Why Computational Actinide Chemistry Needs Flops (& Memory & Interconnect & Disk)

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ALABAMA
CRIMSON TIDE

Robert Ramsay Chair Fund

ASA

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iic
Institute for Interfacial Catalysis
Control of Chemical Transformations for a Secure Energy Future

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Research Drivers: Science across Scales in Space & Time

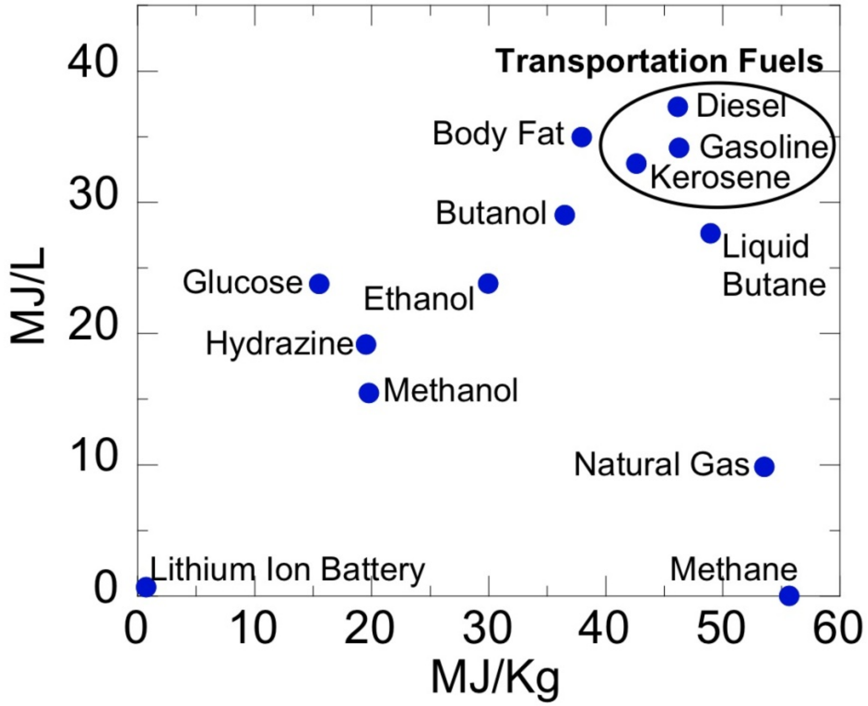
- **Catalysis**: Computational catalysis – transition metal oxides, homogeneous catalysts, metal clusters, site isolated catalysts
- **Nanoscience**: TiO_2 clusters for sensors and photocatalysts; Shape memory alloys (Nitinol) (NASA)
- **Energy**: H_2 storage in chemical systems – organic & inorganic
- **Energy**: Advanced Fuel Cycle Initiative – Metal oxide clusters in solution for new fuels and environmental cleanup – Actinides and Lanthanides
- **Energy**: New sources of energy (solar)
- **Geochemistry**: Geological CO_2 sequestration
- **The Environment**: Atmosphere, Clean Water, Subsurface & Cleanup
- **Biochemistry**: Peptide and amino acid negative ion chemistry
- **Computational main group chemistry** – Fluorine chemistry, acids and bases, other elements
- **Computational thermodynamics and kinetics** – High accuracy, solvation effects.
- **Chemical End Station**: RC^3 & software development

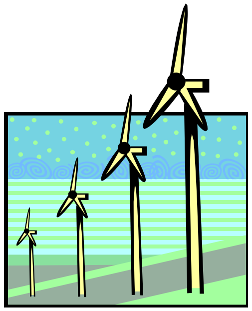
Catalysis: An Essential Science for a Secure Energy Future

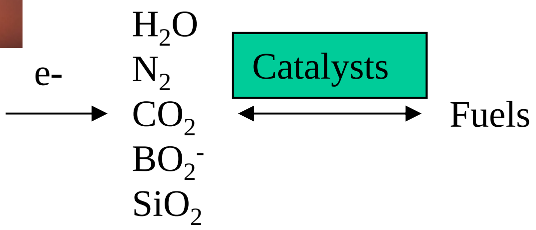
- “Best” energy sources store energy (electrons) in chemical bonds. Catalysts are crucial for making new fuels & storing energy when alternative energy sources are not available or for transportation.
- Catalysts are crucial for interconversion of electric and chemical energy, e.g.,

  Solar fuels

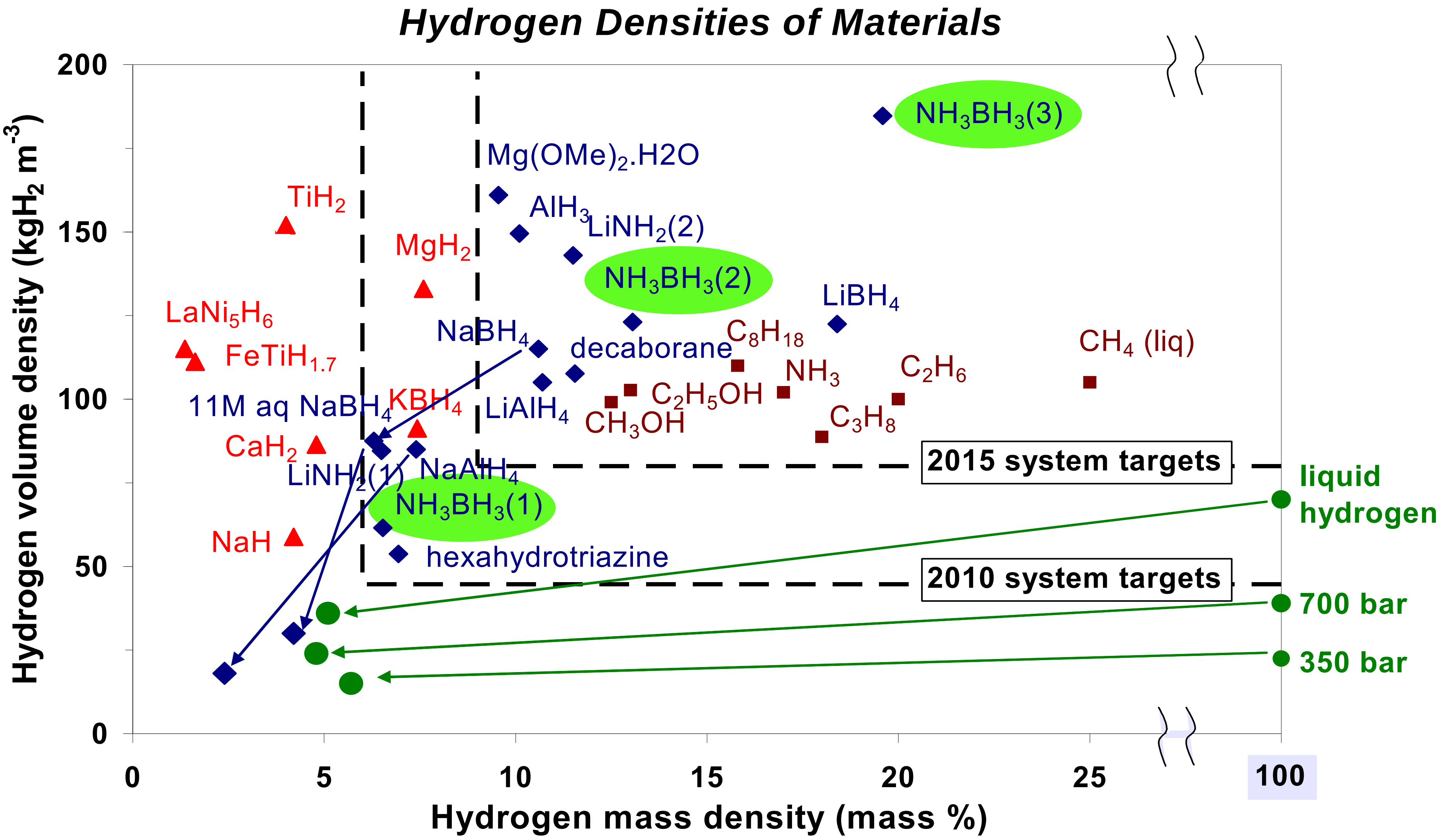
  Fuel cells
- First principles catalyst ***design*** requires quantitative information about ***transition states*** for critical reaction processes. These are *only* accessible by computational methods, which hold the key to the fundamental understanding of catalytic processes thus enabling reliable catalyst design.
- Predict real processes in real environments to proper accuracy.







Chemical Hydrogen Storage Materials



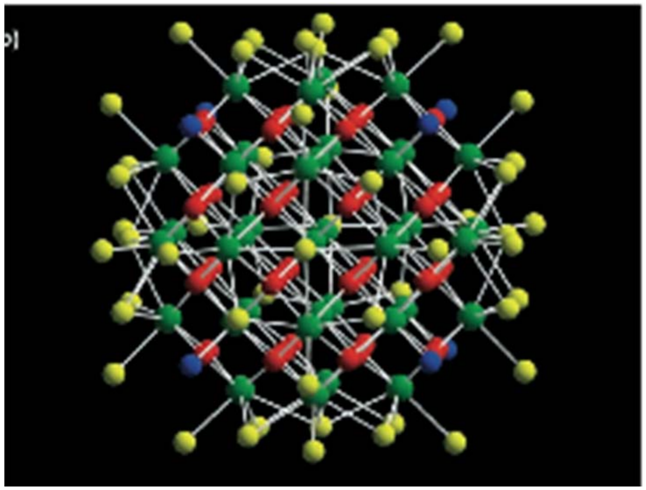
Ammonia-Borane = NH_3BH_3, contains both protic N-H and hydridic B-H hydrogen atoms (19.6 wt % H2, 0.16 kg/L H_2)

George Thomas

Development of New Materials for Energy Applications

- Materials theory/simulation has largely been about materials by design:
  Analysis: *Why does this material have the properties it does?*
  Reverse Engineering: *What material has the properties that I want?*
- Materials theory/simulation rarely contributes to ***how*** to make materials:
  What precursors? What temperature? What pressure? What solvent? What synthesis steps in what order? What yield? What is the resulting concentration of defects?...
- With the advent of large, fast computers and relatively cheap, reliable electronic structure methods, can we develop simulation approaches on how to make "stuff" → Materials Synthesis by Design

An example: Structured precipitates: Particle is $Pu_{38}O_{54}(H_2O)_8^{40+}$ which grows over days from initial solution of solvated Pu^+ ions. How does such a structure grow? Why so long? How can we control it?

