



Impact of the Electronic Properties of Chalcogenide Ligands in their Complexation with Uranyl Nitrate Complexes

May 2023

Changing the World's Energy Future

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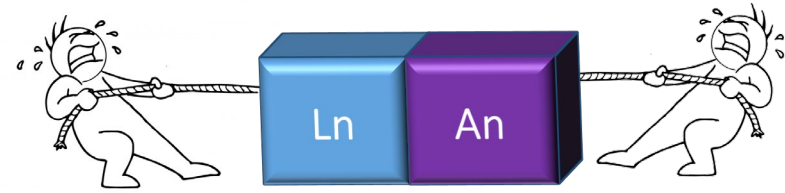
Hydrogen H *** 1.008 1																	Helium He *** 4.003 2						
Lithium Li * 6.941 3	Beryllium Be * 9.012 4																	Boron B * 10.81 5	Carbon C * 12.01 6	Nitrogen N *** 14.01 7	Oxygen O *** 16.00 8	Fluorine F *** 19.00 9	Neon Ne *** 20.18 10
Sodium Na * 22.99 11	Magnesium Mg * 24.31 12																	Aluminium Al * 26.98 13	Silicon Si * 28.09 14	Phosphorus P * 30.97 15	Sulfur S * 32.07 16	Chlorine Cl *** 35.45 17	Argon Ar *** 39.95 18
Potassium K * 39.10 19	Calcium Ca * 40.08 20	Scandium Sc * 44.96 21	Titanium Ti * 47.87 22	Vanadium V * 50.94 23	Chromium Cr * 52.00 24	Manganese Mn * 54.94 25	Iron Fe * 55.84 26	Cobalt Co * 58.93 27	Nickel Ni * 58.69 28	Copper Cu * 63.55 29	Zinc Zn * 65.39 30	Gallium Ga * 69.72 31	Germanium Ge * 72.63 32	Arsenic As * 74.92 33	Selenium Se * 78.96 34	Bromine Br ** 79.90 35	Krypton Kr *** 83.80 36						
Rubidium Rb * 85.47 37	Strontium Sr * 87.62 38	Yttrium Y * 88.91 39	Zirconium Zr * 91.22 40	Niobium Nb * 92.91 41	Molybdenum Mo * 95.94 42	Technetium Tc [98] 43	Ruthenium Ru * 101.07 44	Rhodium Rh * 102.91 45	Palladium Pd * 106.42 46	Silver Ag * 107.87 47	Cadmium Cd * 112.41 48	Indium In * 114.82 49	Tin Sn * 118.71 50	Antimony Sb * 121.76 51	Tellurium Te * 127.60 52	Iodine I ** 126.90 53	Xenon Xe *** 131.29 54						
Actinium Ac [227] 89	Thorium Th 232.04 90	Protactinium Pa 231.04 91	Uranium U 238.03 92	Neptunium Np [237] 93	Plutonium Pu [244] 94	Americium Am [243] 95	Curium Cm [247] 96	Berkelium Bk [247] 97	Californium Cf [251] 98	Einsteinium Es [252] 99	Fermium Fm [257] 100	Mendelevium Md [258] 101	Nobelium No [259] 102	Lawrencium Lr [262] 103									
Francium Fr * [223] 87	Radium Ra * [226] 88	↓	Rf * [267] 104	Db * [268] 105	Sg * [269] 106	Bh * [270] 107	Hs * [269] 108	Mt * [278] 109	Ds * [281] 110	Rg * [281] 111	Cn * [285] 112	Nh * [286] 113	Fl * [289] 114	Mc * [289] 115	Lv * [293] 116	Ts * [294] 117	Og *** [294] 118						

SEPARATION LIGANDS

Rationalizing the driving forces for actinide selectivity

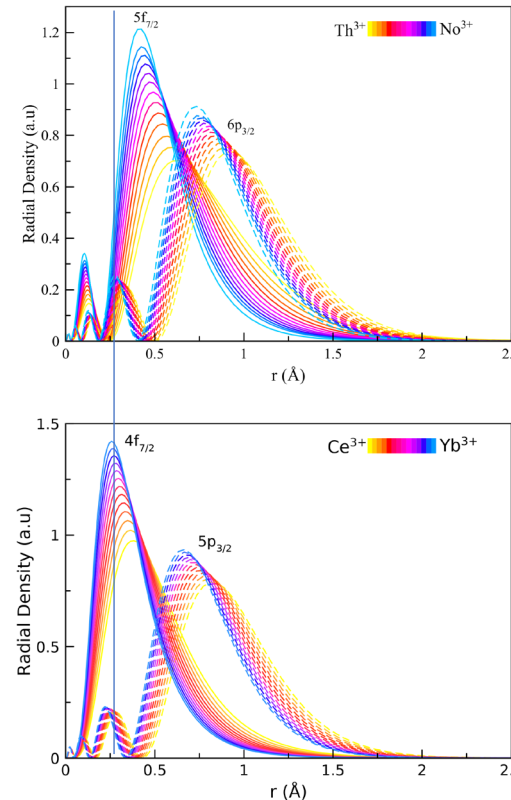
Ln/An SEPARATION

fundamental viewpoint



Rationale

- 5f orbitals radially more exposed than 4f
- 5f shell softer than 4f
- Softer-donor ligands would...
 - Enhance selectivity for actinides over lanthanides
 - Increase covalency with the metal center



HARD SOFT(ER)

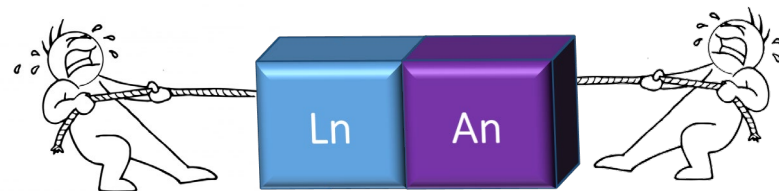
Metal center Ln^{3+} An^{3+}

Preferred Ligand (L) LO LN LS LSe

IONIC COVALENT

Ln/An SEPARATION

fundamental viewpoint



Chemical bond = electrostatic + covalency + dispersion + hyperconjugation + ...

Classical Mechanics

Quantum Mechanics

Sadhu, B., Dolg, M. *Inorganic Chemistry*, **2019**, 58, 9738-97-48.

