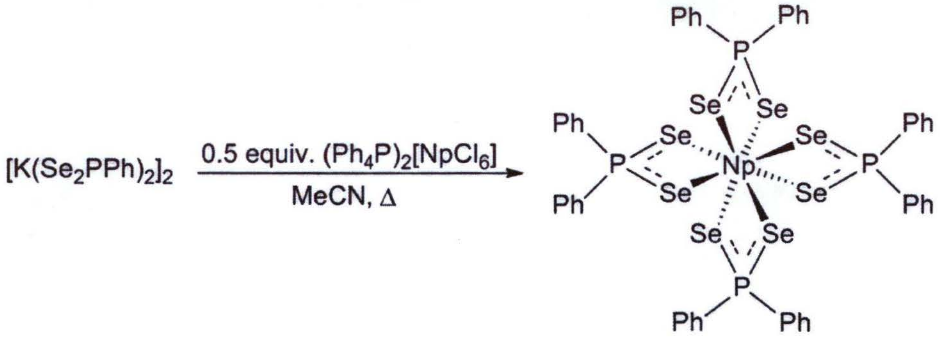
Bonds (Å)	$Et_4N[Ce^{III}(Se_2PPh_2)_4]$	$Et_4N[Pu^{III}(Se_2PPh_2)_4]$	ΔM-L
M—Se	3.0853(1)	3.0554(5)	+ 0.0299