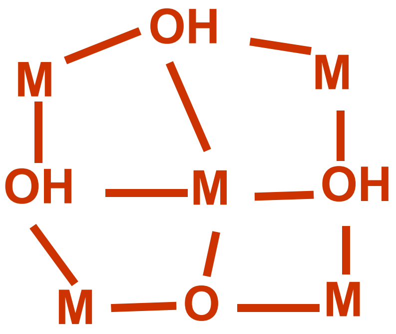


Molecular Aggregation: Formation of Polynuclear Species

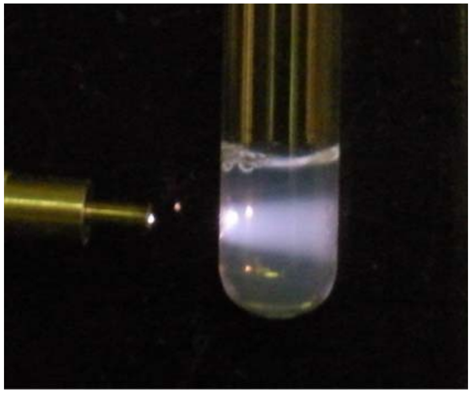
Deprotonation of water molecules attached to metal cation gives hydroxides

$[M(OH_2)_m]^{n+} \rightarrow [M(OH_2)_{m-h}(OH)_h]^{(n-h)+} + hH^+$

Olation: M-OH + M-(H_2O) → M-(OH)-M + H_2O

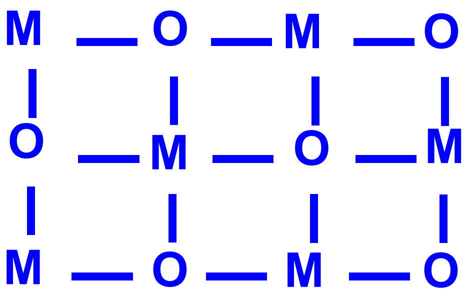


"Amorphous" hydroxide
Chemically – poorly defined

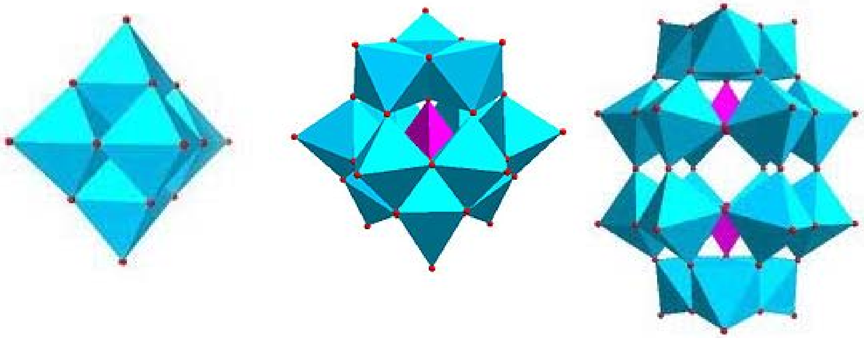


colloids

Oxolation: M-OH + M-OH → M-O-M + H_2O



Crystalline oxide
Well defined structures
Well defined chemistry

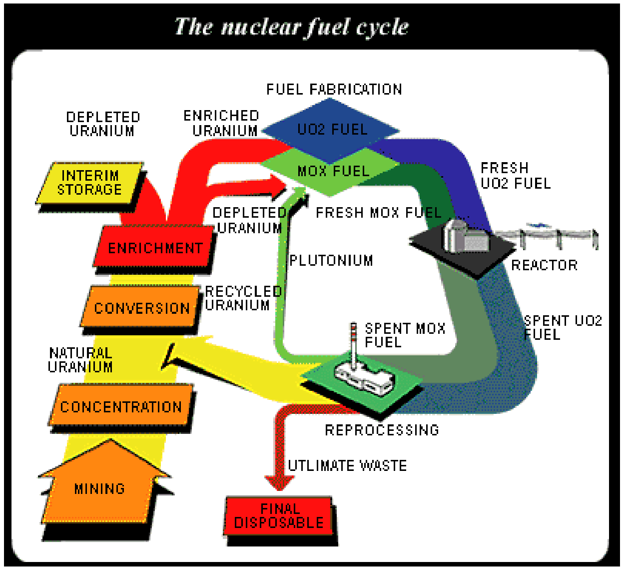


Which reaction occurs depends on effects including ion hardness and electronegativity and M-OH_2 stability to deprotonation

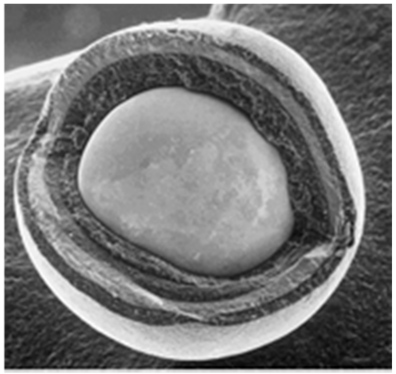
Importance of Actinide Chemistry

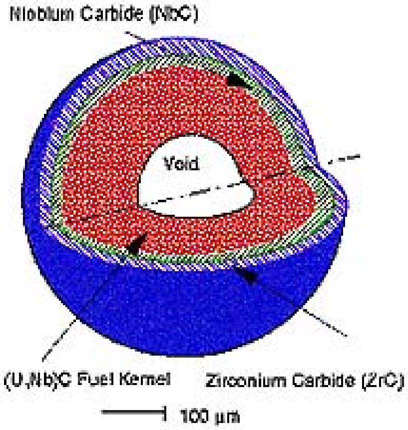
Waste management/ cleanup

Fuel reprocessing

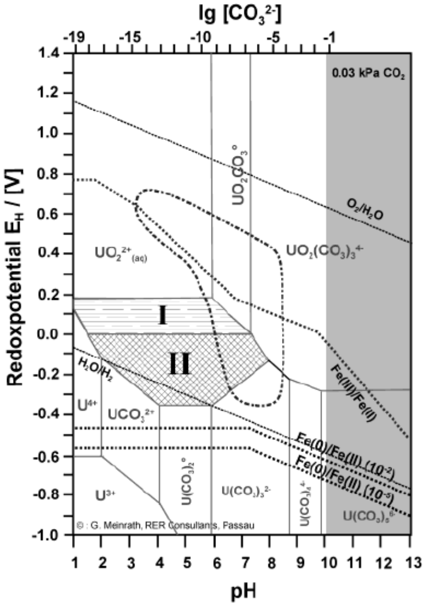


Fuel development

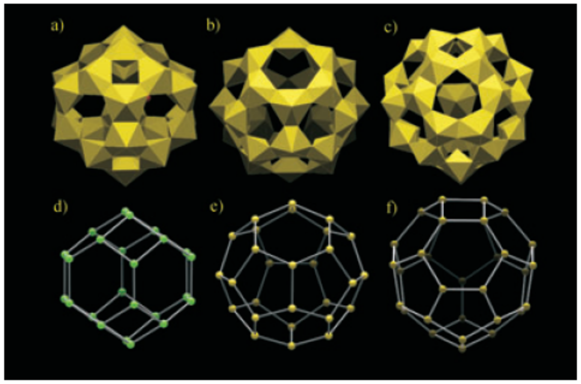




Environment

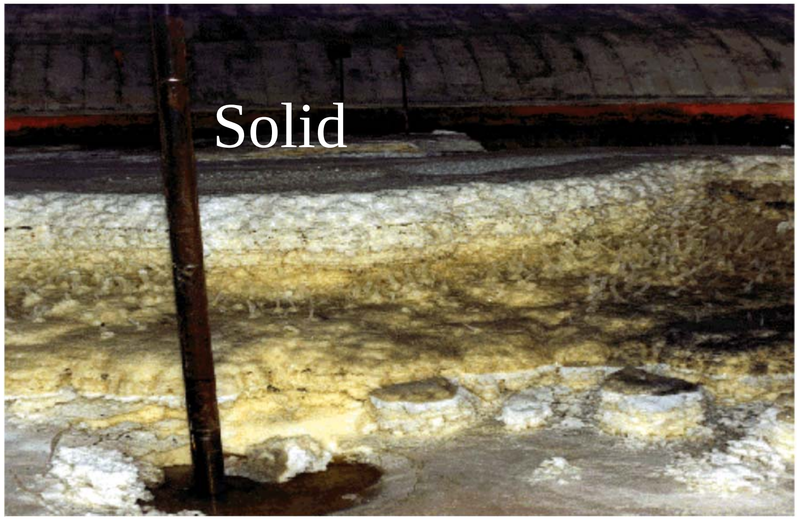


Basic science



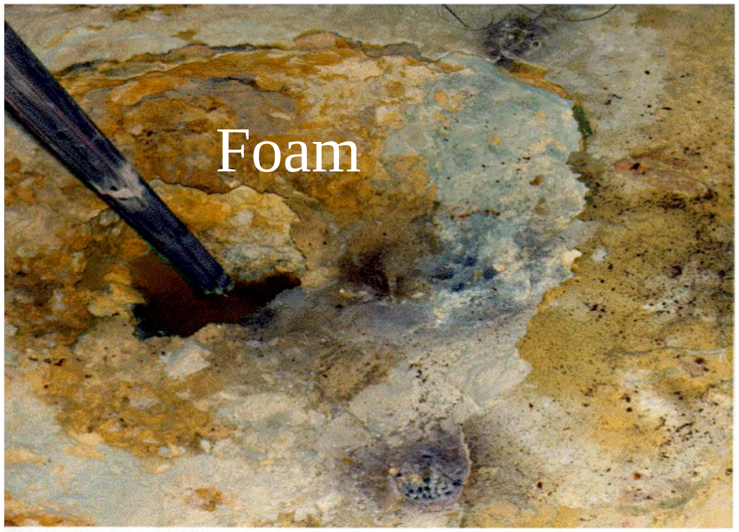
“Actinide Peroxide Nanospheres” Burns et al., *Angew. Chem.* **2005**, *117*, 2173.

Hanford Tanks



Solid

Liquid



Foam

What’s needed for chemical accuracy?

Example: the design of catalysts and separations systems

A Scientific Grand Challenge is the precise control of molecular processes by using catalysts.

Predict equilibrium chemistry: *Selectivity*

Change in K_{eq} @ 298 K

$K_{eq} = 1$	50:50	$\Delta G =$ 0 kcal/mol
$K_{eq} = 10$	90:10	$\Delta G =$ 1.4 kcal/mol
$K_{eq} = 100$	99:1	$\Delta G =$ 2.8 kcal/mol

Predict accurate rates: *Reactivity*

Absolute Rates @ 298 K

Factor of 10 in rate @ 25^{o}C is a change in E_a of 1.4 kcal/mol

Molecular design will require performing accurate calculations and building the correct physical model.

Issues:

- Uncertainty in models
- Errors in calculations and experiments
- Maintaining accuracy across length scales: molecular→nano→micro→macro
- How do we incorporate error bars in simulations?

How do we get the right answer for the right reason and know it?

How do we get accurate results from computational studies with specified small error bars?