Inorganic Chemistry

Cite This: *Inorg. Chem.* 2019, 58, 9738–9748

Article
pubs.acs.org/IC

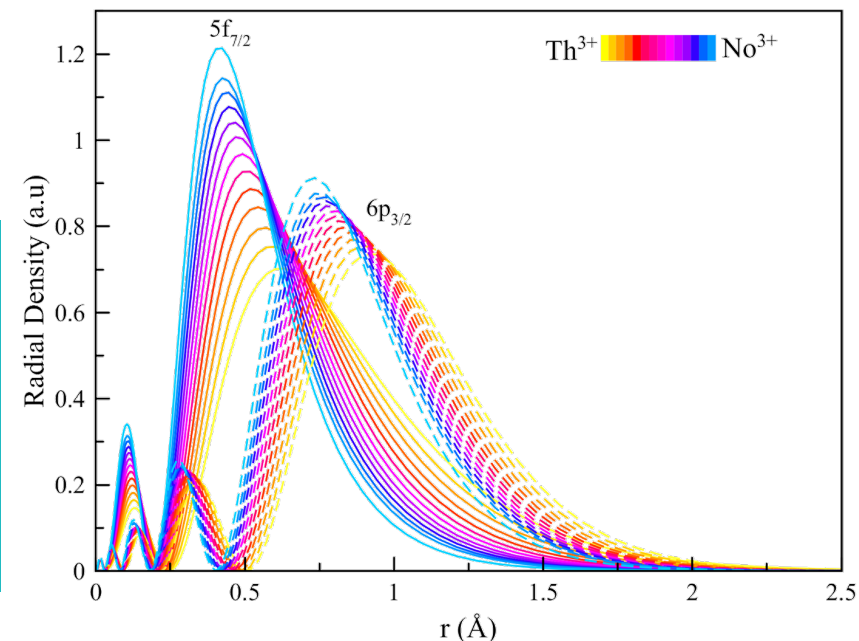
Enhancing Actinide(III) over Lanthanide(III) Selectivity through Hard-by-Soft Donor Substitution: Exploitation and Implication of Near-Degeneracy-Driven Covalency

Biswajit Sadhu^{*,†} and Michael Dolg^{*,‡}

[†]Health Physics Division, Health Safety & Environment Group, Bhabha Atomic Research Center (BARC), Mumbai 400 085, India

[‡]Institute for Theoretical Chemistry, University of Cologne, Greinstrasse 4, 50939 Cologne, Germany

**SOMETHING
MISSING from the
rationale**



- Softer-donor ligands DO increase covalency
- BUT...they also decrease electrostatic interaction
- MAY lead to a weaker complex

Ligands have to "deal" with the semi-core shells prior to interacting with the metal center

</

SOFT- VS HARD-DONORS?

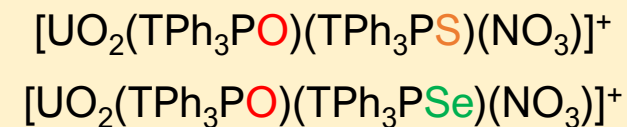
$[\text{UO}_2(\text{NO}_3)]^+$ and chalcogenide systems

EXPERIMENT AND THEORY

determining bonding properties and energies

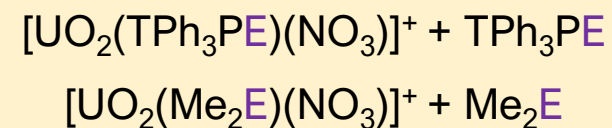
EXPERIMENT

Collision-induced
dissociation



THEORY

Complexation free
energies



Energy
decomposition
analysis

Pauli + Electrostatic + Orbital +
Dispersion

Topology of the
electron density of
the bond

Electron density
Total energy density

COVALENCY

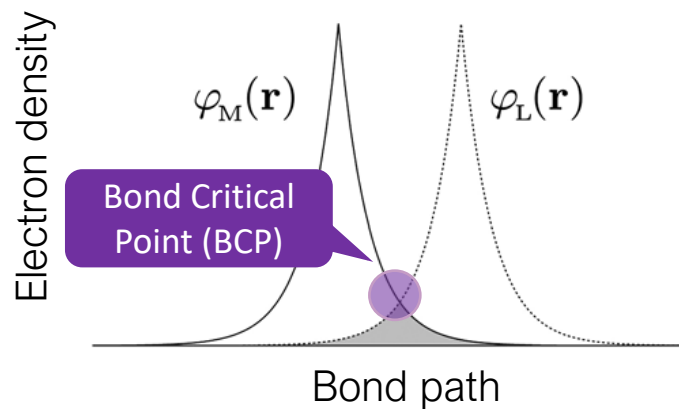
Energy decomposition analysis

Pauli + Electrostatic + Orbital + Dispersion

Topology of the electron density of the bond

Electron density
Total energy density

Pauli → Antisymmetrization of wave functions
Electrostatic → Coulomb interaction between nuclei and electrons
Orbital → Covalency through orbital mixing
Dispersion → Non-bonding attractive forces