An(IV) 4:1 Complexes

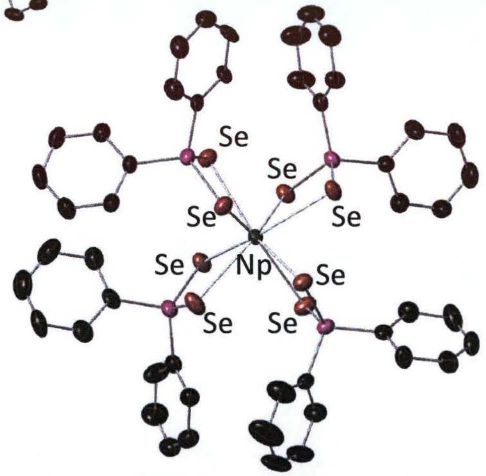


$[U^{IV}(Se_2PPh_2)_4]$





$[Np^{IV}(Se_2PPh_2)_4]$

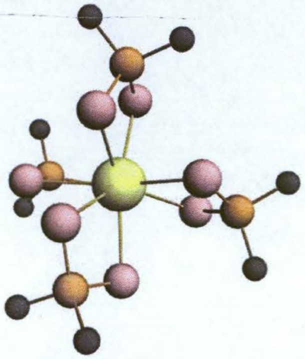


- ^{31}P NMR: U, -820 ppm
  Np, -902 ppm

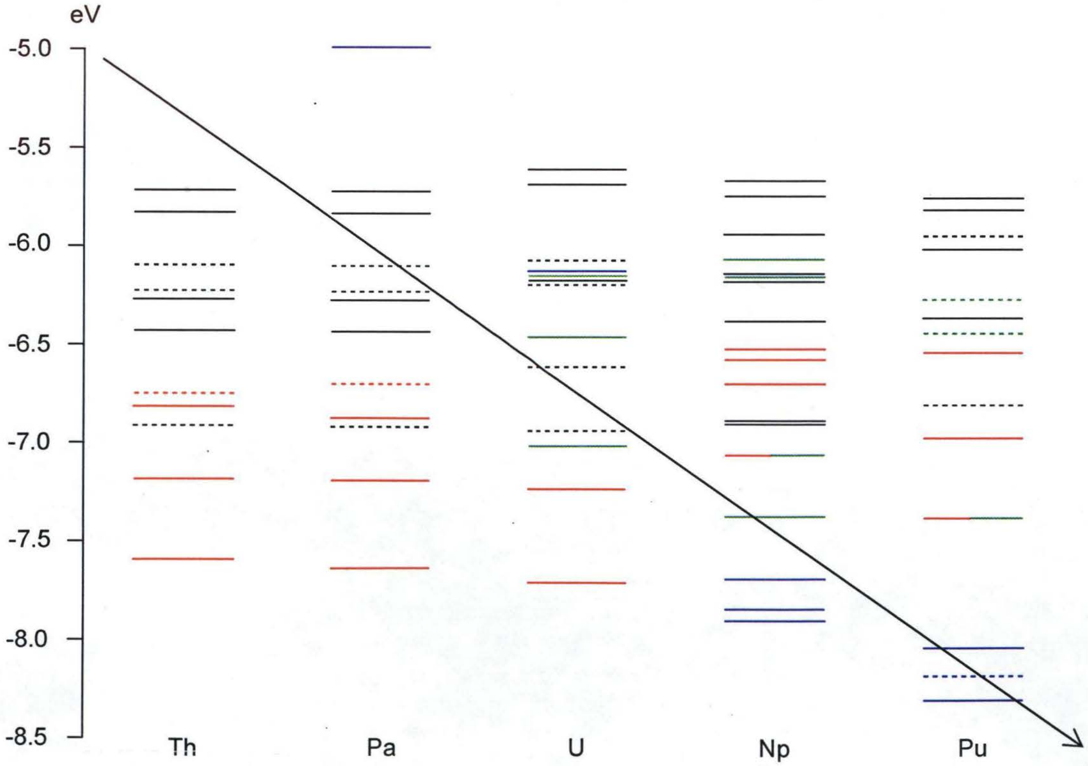
Bonds (Å)	$[U^{IV}(Se_2PPh_2)_4]$	$[Np^{IV}(Se_2PPh_2)_4]$	$[U^{IV}(S_2PPh_2)_4]$	$[Np^{IV}(S_2PPh_2)_4]$
M—E	2.970(1)	2.9585(9)	2.844(3)	2.832(10)
Δ	- 0.012		-0.012	

Initial Computational Findings

- N. Kaltsoyannis, UCL
- Pu(IV) complex not isolated
- Greater 5f orbital mixing across An series



	Calc (Å)	Exp(Å)
$Th(Se_2PMe_2)_4$	3.053	
$Pa(Se_2PMe_2)_4$	3.012	
$U(Se_2PMe_2)_4$	2.994	2.97
$Np(Se_2PMe_2)_4$	2.989	2.959
$Pu(Se_2PMe_2)_4$	2.993	