Schrödinger Equation for the Electronic Structure of Molecules

- Born-Oppenheimer Approximation

$$H = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{(r_i - R_A)} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

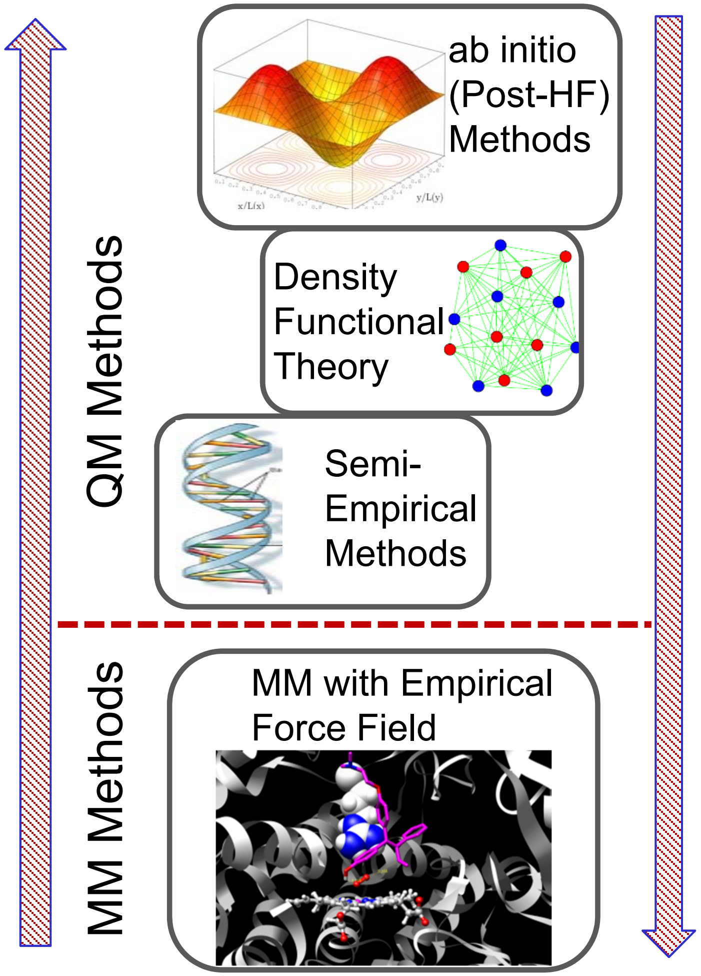
↑	↑	↑
kinetic energy of electrons	nuclear-electron attraction energy	electron-electron repulsion energy
repulsive	attractive	repulsive

$$H\psi = E\psi$$

- Expand ψ in terms of molecular orbitals (Slater determinants)
- Expand each spatial M.O. as Linear Combination of Atomic Orbitals
- Generates a complicated set of coupled integro-differential equations which we solve using linear algebra methods on high performance computers.

$$\phi = \sum_{i=1}^{N} c_i \varphi_i$$

Computational Methods



ab initio
(Post-HF)
Methods

Density
Functional
Theory

Semi-
Empirical
Methods

QM Methods

MM Methods

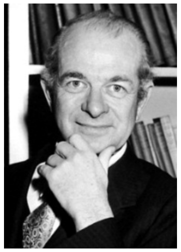
MM with Empirical
Force Field

Accuracy & Cost

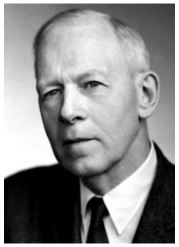
System Size
~10^2 to10^6 atoms

QM: Quantum Mechanics
MM: Molecular Mechanics

Nobel prizes in theoretical chemistry

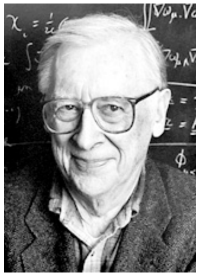


Linus Pauling
1954



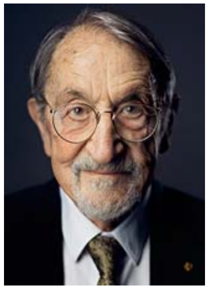
Robert S. Mulliken
1966

Walter Kohn



John A. Pople

1998



Martin Karplus

Michael Levitt

Arieh Warshel

2013

Solving the Schrödinger Equation

Schrödinger Equation

Molecular Orbital Theory

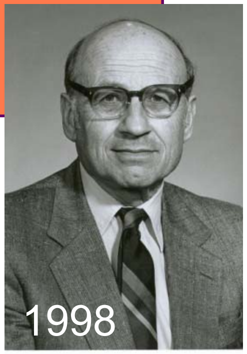
- Correlation Energy – CCSD(T), MPn, CASPT@, MRCI
- Basis set – aug-ccpVnZ
- Environment
- Relativity

Density Functional Theory

- Exchange-Correlation Functional
  - Local
  - Gradient corrected
    - Becke-Perdew
    - B3LYP
    - Handy, etc
  - New approaches: OEP for exchange, new correlation
- Basis set
- Environment
- Relativity

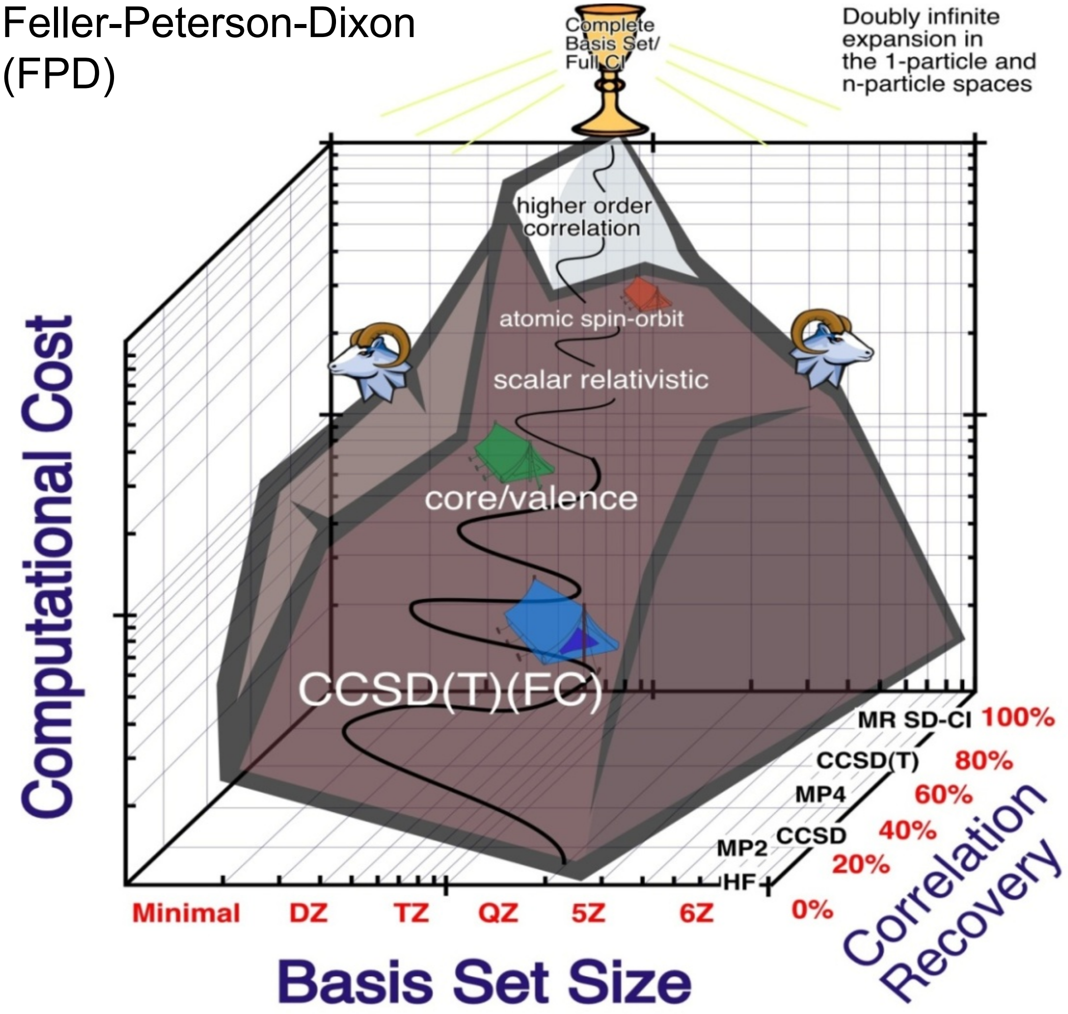
Full CI


1998


1998

High Level Computational Thermochemistry: FPD

Feller-Peterson-Dixon (FPD)



Gaussian09, MOLPRO, NWChem

$$E = E_{CBS} + E_{core} + E_{SR} + E_{SO} + E_{ZPE}$$

$$E_{atomization} = E_{atoms} - E_{molecule}$$

Total atomization energy (TAE) calculated at the CCSD(T) level extrapolated to the complete basis set limit (CBS) using the augmented-correlation consistent basis sets

\+ **Core corrections** – CCSD(T)/cc-pwCVTZ level

\+ **Scalar relativistic correction** – CI(SD)/cc-pVTZ (MVD) or MP2/cc-pVTZ DK (DKH)

\+ **Atomic/Molecular = Total spin orbit correction**

\+ **Zero point energy** – MP2/aug-cc-pVTZ level

\+ **Thermal correction (0K → 298 K)** – MP2/aug-cc-pVTZ level.

Atomic heats of formation ΔH_f to get molecular heats of formation ΔH_f

N^7 method

Reliable Computational Chemistry Energy Components (kcal/mol)

MX_4	ΔE_{CBS}	$\Delta E_{(SR)}$	$\Delta E_{(PP,corr)}$	$\Delta E_{(CV)}$	$\Delta E_{(ZPE)}$	$\Delta E_{so(atomic)}$	ΣD_0
TiF_4	570.71	-1.83	-1.28		-5.93	-2.20	559.47
ZrF_4	627.42	-1.10	-1.37		-4.67	-3.62	616.66
HfF_4	650.54	-1.07	-8.40		-4.79	-9.40	626.88
ThF_4	646.36	-1.03		3.80	-3.98	-10.36	634.80
$TiCl_4$	417.42	-1.46	-1.18	1.15	-3.73	-4.00	408.21
$ZrCl_4$	475.54	-0.81	-1.24	1.07	-3.10	-5.42	466.03
$HfCl_4$	493.19	-0.74	-3.44	1.08	-3.03	-11.20	475.86
$ThCl_4$	504.69	-0.87		4.18	-2.34	-12.16	493.50

Heats of Formation (kcal/mol)

molecule	ΔH_f,0K calc	ΔH_f,0K expt	ΔH_f, 298K calc	ΔH_f,298K expt	Ave BDE calc
TiF_4	-373.2	-369.9 ± 1.0	-374.2	-370.8 ± 1.0	139.9
ZrF_4	-397.3	-399.0 ± 0.8	-398.0	-400.0 ± 0.8 -399.4 ± 0.2	154.2
HfF_4	-405.3		-406.3	-399.1	156.7
ThF_4	-417.0		-417.7	418.4 ± 2.4 -420.4 ± 1.0	158.7
$TiCl_4$	-181.4 -181.0	-182 ± 0.9	-181.9 -181.5	-182.4 ± 0.7	102.1
$ZrCl_4$	-206.2 -209.4	-207.6 ± 0.5	-206.5 -209.7	-207.9 ± 0.5 -208.3 ±0.2	116.5
$HfCl_4$	-213.8 -213.4		-214.2 -213.7	-212.9 ± 0.3 -211.4	119.0
$ThCl_4$	-235.2		-235.4	-227.4 ± 1.2 -230.0 ± 1.0	123.4