Orbital overlap
Accidental degeneracy
Electrostatic



Total energy density

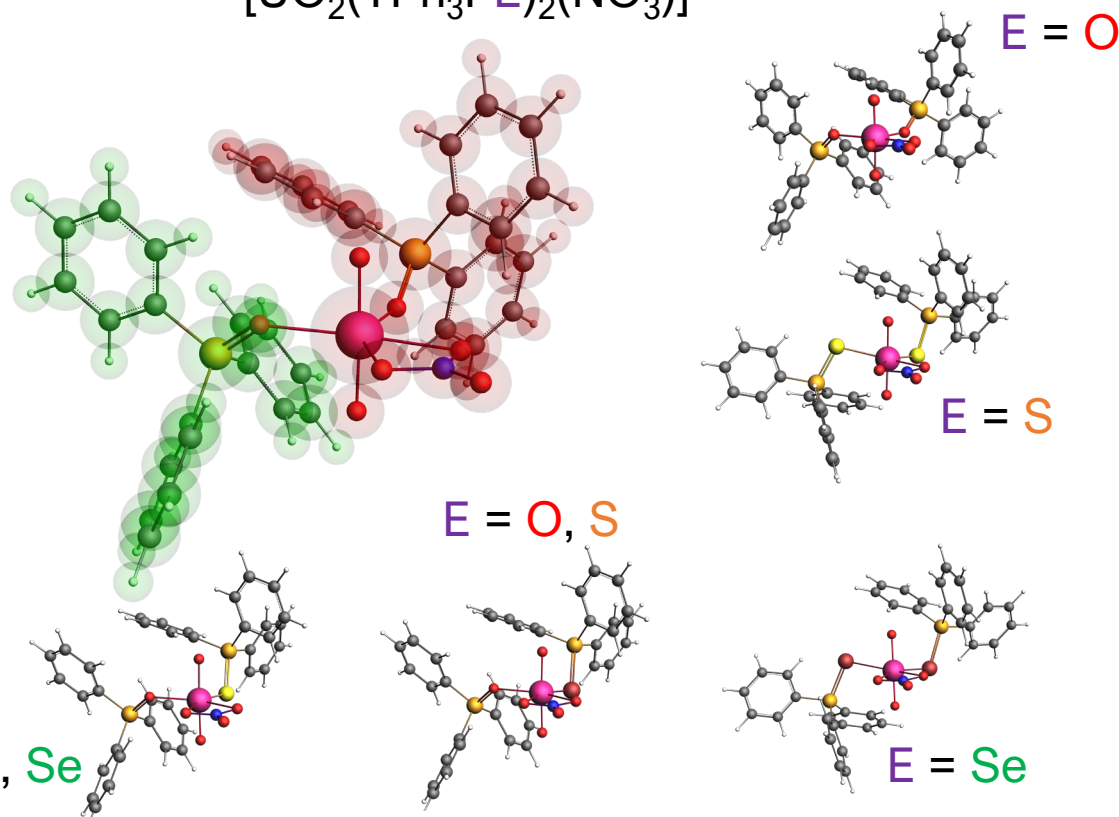
$$H(r) = G(r) + V(r)$$

Kinetic
energy
density

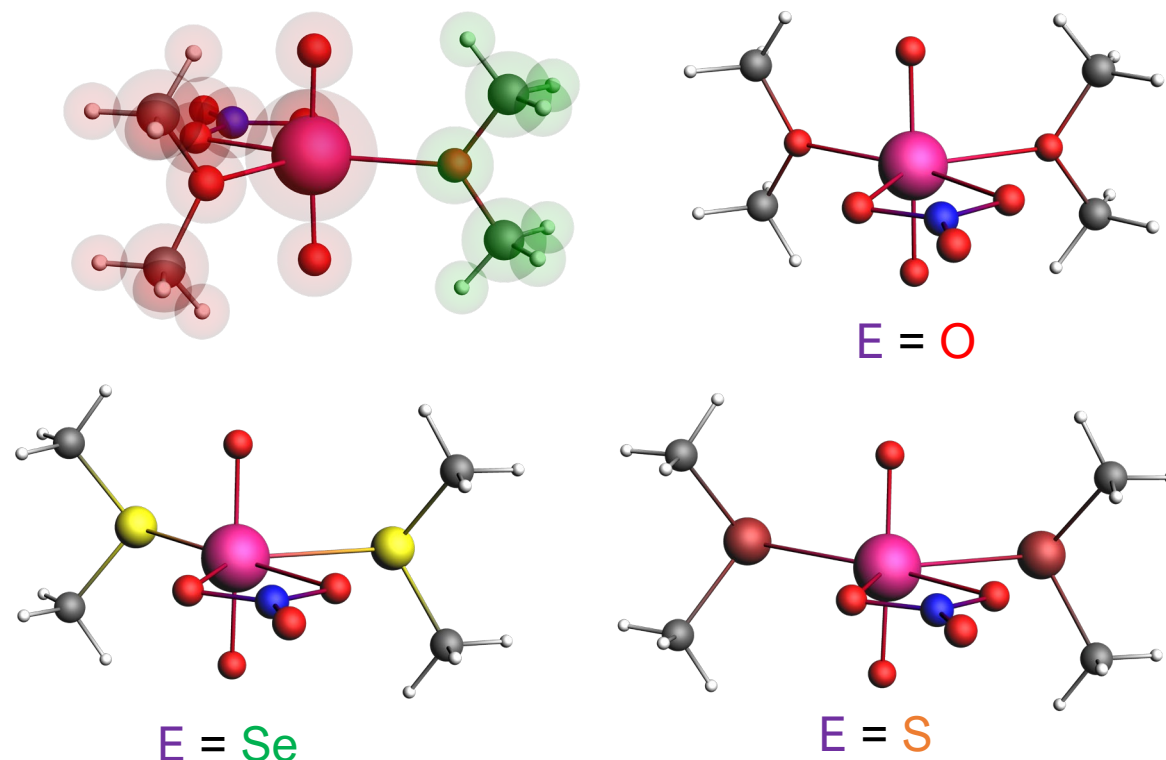
Potential
energy
density

MOLECULAR SYSTEMS

Triphenyl phosphine chalcogenide

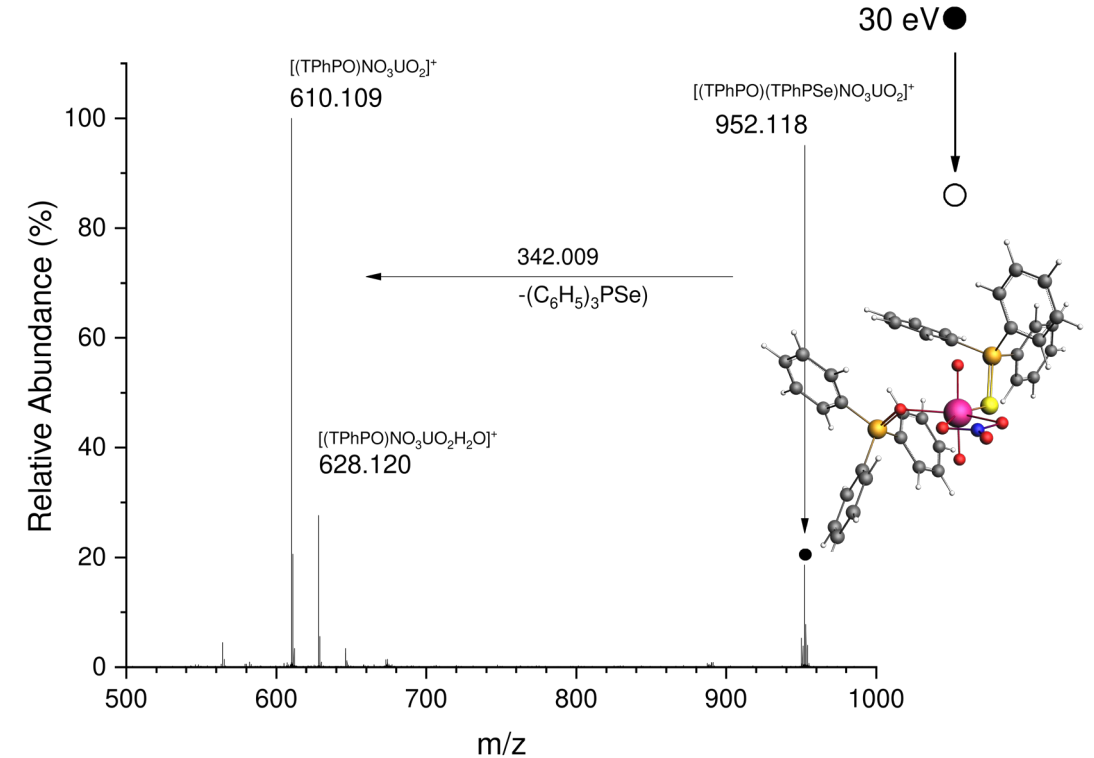
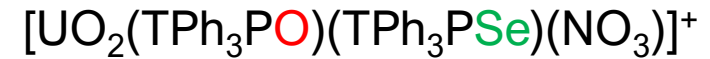