Red, > 10% d

Green, > 10% f

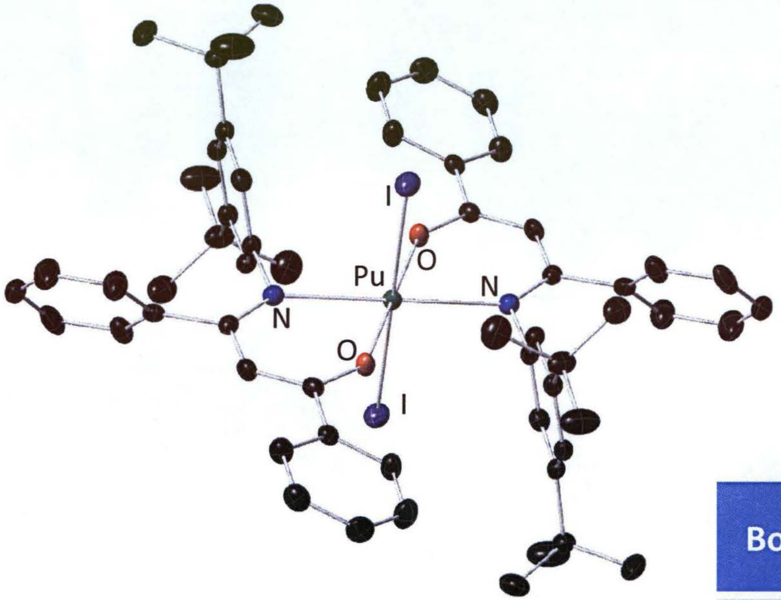
Blue, > 50% f

Dashed lines are doubly degenerate

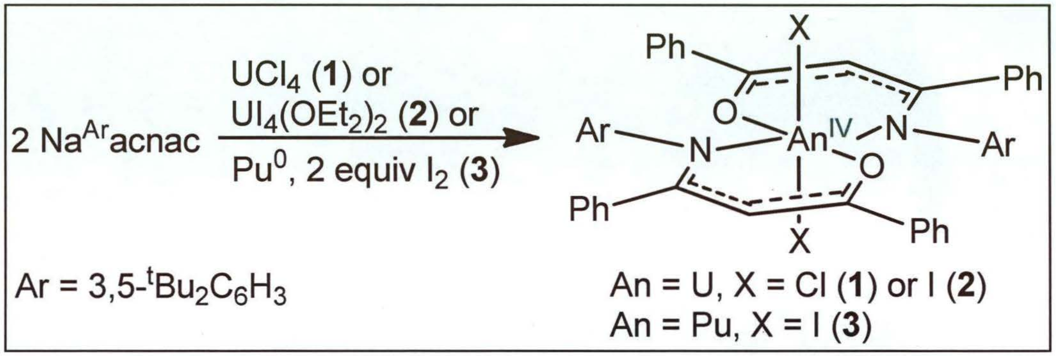
- An(III) versus Ln(III) calculations are underway

β-ketoiminate N,O Donor Complexes

- ^{Ar}acnac ligand gives access to very rare U(IV) *vs* Pu(IV) isostructural molecular comparison
- T. Hayton and D. Schnaars, UCSB



PuI$_2$(^{Ar}acnac)$_2$



$$2\ \mathrm{Na}^{Ar}\mathrm{acnac} \xrightarrow[\mathrm{Pu}^0,\ 2\ \mathrm{equiv}\ \mathrm{I}_2\ (\mathbf{3})]{\mathrm{UCl}_4\ (\mathbf{1})\ \mathrm{or}\ \mathrm{UI}_4(\mathrm{OEt}_2)_2\ (\mathbf{2})\ \mathrm{or}}$$

Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

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

Coordination number = 6

Distorted octahedral geometry

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

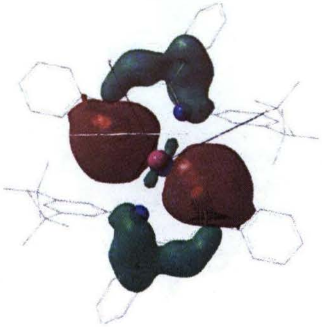
- U-O *vs* Pu-O and U-N *vs* Pu-N changes not explained well by ionic bonding alone

Gaunt, Hayton, Schnaars, Batista, et al, Chem. Commun., ***2011****, 47(27), 7647.*

β-ketoiminate N,O Donor Complexes

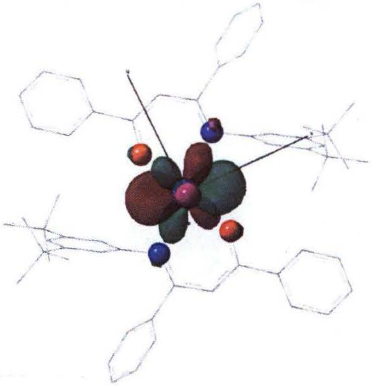
- Turned to DFT modeling to look for any 5f or 6d orbital interaction differences
  -(Batista, LANL)

- 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

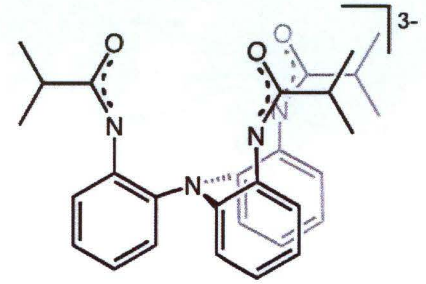
100% **6d**,
metal character

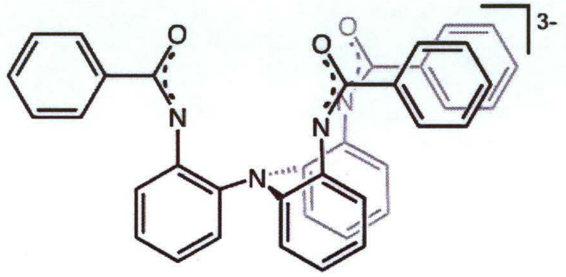
- Stronger U-O *vs* Pu-O orbital interactions lead to shorter U-O bond
  - the O atom carries 17% greater charge than the N atom in the ^{Ar}acnac ligand
  - it is the 'hard' O donor rather than the 'softer' N donor that exhibits 'covalency' differences!