Inversion Barriers $T_d \rightarrow D_{4h}$ (kcal/mol)

Molecule	**ΔE (CBS+corrections)**	**Imaginary freq (cm^{-1}) MP2/aT)**
CF_4	130.1	-370i
SiF_4	67.3	-225i
GeF_4	46.3	-192i
SnF_4	32.3	-138i
PbF_4	21.4	-110i
TiF_4	55.7	-195i
ZrF_4	47.4	-148i
HfF_4	49.9	-175i
CeF_4	24.9	-106i
ThF_4	25.2	-105i

Actinide(IV) Colloid Formation: Waste Management & Separations

- Formation of hydrolysis products impedes current separation scenarios and nuclear fuel reprocessing schemes
- Colloids known to prevent complete extraction of Pu from liquid waste
- Waste streams remain contaminated
- Clog transfer pipes
- Plug ion exchange columns
- Increase treatment and processing costs
- Pu accounting – lose Pu in the process
    - Nevada Test Site (828 underground nuclear tests 1956-1992): Pu found 1.3 km from source
    - Lake Karachai, Russia: Pu migrated 4 km within 55 years

J. Roberto, T.D. de La Rubia, Eds. *Basic Research Needs of Advanced Nuclear Energy Systems*, 2006, Office of Basic Energy Sciences, U.S. Dept. of Energy; Kersting et al. Nature 1999 vol 397, 56-59; Novikov et al. Science 2006

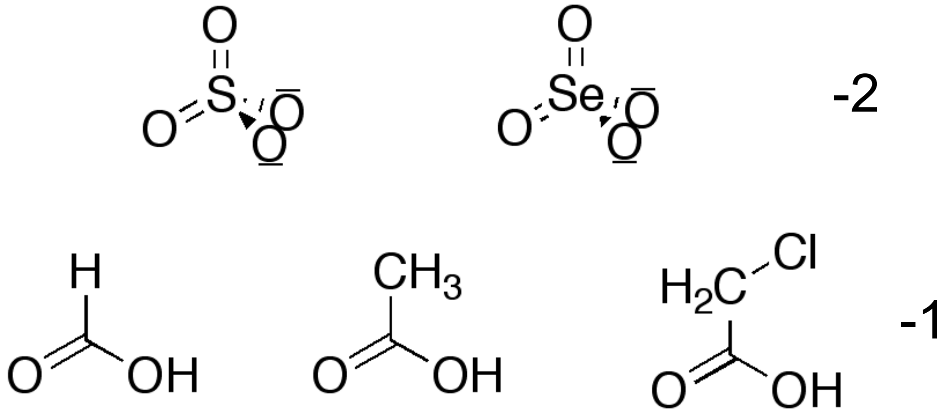
ANL Concepts for Actinide Oligomer Synthesis

Enhance Hydrolysis using control of pH and T

$$[M(H_2O)_m]^{n+} \rightarrow [M(OH_2)_{m-h}(OH)_h]^{(n-h)+} + hH^+$$

$$2An(OH)_2(H_2O)_6^{2+} + xH_2O \leftrightarrows An_2O_p(OH)_{8-2p}(OH_2)^{6+p} + 4H^+ + (2+x)H_2O$$

Capture condensation products using oxygen donor ligands



Use the APS to identify products using x-ray scattering such as HEXS

“Thorium(IV) molecular clusters with a hexanuclear core,” K. E. Knope, R. E. Wilson, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem.*, **2011**, *50*, 9696-9704

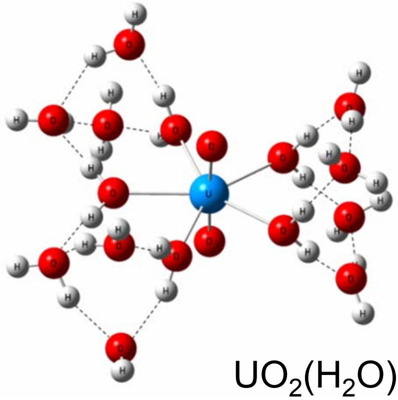
“Thorium(IV)-Selenate Clusters containing an Octanuclear Th(IV) Hydroxide/Oxide Core,” K. E. Knope, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem.* **2012**, *51*, 4239-4249

Computational Studies of Actinide Aggregation

- Benchmarks of DFT methods against experiment and CCSD(T)
- $Th_6O_8^{8+}$ clusters
- $Th_8O_{12}^{8+}$ clusters
- $(ThO_2)_n$ cluster structures and hydrolysis of clusters – estimates of physisorption and chemisorption energies
- Th reactions with CH_3OH (CCSD(T) potential energy surface for actinide reaction)
- Th hydrolysis reaction products and complexes with SeO_4^{2-}
- **How do $Th_xO_y^{z+}$ clusters form in aqueous solution?**
- **What is the role of the counter-anions?**
- **How does proton loss occur?**
- **What drives the difference between oxolation and olation?**
- **How does the reactivity change from Th(IV) to U(IV) to Pu(IV)?**

Aqueous Uranyl Chemistry

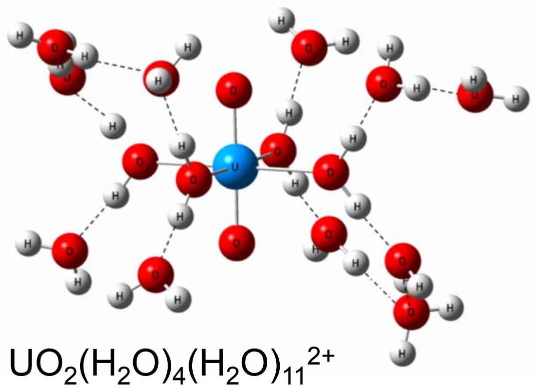
UO_2^{2+} is mostly 5-coordinate in aqueous solution in equilibrium with 4-coordinate



HEXS : ΔG =
-1.19 ± 0.42 kcal/mol

$\longrightarrow$

MP2/COSMO
ΔG = -2.0 kcal/mol



$UO_2(H_2O)_5(H_2O)_{10}^{2+}$ $UO_2(H_2O)_4(H_2O)_{11}^{2+}$

HEXS: L. Soderholm, S. Skanthakumar, J. Neuefeind, *Anal. Bioanal. Chem*. **2005**, *383*, 48
Calc: K. E. Gutowski, and D. A Dixon, *J. Phys. Chem. A*, **2006**, *110*, 8840

Free Energy of solvation of UO_2^{2+}

MP2/COSMO = -411.0 kcal/mol

Expt = -421 ± 15 kcal/mol

Gibson, J. K.; Haire, R. G.; Santos, M.; Marçalo, J.; de Matos, A. P. *J. Phys. Chem. A* **2005**, *109*, 2768-81. ($\Delta H_{solv}(UO_2^{2+})$)
Marcus, Y. *J. Inorg. Nucl. Chem.* **1975**, *37*, 493-501 ($\Delta S_{solv}(UO_2^{2+})$)

The splitting between the anharmonic asymm & symm stretches in UO_2^{2+} is 80 to 83 cm^{-1}

CCSD(T)/SO/aVQZ: asym str: 1113.0 cm^{-1} sym str = 1031.6 cm^{-1} bend = 174.5 cm^{-1}

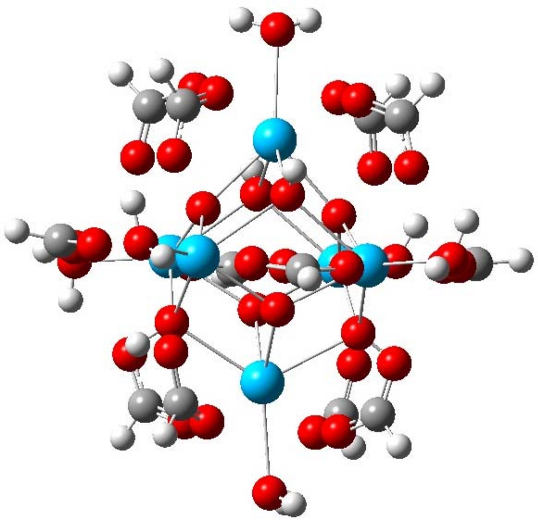
ThO_2 (bent) benchmark

CCSD(T)/SO/aVTZ asym str: 807.7 cm^{-1} sym str = 756.0 cm^{-1} bend = 165.3 cm^{-1}

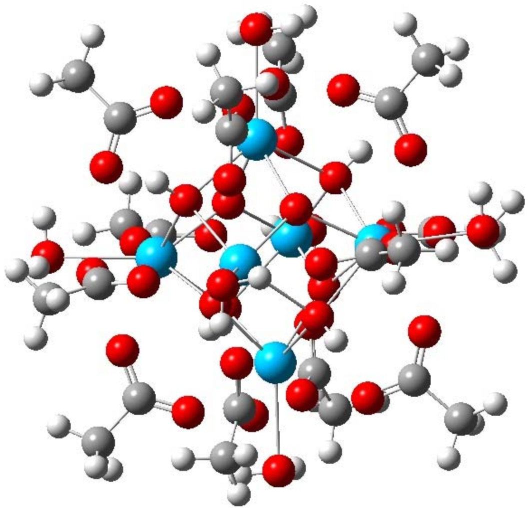
Expt(Ne matrix) asym str: 808.3 cm^{-1} sym str = 756.8 cm^{-1}

“The Vibrational Spectra of UO_2^{2+} Predicted at the CCSD(T) Level,” V. E. Jackson, R. Craciun, D. A. Dixon, K. A. Peterson, W.A. de Jong, *J. Phys. Chem. A*, **2008**, *112*, 4095

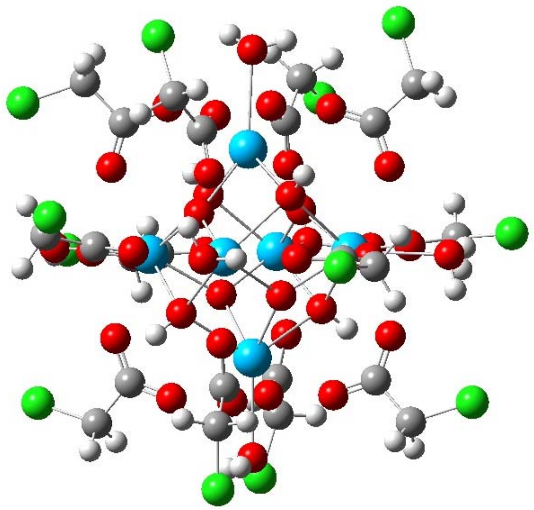
Thorium hydrolysis and condensation: Hexamers