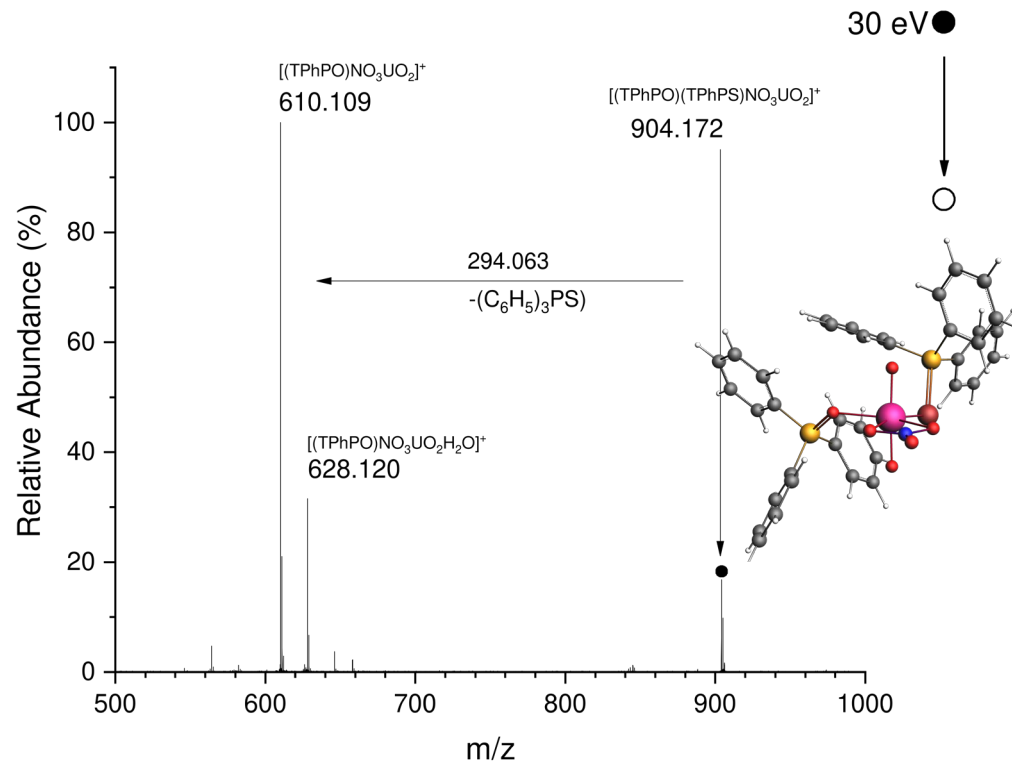


Dimethyl chalcogenide

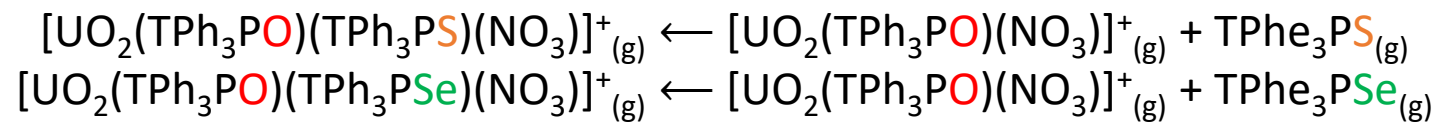


COLLISION INDUCED DISSOCIATION

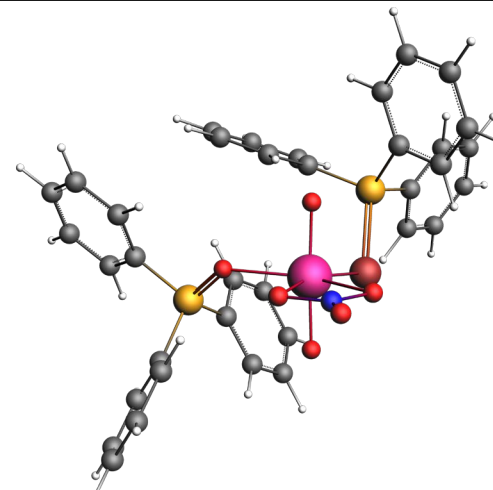
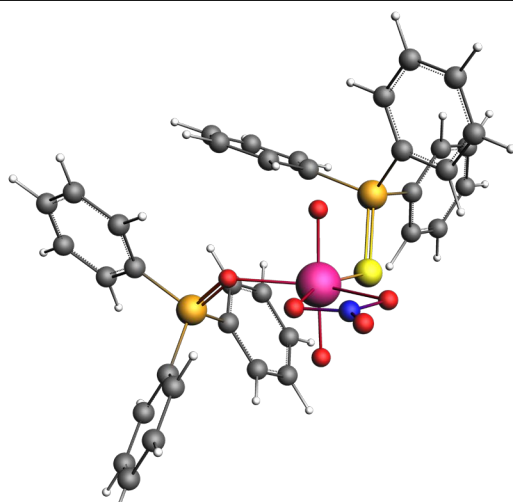
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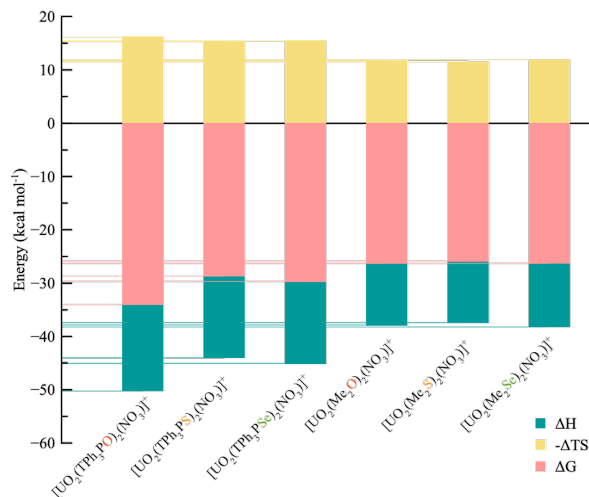
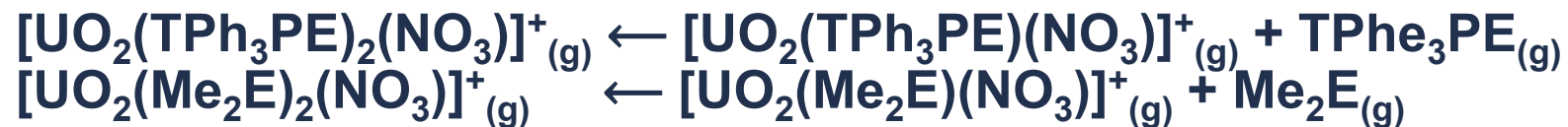
COMPLEXATION FREE ENERGIES