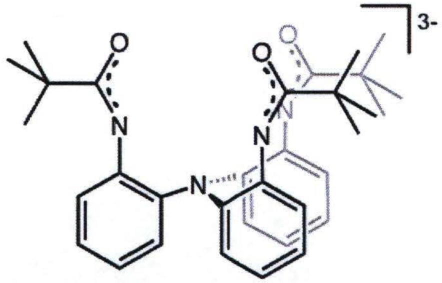
Gaunt, Hayton, Schnaars, Batista, et al, Chem. Commun., ***2011****, 47(27), 7647.*

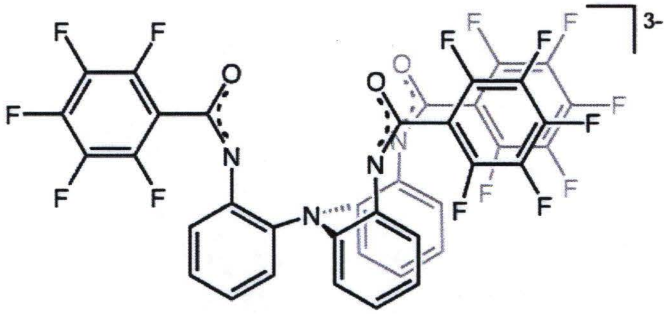
Other N,O Donor Complexes

- Do other N,O donors also exhibit interesting actinide-ligand orbital interactions?
- Trianionic triamidatoamine ligands offer tunable frameworks
  - collaboration with Cora MacBeth (Emory)





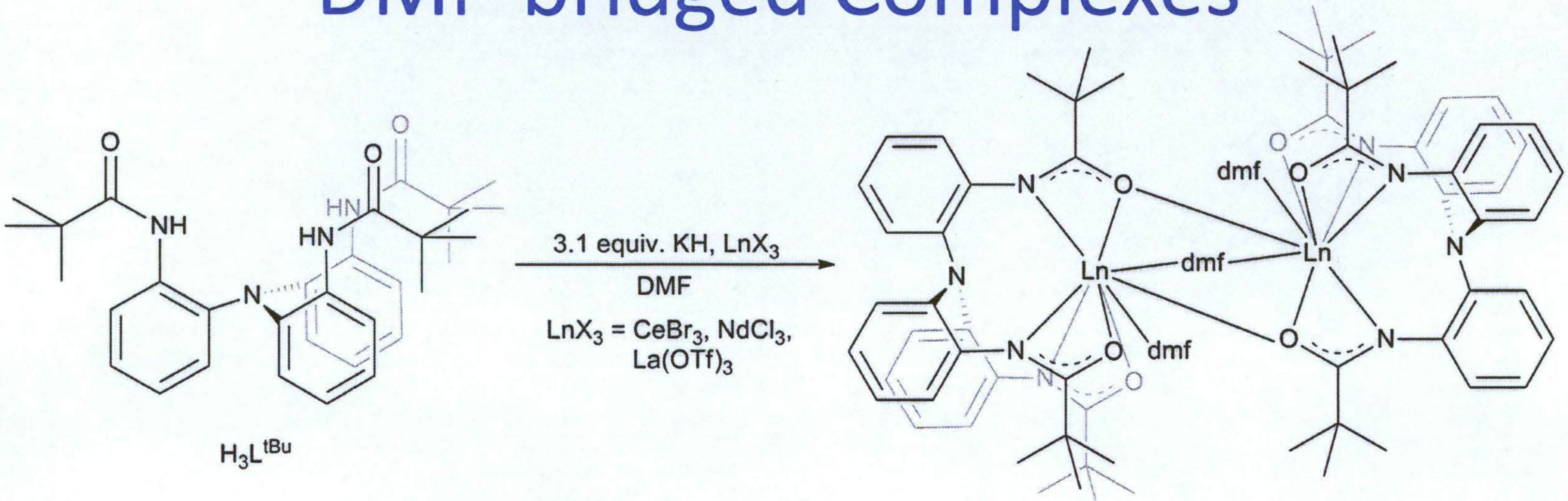




- No previous f-element complexes known – aim to compare Ln(III), An(III), An(IV)