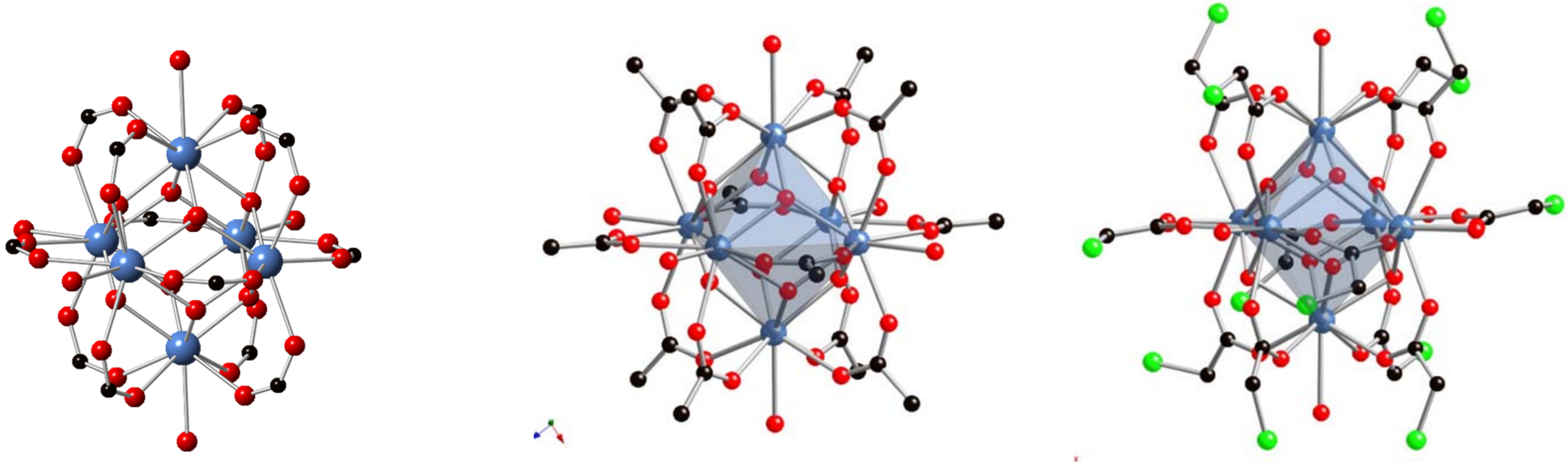
$Th_6(OH)_4O_4(H_2O)_6(HCOO)_{12}$



$Th_6(OH)_4O_4(H_2O)_6(CH_3COO)_{12}$



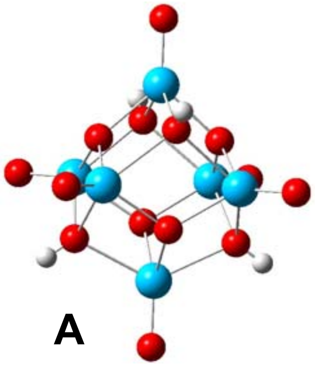
$Th_6(OH)_4O_4(H_2O)_6(ClCH_2COO)_{12}$

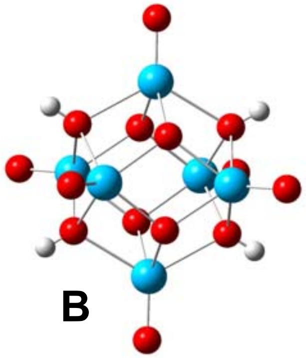


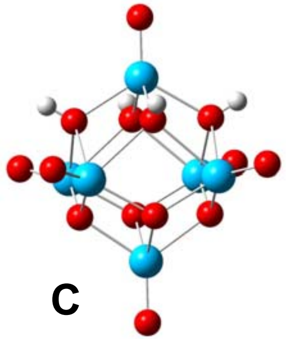
Use computational chemistry to assign the proton positions.

“Thorium(IV) molecular clusters with a hexanuclear core,” K. E. Knope, R. E. Wilson, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem*., **2011**, *50*, 9696-9704

$Th_6(OH)_4O_4O_6$ (0) Isomers: $Th_6O_8^{8+}$ core


A


B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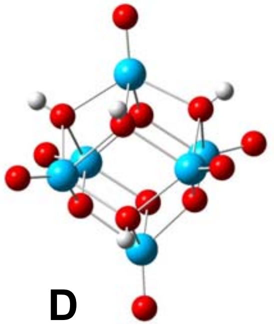
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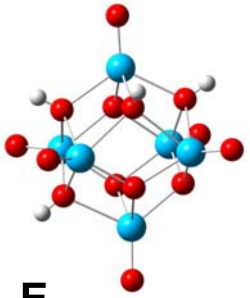
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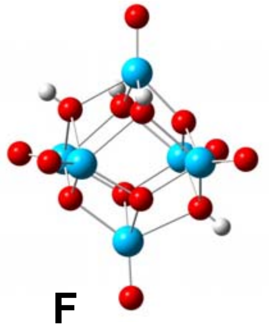

F

Isomer	$Th_6(OH)_4O_4O_6$	$Th_6O_4(OH)_4(HCOO)_{12}$	$Th_6O_4(OH)_4(H_2O)_6(HCOO)_{12}$
A	0.0	0.0	0.0
B	7.4	20.4	17.3
C	23.4	31.5	27.7
D	15.4	19.7	16.6
E	15.0	25.0	21.6
F	9.3	16.1	13.5

- Calculated relative energies in kcal/mol at B3LYP/DZVP/Stuttgart+2f for Th
- Clear computational evidence to put the 4 protons in the most symmetrical position
- Use computational chemistry to assign the structures
- Determine the role of different counter-anions. Determine the role of water in the inner shell.

Comparison of average experimental and calculated bond distances (Å) of $Th_6(OH)_4O_4(H_2O)_6(RCOO)_{12}$

Distance	R = H			R = CH_3			R = $ClCH_2$		
	Expt	B3LYP	LDA	Expt	B3LYP	LDA	Expt	B3LYP	LDA
Th- μ_3-O	2.38	2.323	2.287	2.387	2.321	2.287	2.30	2.325	2.290
Th - μ_3-OH	2.38	2.537	2.493	2.387	2.533	2.488	2.50	2.535	2.486
Th-O-COH	2.50	2.543	2.493	2.479	2.540	2.487	2.50	2.530	2.477
Th-OH_2	2.67	2.726	2.616	2.621	2.752	2.641	2.66	2.712	2.595
C-O	-	1.264	1.263	1.254	1.270	1.269	1.268	1.263	1.263
Th-Th (edge)	3.90-3.94	3.981	3.911	3.97	3.977	3.908	3.92	3.987	3.911
Th-Th(vertex)	5.53-5.57	5.631	5.529	5.62	5.625	5.527	5.56	5.638	5.532

Comparison of average experimental and calculated bond distances (Å) of neutral complexes

Distance	$Th_6(OH)_4O_4(H_2O)_6(HCOO)_{12}$			$Th_6(OH)_4O_4(HCOO)_{12}$		$Th_6(OH)_4O_4O_6$	
	Expt	B3LYP	SVWN5	B3LYP	SVWN5	B3LYP	SVWN5
Th- μ_3-O	2.38	2.323	2.287	2.306	2.274	2.375	2.329
Th - μ_3-OH	2.38	2.537	2.493	2.520	2.476	2.629	2.559
Th-O-COH	2.50	2.543	2.493	2.497	2.442	-	-
$Th\text{-}OH_2$	2.67	2.726	2.616	-	-	-	-
Th=O	-	-	-	-	-	1.902	1.891
C-O	-	1.264	1.263	1.267	1.264	-	-
Th-Th (edge)	3.90-3.94	3.981	3.911	3.958	3.896	4.005	3.932
Th-Th(vertex)	5.53-5.57	5.631	5.529	5.597	5.510	5.664	5.561

Assignment of Proton NMR Spectra

Molecule	**Organic H**	**OH δ (ppm)**	**H_2O δ (ppm)**
HCO_2^-	8.8/*8.30* (HCO_2^-)	5.1/*6.16*	~ 4.4/*3.32*
$CH_3CO_2^-$	2.0/*1.78* ($CH_3CO_2^-$)	4.9/*5.97*	~ 4.5/*3.3*
$CH_3CO_2^-$	4.1/*3.97*($ClCH_2CO_2^-$)	5.0/*6.97*	~3.9/*3.3*
HCO_2^- No H_2O	8.6 (HCO_2^-)	5.0	
O^{2-}		6.3	
$ThO(OH)_2$		2.9	
$Th(OH)_4$		1.5	
$ThO_2(H_2O)$			5.7
$Th_2O_2(OH)_4$		0.9 (terminal)	
$Th_2O_2(OH)_4$		6.2 (bridge) 4.3 (terminal)	
$Th_2O_3(OH)_2$		0.7, 1.3	
$Th_2O_4(H_2O)$			3.0, 2.3

- $Th_6(OH)_4O_4(H_2O)_6(RCOO)_{12}$
- ^{1}H-NMR in ppm, ADF (BLYP/TZ2P/ZORA)
- Computations used to assign NMR spectra
- Provides evidence that the solid state structure is maintained in solution
- Relativistic effects from Th on nearby protons can be predicted reliably with ZORA
- Use computational approaches to assign Raman spectra

"Spectroscopic and Energetic Properties of Thorium(IV) Molecular Clusters with a Hexanuclear Core," M. Vasiliu, K. E. Knope, L. Soderholm and D. A. Dixon, *J. Phys. Chem. A*, **2012**, *116,* 6917–6926

Gas Phase Acidities (kcal/mol) and pK$_a$'s

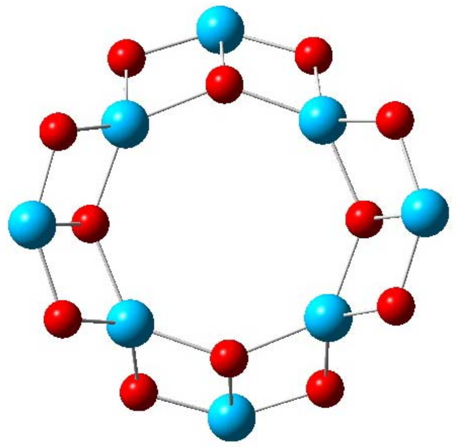
Reaction	**ΔH_{298K} gas**	**ΔG_{298K} gas**	**pK$_a$(H_2O) CH_3COOH**	**pK$_a$(DMSO) CH_3COOH**
$Th_6(OH)_4O_4(H_2O)_6(HCOO)_{12}$ **1**	315.4	308.4	14.1	21.5
$Th_6(OH)_4O_4(H_2O)_6(CH_3COO)_{12}$ **2**	322.9	315.7	16.2	25.6
$Th_6(OH)_4O_4(H_2O)_6(CH_2ClCOO)_{12}$ **3**	306.3	302.2	13.2	21.7
$Th_6(OH)_4O_4(HCOO)_{12}$	308.6	298.2	5.8	12.5
$Th_6(OH)_4O_4O_6$	281.4	272.5	9.5	14.2
$Th_6(OH)_4O_4(CH_3COO)_{12}$	317.0	312.1	10.9	19.1
$Th_6(OH)_4O_4(H_2O)_6(CH_2ClCOO)_{12}$	294.9	286.4	4.4	11.2