	ΔH	$-\Delta TS$	ΔG
$[\text{UO}_2(\text{TPhe}_3\text{P}^{\text{O}})(\text{TPhe}_3\text{P}^{\text{O}})(\text{NO}_3)]^+$	-50.2	16.2	-34.0
$[\text{UO}_2(\text{TPhe}_3\text{P}^{\text{O}})(\text{TPhe}_3\text{P}^{\text{S}})(\text{NO}_3)]^+$	-45.0	16.4	-28.6
$[\text{UO}_2(\text{TPhe}_3\text{P}^{\text{O}})(\text{TPhe}_3\text{P}^{\text{Se}})(\text{NO}_3)]^+$	-46.5	16.4	-30.0

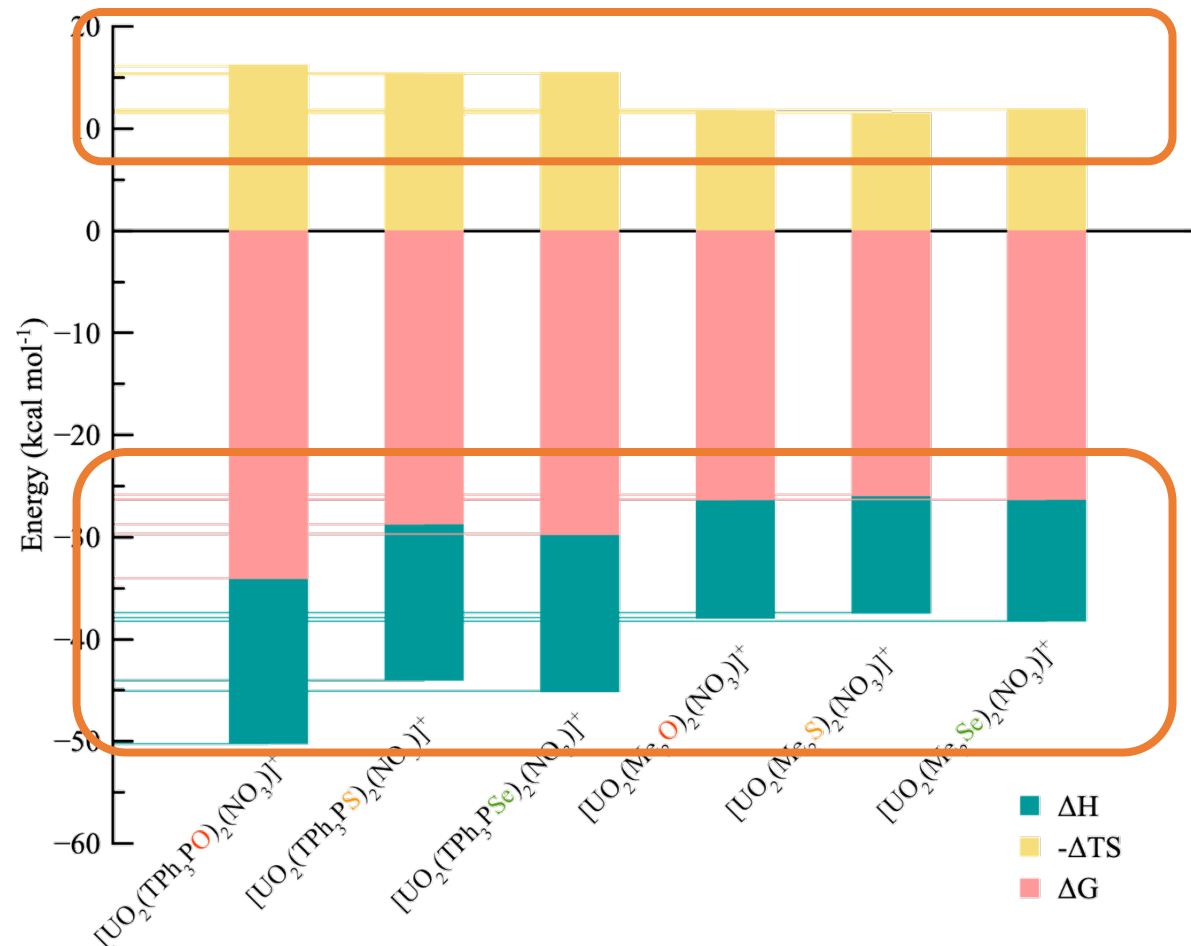
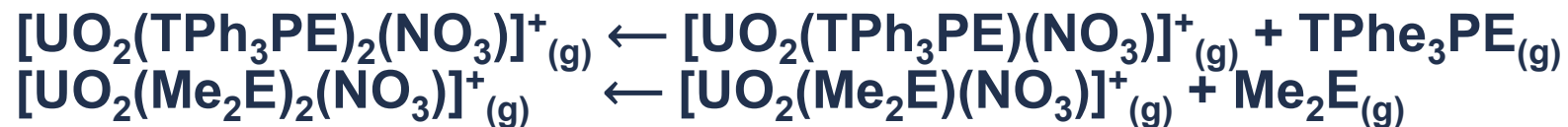