*Jones, MacBeth. Inorg. Chem., **2007**, 46(20), 8117.*

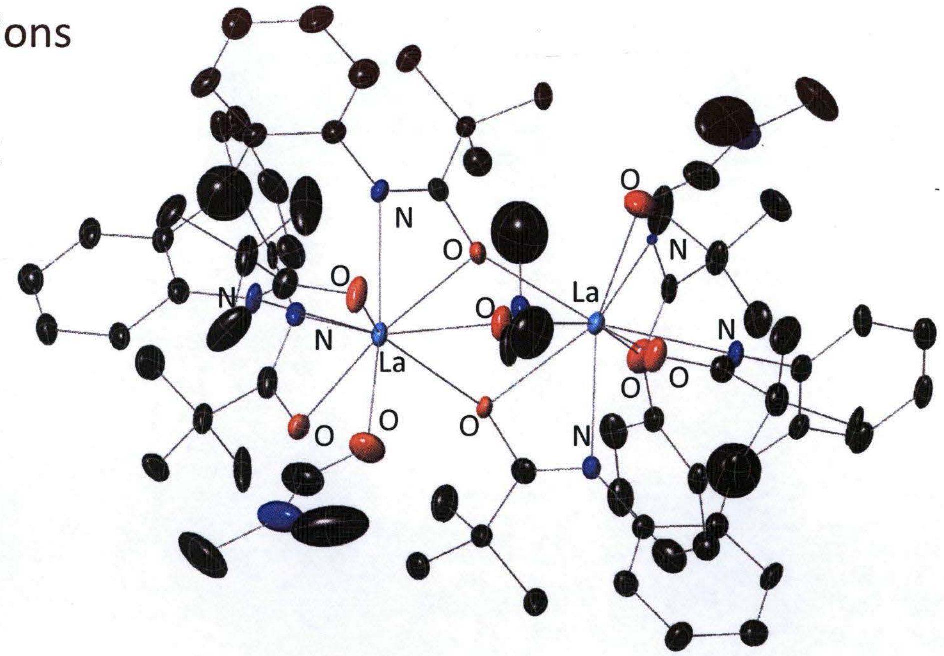
DMF-bridged Complexes



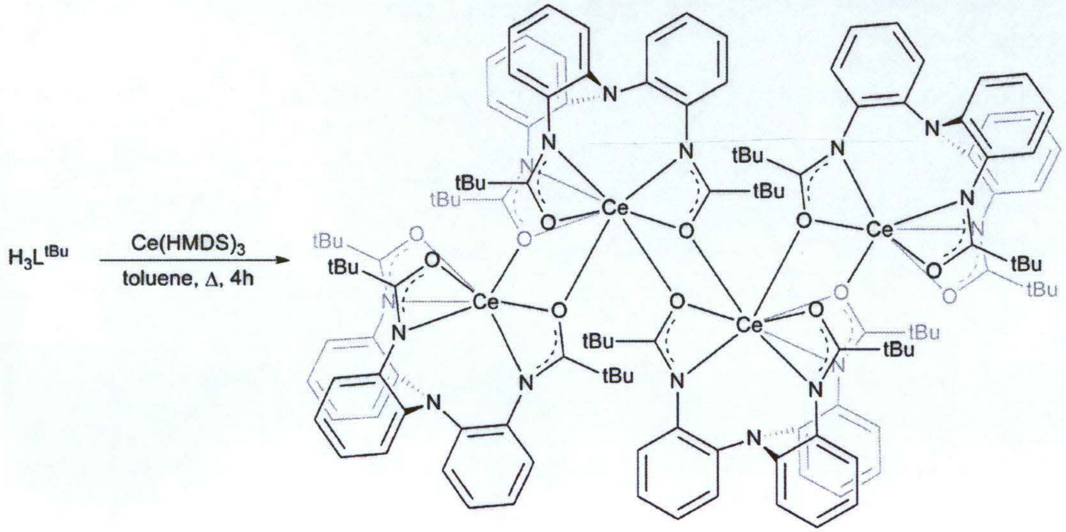
[(LnL^{tBu}(DMF))$_2$(μ-DMF)]

- Appears to remain intact in NMR (CDCl$_3$).
- Bridging DMF disordered over two positions
- No An complexes have been isolated yet