Molecule	**ΔG_{298K}**	**pK$_a$**
$WO_2(OH)_2$	309.6	−1.5
$WO(OH)_4$	305.1	0.3
$W(OH)_6$	303.1	−4.6
$W_2O_5(OH)_2$ (ring)	284.5	−9.2
$W_3O_8(OH)_2$ (ring)	273.8	−10.4
$W_4O_{11}(OH)_2$ (ring)	267.8	−12.9
$W_6O_{19}(H)_2$	261.1	−16.0
H_2SO_4	303.8	−7.0
FSO_3H	294.7	−11.4
CF_3SO_3H	292.4	-12.5
$(CF_3SO_2)_3CH$	274.0	−17.4

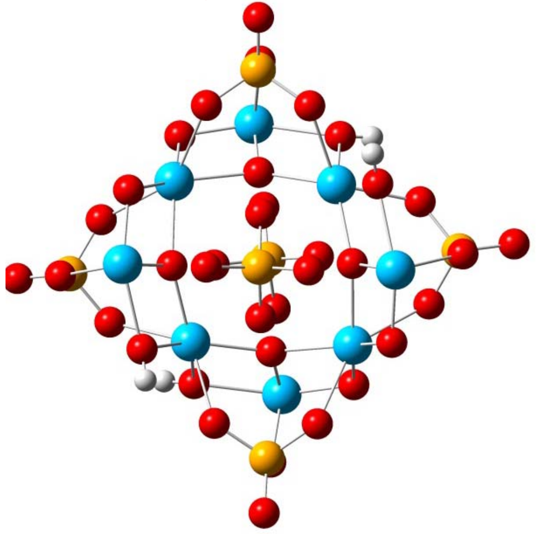
- Solution phase acidities using SCRF complicated by the proper treatment of the Th atomic radius.
- Very strong gas phase acids
- Most are weak acids in solution due to shielding by the outer shell anions.
- How do different anions affect the acidity?

- The average water complexation energies for **1**, **2** and **3** are -14.6, -13.4, and -17.0 kcal/mol for ΔH_{298} and -5.0, -3.6, and -6.8 kcal/mol for ΔG_{298}.
- The H_2O binding energies depend slightly on the nature of the anionic ligand and the water is most strongly bonded to the Th for the chloroacetate ligand.

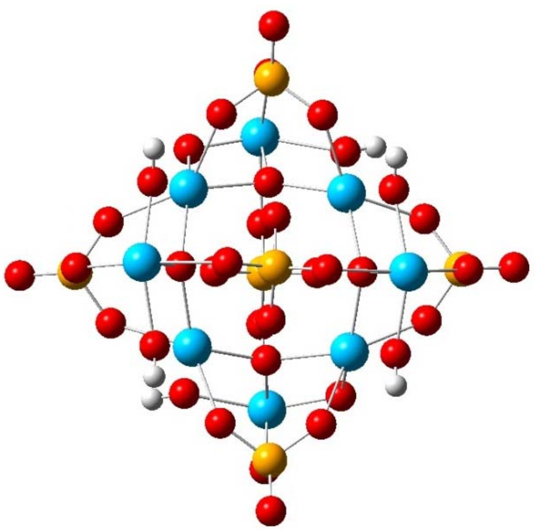
Th_8O_{12} Complexes



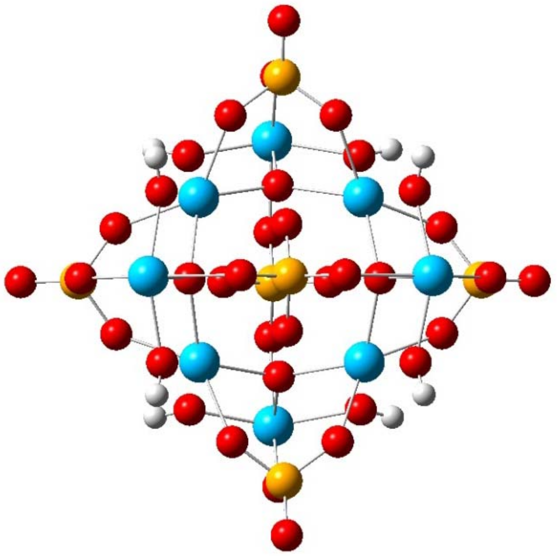
$Th_8O_{12}^{+8}$



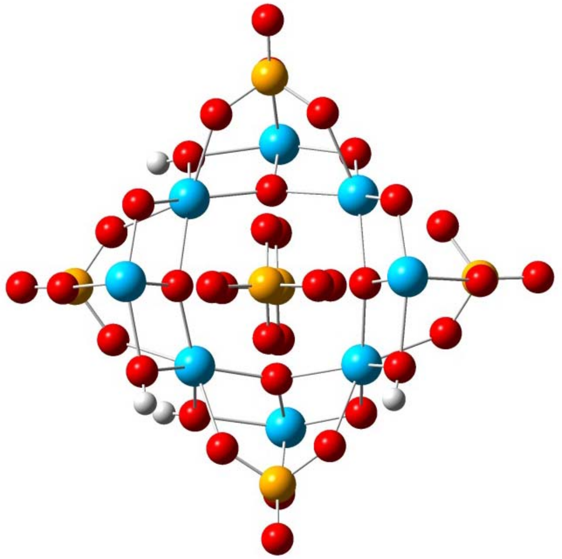
$Th_8O_8(OH)_4(SeO_4)_6$ (A) 0.0



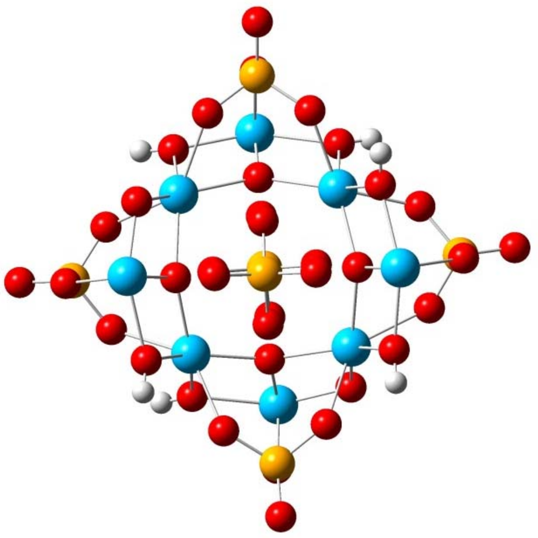
$Th_8O_6(OH)_6(SeO_4)_6^{+2}$ (A) 0.0



$Th_8O_4(OH)_8(SeO_4)_6^{+4}$



$Th_8O_8(OH)_4(SeO_4)_6$ (E) 1.0



$Th_8O_6(OH)_6(SeO_4)_6^{+2}$ (B) 1.0

Comparison of Calculated Bond Distances (Å) for $Th_8O_4(OH)_8(SeO_4)_6^{+4}$ with Average Experimental Values

$Th_8O_4(OH)_8(SeO_4)_6^{+4}$	Calc	1	2	3	4
Th-μ_3-O	2.300	2.304(11)	2.303(10)	2.299(13)	2.298(02)
Th-μ_2-OH	2.398	2.379(23)	2.372(11)	2.363(23)	2.361(15)
Th-O(H_2)	--	2.574(37)	2.566(29)	2.582(67)	2.544(69)
Th-O-(SeO_3)	2.312	2.501(42)	2.501(33)	2.477(49)	2.485(57)
Se-O-(Th)	1.727	1.637(11)	1.641(11)	1.629(13)	1.639(05)
Se-$O_{(unbound)}$	1.601	1.631(11)	1.638(30)	1.619(10)	1.633(60)
Th1-Th8	3.832	3.862	3.874	3.856	3.876
Th1-Th3	4.241	4.204	4.180	4.183	4.175
Th1-Th4	5.998	5.936	5.901	5.913	5.905
Th6-Th8	7.325	7.459	7.390	7.499	7.475
Th5-Th8	7.620	7.513	7.737	7.708	7.714

“Thorium(IV)-Selenate Clusters containing an Octanuclear Th(IV) Hydroxide/Oxide Core,” K. E. Knope, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem.* **2012**, *51*, 4239-4249

Cluster Acidity

- Gas phase acidity of the neutral compound

$$Th_8O_8(OH)_4(SeO_4)_6 \rightarrow Th_8O_9(OH)_3(SeO_4)_6^{-1} + H^+$$

- Anion has two low energy isomers differing by 0.5 kcal/mol with similar proton arrangements.
- The gas phase acidity

$$\Delta H_{298K} = 297.2 \text{ and } \Delta G_{298K} = 289.6 \text{ kcal/mol}$$

shows a strong gas phase acid.

- Calculated pK_a for $Th_8O_8(OH)_4(SeO_4)_6$ in water of 9.5 relative to the known value of acetic acid in water (pK_a = 4.75) – weak acid

Molecule	**ΔG_{298}**	**pKa**	**Molecule**	**ΔG_{298}**	**pKa**
H_2SO_4	301.6	-8.8	$W(OH)_6$	303.1	-4.6
FSO_3H	292.8	-13.0	$W_2O_5(OH)_2$	294.2	2.1
CF_3SO_3H	290.2	-14.2	$W_3O_8(OH)_2$	273.8	-10.4
WO_2OH_2	309.6	-1.5	$W_4O_{11}(OH)_2$	267.8	-12.9
$WO(OH)_4$	305.1	0.3			

Deprotonation Reaction Free Energies ΔG_{298}^{aq} in Aqueous Solution in kcal/mol

Reaction	ΔG_{298}^{aq}
$Th_8O_4(OH)_8(SeO_6)_6^{4+} \rightarrow Th_8O_5(OH)_7(SeO_6)_6^{3+} + H^+$	-6.8
$Th_8O_5(OH)_7(SeO_6)_6^{3+} \rightarrow Th_8O_6(OH)_6(SeO_6)_6^{2+} + H^+$	-3.6
$Th_8O_6(OH)_6(SeO_6)_6^{2+} \rightarrow Th_8O_7(OH)_5(SeO_6)_6^{+} + H^+$	2.3
$Th_8O_7(OH)_5(SeO_6)_6^{+} \rightarrow Th_8O_8(OH)_4(SeO_6)_6 + H^+$	1.0
$Th_8O_8(OH)_4(SeO_6)_6 \rightarrow Th_8O_9(OH)_3(SeO_6)_6^{-} + H^+$	14.1

- Exothermic to lose a proton from the +4 and +3 cations to form the +3 and +2 cations
- Formation of the +1 and the neutral from the +2 and +1 cores are predicted to be slightly endothermic.
- Most stable species in solution with no counterions present is +2 core.
- Free energy differences are small enough that that there is some $Th_8O_7(OH)_5(SeO_6)_6^{+}$ ($K_{eq} \sim 0.02$), $Th_8O_5(OH)_7(SeO_6)_6^{3+}$ ($K_{eq} \sim 0.002$) , and $Th_8O_8(OH)_4(SeO_6)_6$ ($K_{eq} \sim 0.004$).
- +4 cluster is not predicted to be present to any substantial amount, hence the need for the two additional coordinating SeO_4^{2-} groups found in the solid state. The additional anions lead to the precipitation process.