COMPLEXATION FREE ENERGIES



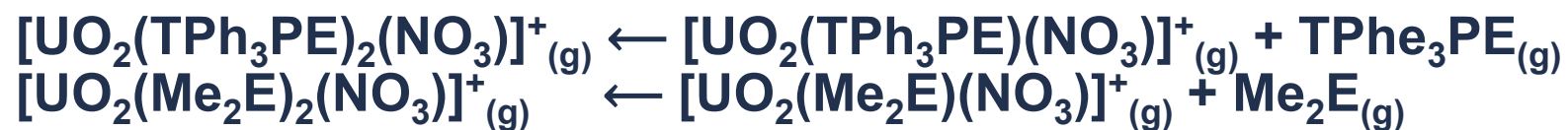
	ΔH	-ΔTS	ΔG
[UO ₂ (TPh ₃ PO) ₂ (NO ₃)] ⁺	-50.2	16.2	-34.0
[UO ₂ (TPh ₃ PS) ₂ (NO ₃)] ⁺	-44.0	15.3	-28.7
[UO ₂ (TPh ₃ PSe) ₂ (NO ₃)] ⁺	-45.1	15.5	-29.7
[UO ₂ (Me ₂ O) ₂ (NO ₃)] ⁺	-37.9	11.7	-26.3
[UO ₂ (Me ₂ S) ₂ (NO ₃)] ⁺	-37.4	11.5	-25.9
[UO ₂ (Me ₂ Se) ₂ (NO ₃)] ⁺	-38.2	11.9	-26.3

COMPLEXATION FREE ENERGIES

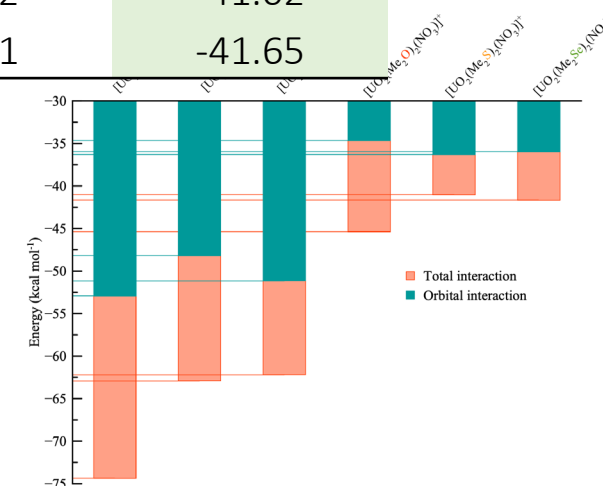


	ΔH	-ΔTS	ΔG
$[\text{UO}_2(\text{TPh}_3\text{PO})_2(\text{NO}_3)]^+$	-50.2	16.2	-34.0
$[\text{UO}_2(\text{TPh}_3\text{PS})_2(\text{NO}_3)]^+$	-44.0	15.3	-28.7
$[\text{UO}_2(\text{TPh}_3\text{PSe})_2(\text{NO}_3)]^+$	-45.1	15.5	-29.7
$[\text{UO}_2(\text{Me}_2\text{O})_2(\text{NO}_3)]^+$	-37.9	11.7	-26.3
$[\text{UO}_2(\text{Me}_2\text{S})_2(\text{NO}_3)]^+$	-37.4	11.5	-25.9
$[\text{UO}_2(\text{Me}_2\text{Se})_2(\text{NO}_3)]^+$	-38.2	11.9	-26.3

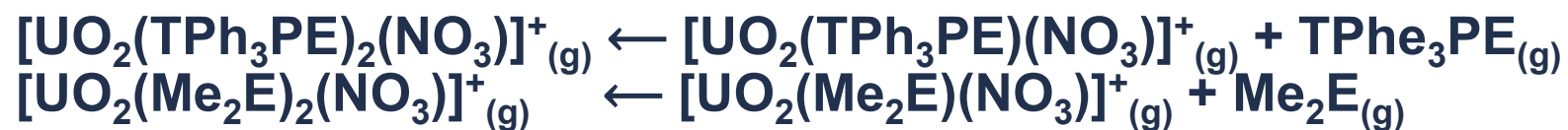
ENERGY DECOMPOSITION



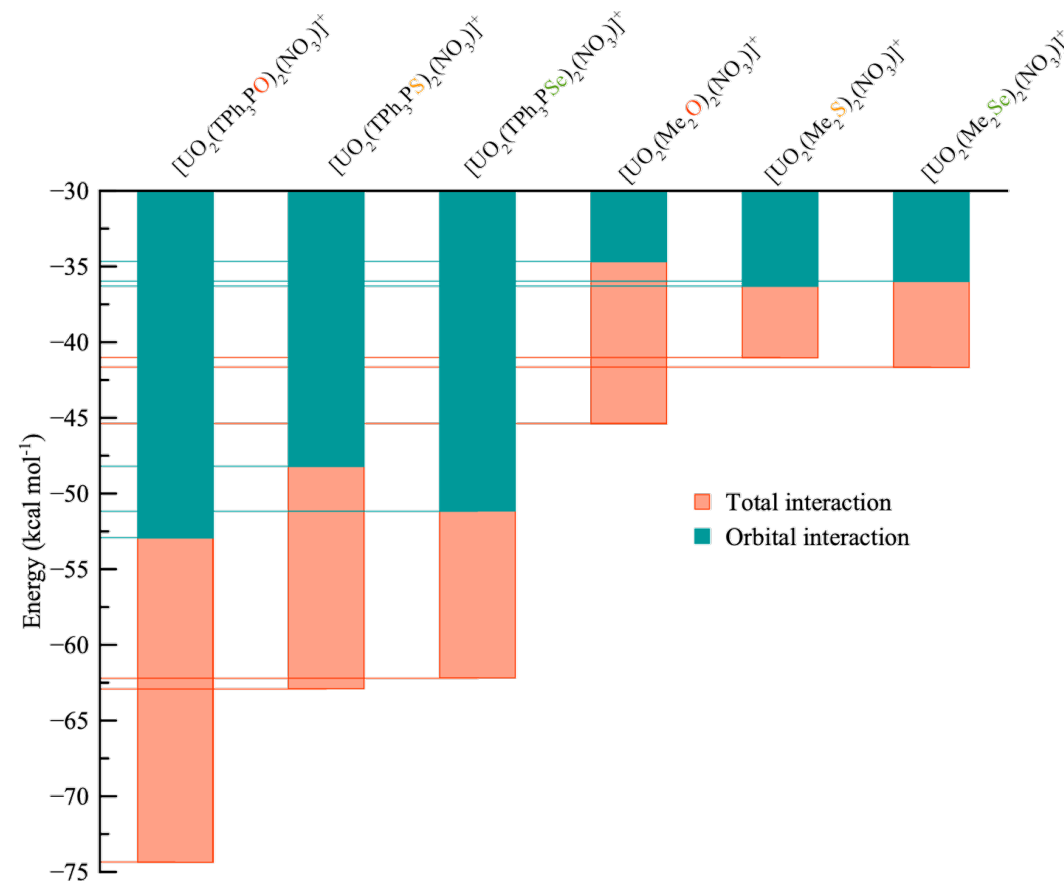
	Pauli	Electrostatic	Steric	Orbital	Dispersion	Total
$[\text{UO}_2(\text{TPh}_3\text{P}\text{O})_2(\text{NO}_3)]^+$	73.38	-82.42	-9.04	-52.91	-12.41	-74.36
$[\text{UO}_2(\text{TPh}_3\text{P}\text{S})_2(\text{NO}_3)]^+$	63.38	-66.01	-2.63	-48.19	-12.08	-62.90
$[\text{UO}_2(\text{TPh}_3\text{P}\text{Se})_2(\text{NO}_3)]^+$	66.33	-68.63	-2.30	-51.15	-8.75	-62.19
$[\text{UO}_2(\text{Me}_2\text{O})_2(\text{NO}_3)]^+$	45.59	-53.48	-7.89	-34.67	-2.81	-45.37
$[\text{UO}_2(\text{Me}_2\text{S})_2(\text{NO}_3)]^+$	44.37	-46.39	-2.02	-36.28	-2.72	-41.02
$[\text{UO}_2(\text{Me}_2\text{Se})_2(\text{NO}_3)]^+$	42.88	-45.66	-2.78	-35.97	-2.91	-41.65