Bonds (Å)	La(III)	Ce(III)
M—O$_{dmf}$	2.602(4)	2.587(5)
M—O$_{\mu\text{-dmf}}$	2.596(2)	2.578(3)
M—O	2.537(3)	2.512(3)
M—O'	2.526(3)	2.502(4)
M—N	2.619(4)	2.594(4)



Cerium Tetramer



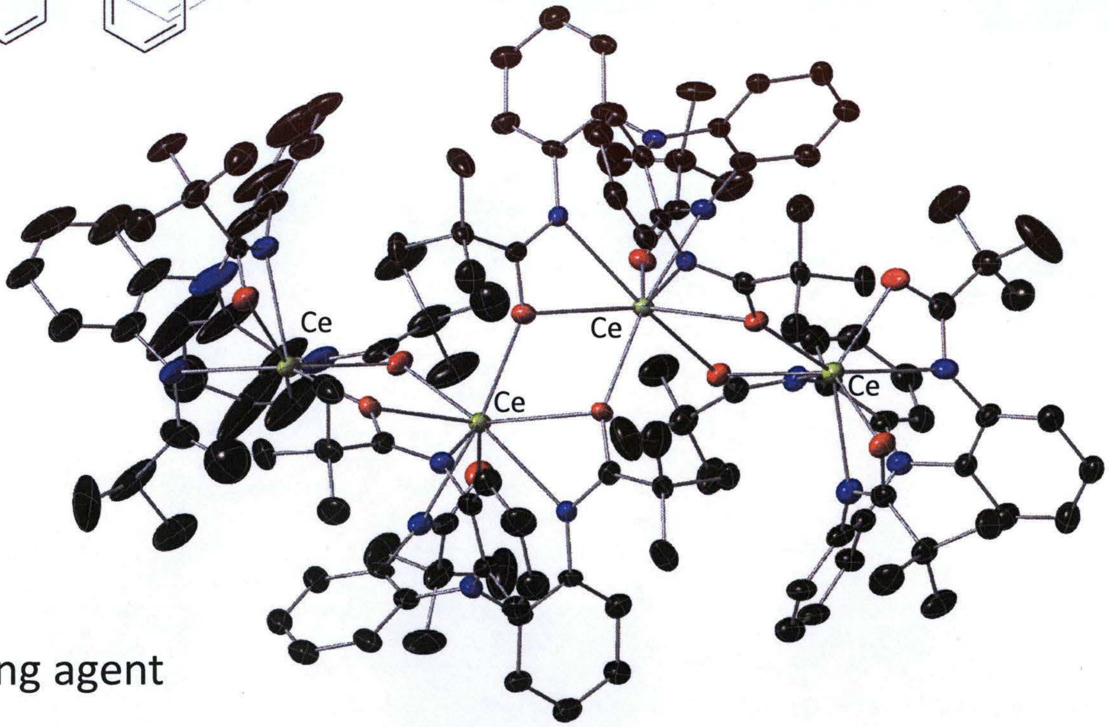
- Tetramer breaks up in solution NMR ($CDCl_3$).

- No An complexes yet

Bonds	Length (Å)
M—N	2.557(8)
M—O$_\mu$	2.535(6)
M—O	2.408(7)

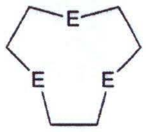
- Pu analog needs to be made

- Break up tetramer with capping agent



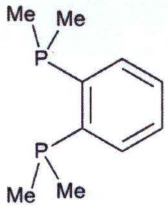
Future Directions

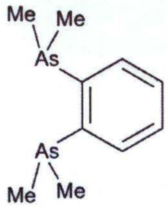
- Complete characterization of selenophosphinate complexes of Pu(III/IV), Np(IV) and Ln(III) ions
  - integrate all of the structural data with DFT modeling (Kaltsoyannis)
  - identify candidates for Se K-edge XAS measurements (Kozimor, LANL)
  - look towards ultra-soft, neutral-donor ligands



E = Se, Te

E = S, Se, Te
R = bulky group





- Further coordination of tripodal amidates
  - analogous Pu(III) dimer and tetrameric complexes
  - make monomeric Ce(III) complex
  - explore redox chemistry of the resulting complexes
  - look at the effect varying the ligand R group has on these complexes

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