Mechanistic Concepts

$6Th(H_2O)_{10}^{4+} \rightarrow Th_6O_4(OH)_4^{12+}(H_2O)_6 + 12H^+ + 46H_2O$ +”anions”

Solid is ThO_2 so Th_4O_8, Th_6O_{12}, Th_8O_{16}, etc.

$Th_6O_8^{8+} = (ThO_{1.25})_6^{8+}$ and $Th_8O_{12}^{8+} = (ThO_{1.5})_8^{8+}$

Th_2O_y?, Th_4O_x?, $Th_{12}O_{20}^{8+} = (ThO_{1.67})_{12}^{8+}$, $Th_{16}O_{20}^{8+} = (ThO_{1.75})_{16}^{8+}$???

- When do the protons come off to remove the excess charge?
- What is role of the counter-anions and of different charged counter-anions? What solvent shell are they in and how/when do they move to the 1st shell?
- What happens for U(IV) and Pu(IV)?
- What size solvent shells are controlling the reactions?
- Are there computational ion descriptors that can be used to help predict reactivity?

Electronic Structure Descriptors (from DFT)

- Hardness:
  $\eta = (\text{I.P.} - \text{E.A.})/2 \sim (\varepsilon_{HOMO} - \varepsilon_{LUMO})/2$
- Softness
  $\sigma = 1/\eta \sim 2/\ (\varepsilon_{HOMO} + \varepsilon_{LUMO})$
- Electronegativity
  $x = (\text{I.P.} + \text{E.A.})/2 \sim (\varepsilon_{HOMO} + \varepsilon_{LUMO})/2$
  for the Mulliken electronegativity

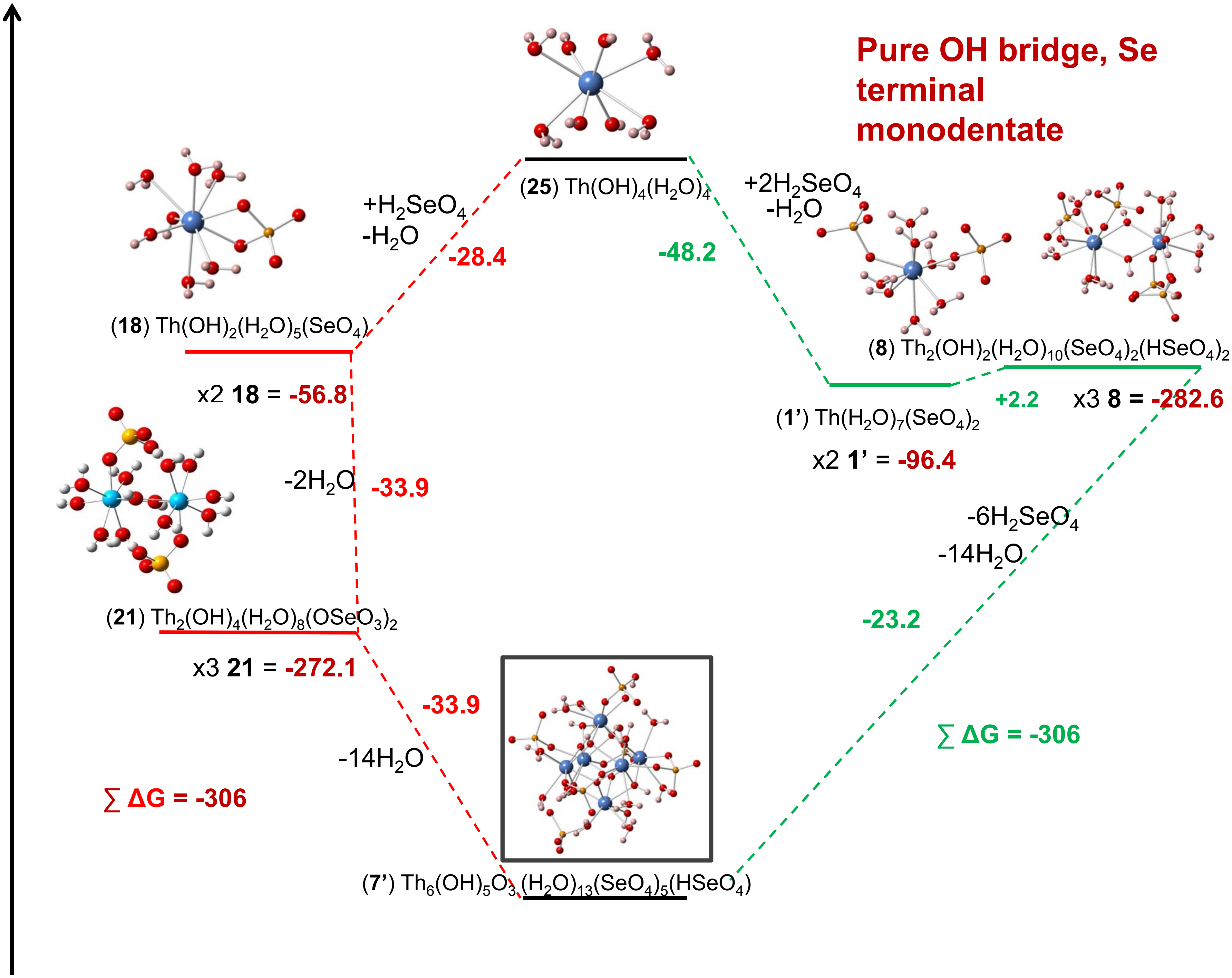
- Properties can be defined for an atom, molecule, etc.
- With DFT assumes that E_{HOMO} can be obtained and that E_{LUMO} is <0 and that it represents an E.A.

- Acidity
  $AH \rightarrow A^- + H^+$ (ΔH or ΔG for the reaction at 298 K)

- For Th^{4+}: $\eta = (\text{IP.5} - \text{IP.4})/2 = 18.1$ eV, $x = 46.9$ eV; $\sigma = 0.055$ eV

- Need to calculate the IP.5 value to get a better value and do so for the other actinides.
- Need to examine properties of clusters. Expand the descriptor concept. Also examine the role of “local” quantities.