ENERGY DECOMPOSITION

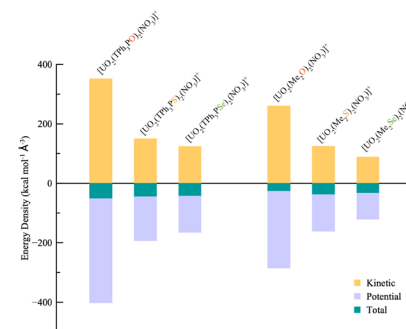
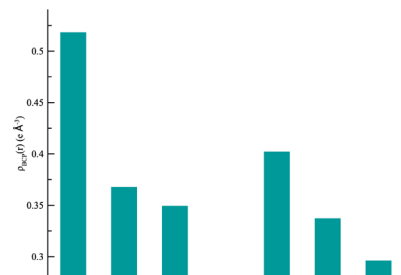


	Pauli	Electrostatic	Steric	Orbital	Dispersion	Total
$[\text{UO}_2(\text{TPh}_3\text{PO})_2(\text{NO}_3)]^+$	73.38	-82.42	-9.04	-52.91	-12.41	-74.36
$[\text{UO}_2(\text{TPh}_3\text{PS})_2(\text{NO}_3)]^+$	63.38	-66.01	-2.63	-48.19	-12.08	-62.90
$[\text{UO}_2(\text{TPh}_3\text{PSe})_2(\text{NO}_3)]^+$	66.33	-68.63	-2.30	-51.15	-8.75	-62.19
$[\text{UO}_2(\text{Me}_2\text{O})_2(\text{NO}_3)]^+$	45.59	-53.48	-7.89	-34.67	-2.81	-45.37
$[\text{UO}_2(\text{Me}_2\text{S})_2(\text{NO}_3)]^+$	44.37	-46.39	-2.02	-36.28	-2.72	-41.02
$[\text{UO}_2(\text{Me}_2\text{Se})_2(\text{NO}_3)]^+$	42.88	-45.66	-2.78	-35.97	-2.91	-41.65

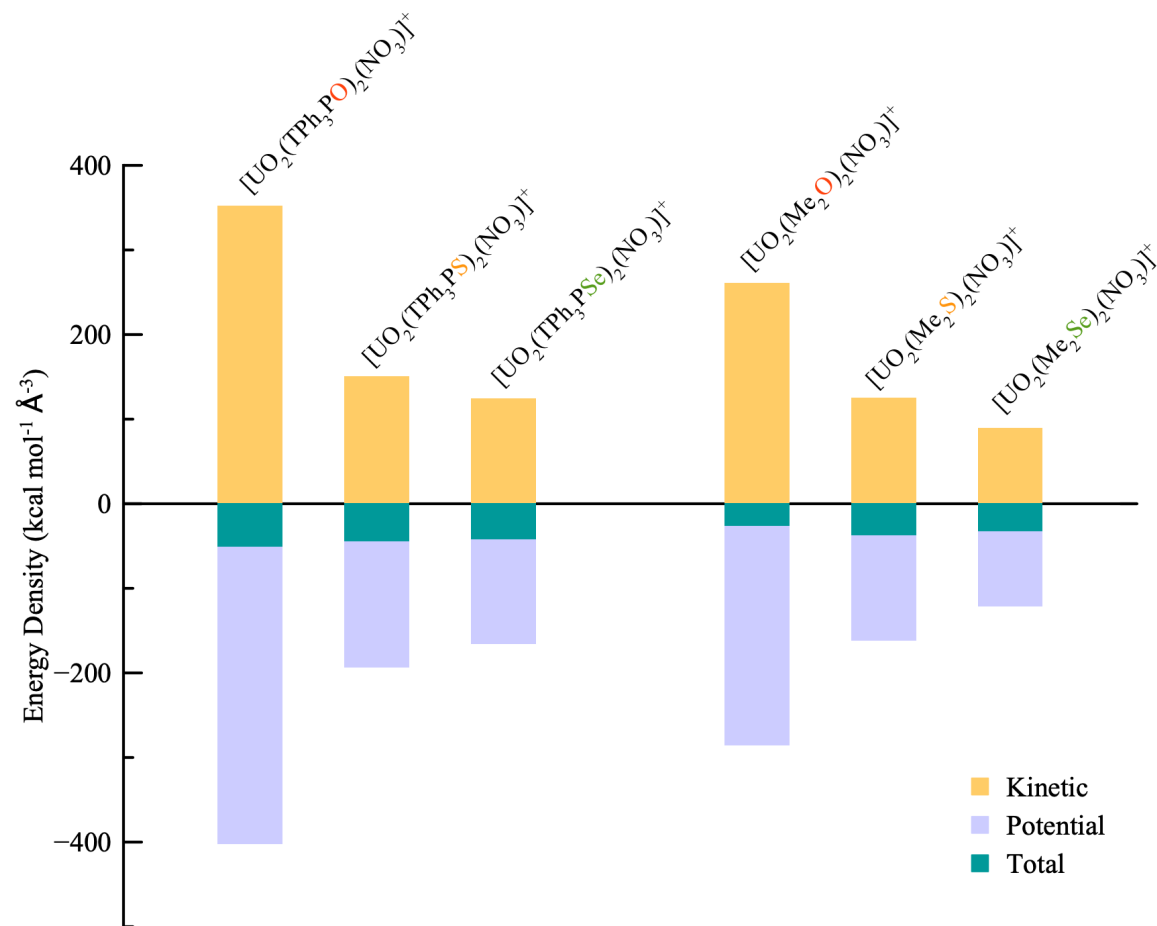
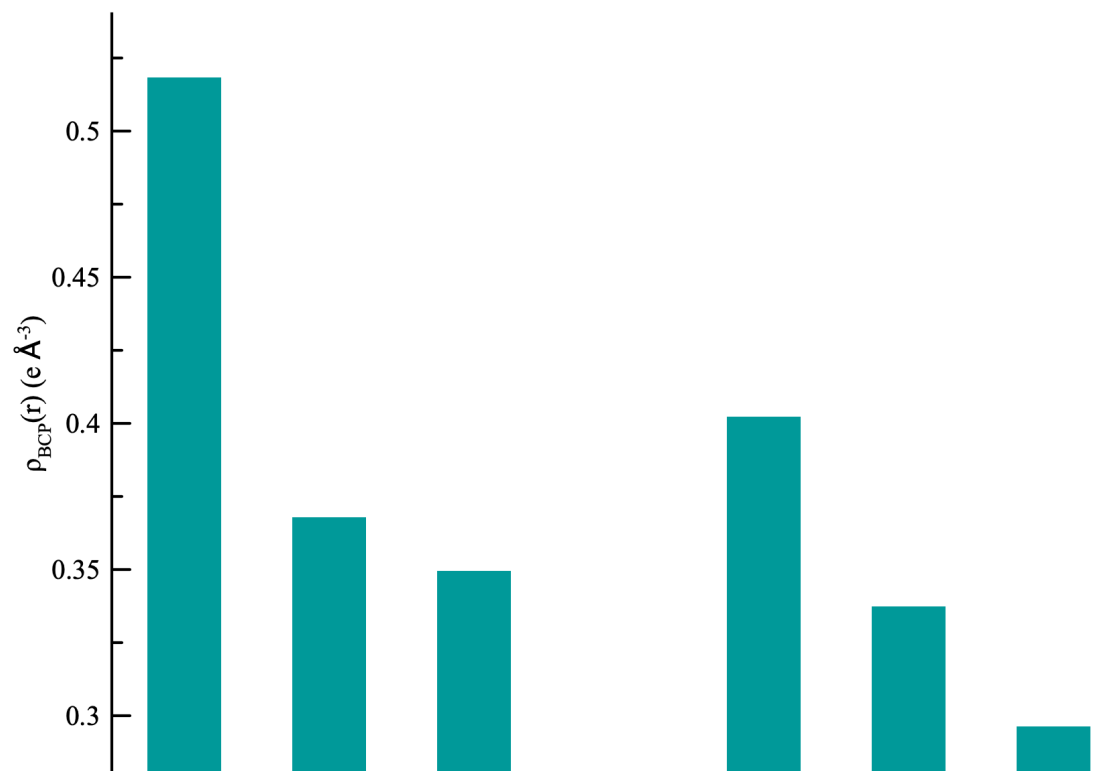


TOPOLOGICAL ANALYSIS - QTAIM

	$\rho(r)$	$G(r)$	$V(r)$	$H(r)$
$[\text{UO}_2(\text{TPh}_3\text{P}\text{O})_2(\text{NO}_3)]^+$	0.5181	351.57	-401.26	-49.69
$[\text{UO}_2(\text{TPh}_3\text{P}\text{S})_2(\text{NO}_3)]^+$	0.3675	149.74	-193.07	-43.33
$[\text{UO}_2(\text{TPh}_3\text{P}\text{Se})_2(\text{NO}_3)]^+$	0.3492	124.16	-165.23	-41.07
$[\text{UO}_2(\text{Me}_2\text{O})_2(\text{NO}_3)]^+$	0.4019	260.18	-285.27	-25.09
$[\text{UO}_2(\text{Me}_2\text{S})_2(\text{NO}_3)]^+$	0.3370	124.61	-161.37	-36.76
$[\text{UO}_2(\text{Me}_2\text{Se})_2(\text{NO}_3)]^+$	0.2960	89.20	-120.72	-31.52



TOPOLOGICAL ANALYSIS - QTAIM



LIGAND POLARIZABILITY

Average Localized Ionization Energies (ALIEs)

$$\bar{I}(\mathbf{r}) = \frac{\sum_i \rho_i(\mathbf{r}) |\varepsilon_i|}{\rho(\mathbf{r})}$$

Quantification of how
loosely bound electrons are

Inversely proportional to
LOCAL POLARIZABILITY

	ALIE (kcal/mol)		
	E1	E2	E3
TPh3P=O	207.5	207.6	207.6
TPh3P=S	163.3	163.7	163.9
TPh3P=Se	148.6	149.1	149.3
Me ₂ O	227.6	227.8	
Me ₂ S	165.6	165.6	
Me ₂ Se	153.8	154.0	

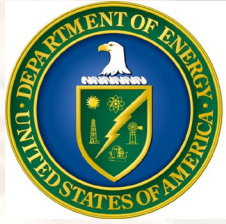
	Mulliken charge
	q(E)
TPh3P=O	-0.839
TPh3P=S	-0.566
TPh3P=Se	-0.669
Me ₂ O	-0.546
Me ₂ S	-0.012
Me ₂ Se	-0.076

SUMMARY AND OVERLOOK

TPh₃P=O

- More negatively charged oxygen atom
- More polarizable than O atom in dimethyl ether
- Increased coulomb and covalent interactions

- HSAB theory is ONLY part of the equation for rational design of ligands
- Expand this work to different chalcogenide ligands and trivalent transU actinides



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ENERGY



COLORADO SCHOOL OF MINES



Idaho National Laboratory

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- Thomas Albrecht-Shoenzart

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THANK YOU!