Pure OH bridge, Se terminal monodentate



(**25**) $Th(OH)_4(H_2O)_4$

$+H_2SeO_4$
$-H_2O$

-28.4

(**18**) $Th(OH)_2(H_2O)_5(SeO_4)$

x2 **18** = -56.8

$-2H_2O$

-33.9

(**21**) $Th_2(OH)_4(H_2O)_8(OSeO_3)_2$

x3 **21** = -272.1

-33.9

$-14H_2O$

∑ ΔG = -306

(**7’**) $Th_6(OH)_5O_3(H_2O)_{13}(SeO_4)_5(HSeO_4)$

-48.2

$+2H_2SeO_4$
$-H_2O$

(**8**) $Th_2(OH)_2(H_2O)_{10}(SeO_4)_2(HSeO_4)_2$

(**1’**) $Th(H_2O)_7(SeO_4)_2$

+2.2

x3 **8** = -282.6

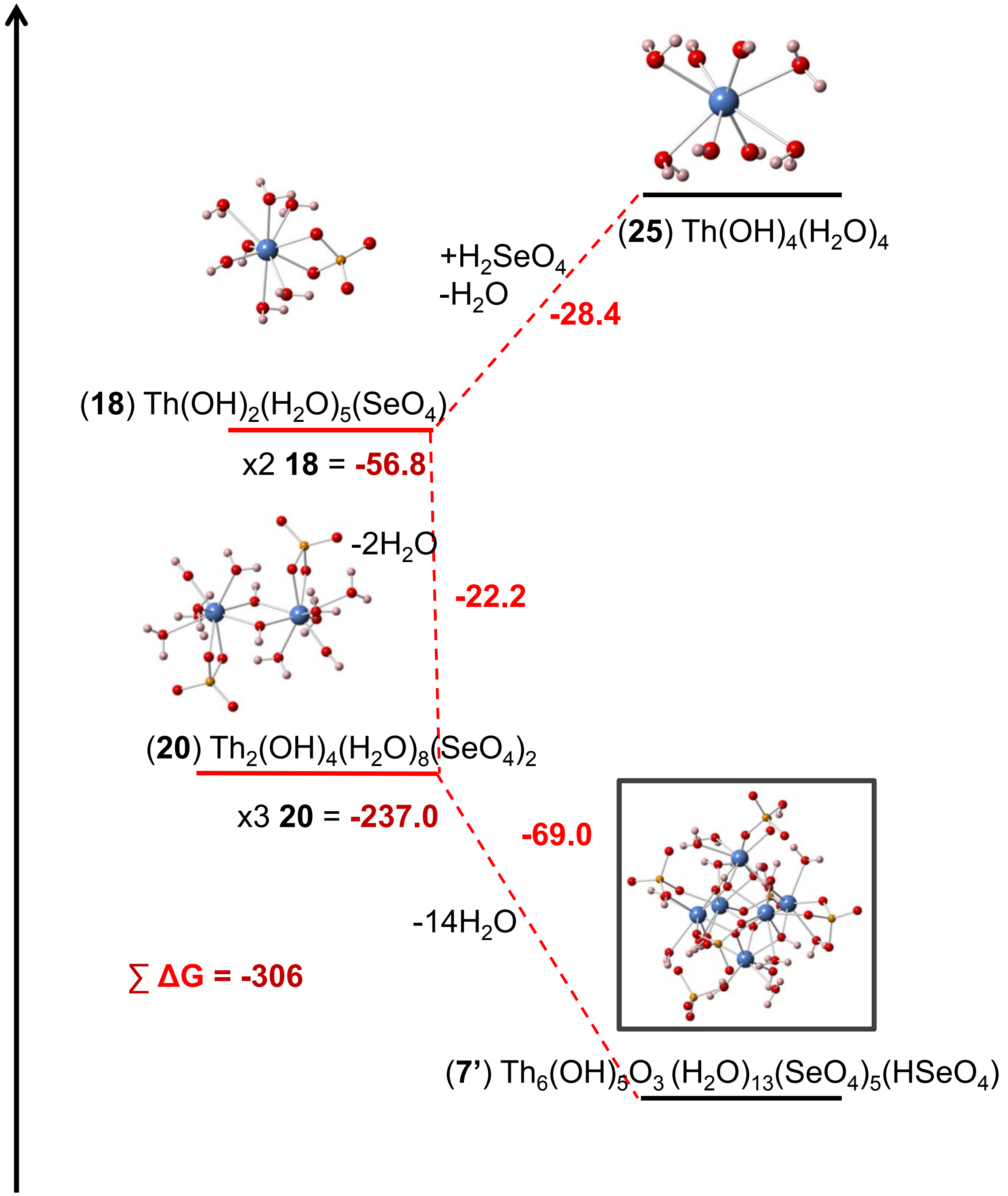
x2 **1’** = -96.4

$-6H_2SeO_4$
$-14H_2O$

-23.2

∑ ΔG = -306

Pure OH bridge, Se terminal bidentate



(25) $Th(OH)_4(H_2O)_4$

$+H_2SeO_4$
$-H_2O$

-28.4

(18) $Th(OH)_2(H_2O)_5(SeO_4)$

x2 **18** = **-56.8**

$-2H_2O$

-22.2

(20) $Th_2(OH)_4(H_2O)_8(SeO_4)_2$

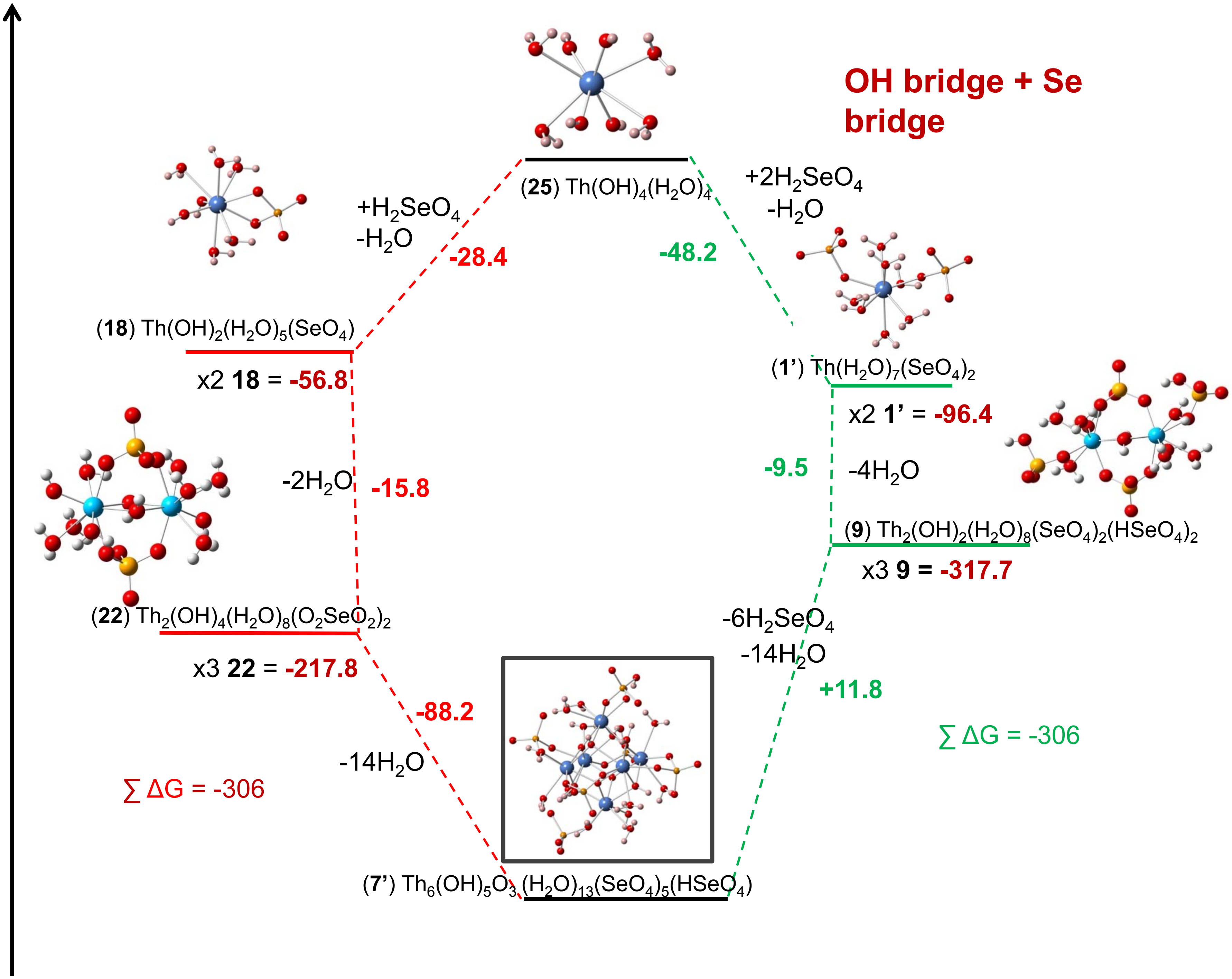
x3 **20** = **-237.0**

-69.0

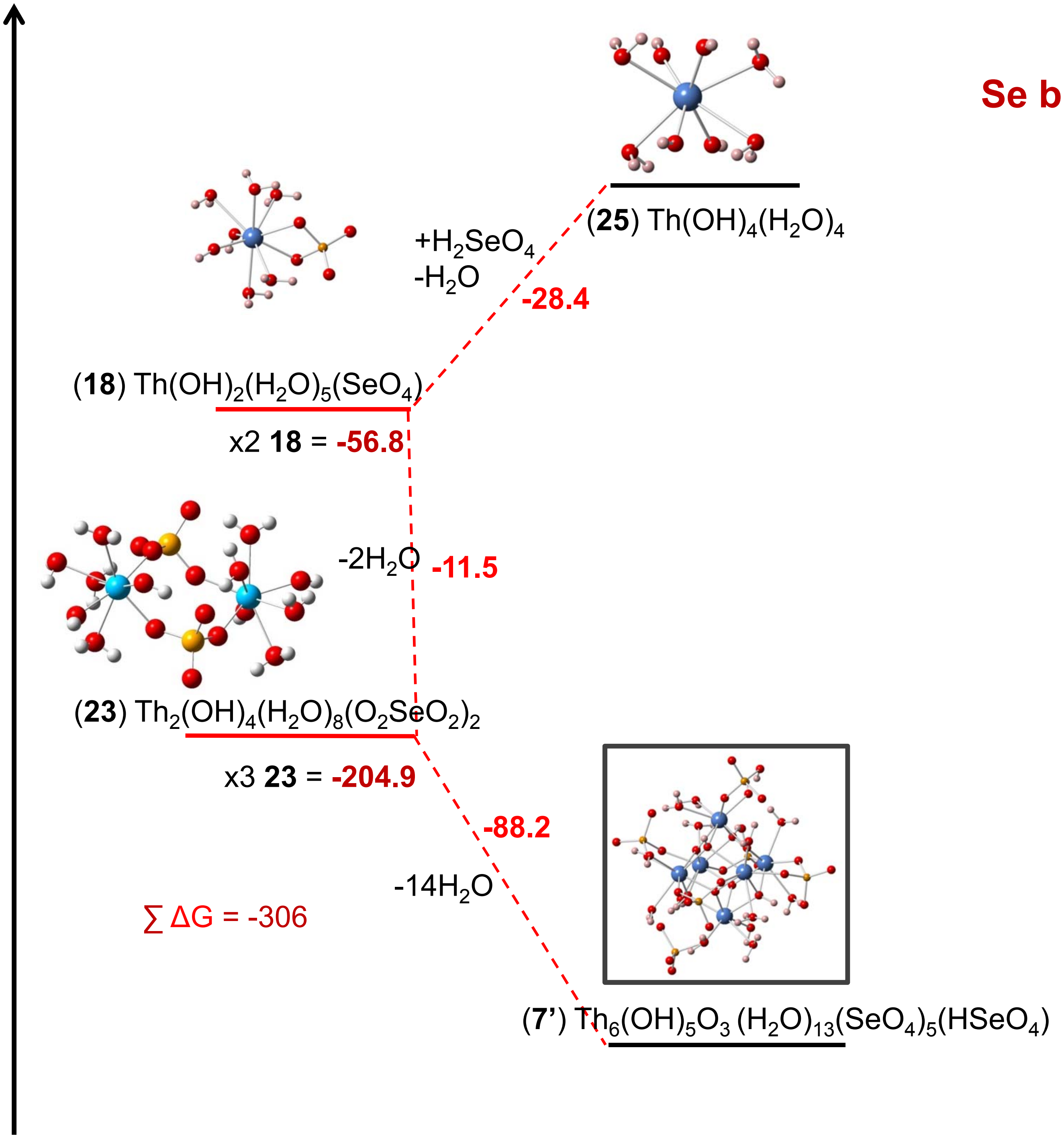
$-14H_2O$

(7') $Th_6(OH)_5O_3\,(H_2O)_{13}(SeO_4)_5(HSeO_4)$

∑ ΔG = -306


OH bridge + Se bridge
(**25**) $Th(OH)_4(H_2O)_4$
$+H_2SeO_4$
$-H_2O$
-28.4
$+2H_2SeO_4$
$-H_2O$
-48.2
(**18**) $Th(OH)_2(H_2O)_5(SeO_4)$
x2 **18** = -56.8
(**1’**) $Th(H_2O)_7(SeO_4)_2$
x2 **1’** = -96.4
$-2H_2O$
-15.8
-9.5
$-4H_2O$
(**9**) $Th_2(OH)_2(H_2O)_8(SeO_4)_2(HSeO_4)_2$
x3 **9** = -317.7
(**22**) $Th_2(OH)_4(H_2O)_8(O_2SeO_2)_2$
x3 **22** = -217.8
$-6H_2SeO_4$
$-14H_2O$
+11.8
-88.2
$-14H_2O$
$\sum \Delta G = -306$
$\sum \Delta G = -306$
(**7’**) $Th_6(OH)_5O_3(H_2O)_{13}(SeO_4)_5(HSeO_4)$

Se bridge



($\mathbf{25}$) $Th(OH)_4(H_2O)_4$

$+H_2SeO_4$

$-H_2O$

-28.4

($\mathbf{18}$) $Th(OH)_2(H_2O)_5(SeO_4)$

x2 **18** = **-56.8**

$-2H_2O$

-11.5

($\mathbf{23}$) $Th_2(OH)_4(H_2O)_8(O_2SeO_2)_2$

x3 **23** = **-204.9**

-88.2

$-14H_2O$

$\sum \Delta G = -306$

(**7'**) $Th_6(OH)_5O_3\,(H_2O)_{13}(SeO_4)_5(HSeO_4)$

Mechanism: Role of Anions (SeO_4^{2-}), Monomers

2 (**1'**) $Th(H_2O)_7(SeO_4)_2 \xrightarrow[-2H_2O]{-32.4/2.2}$ (**8**) $Th_2(OH)_2(H_2O)_{10}(SeO_4)_2(HSeO_4)_2 \xrightarrow[-2H_2O]{-8.2/-11.7}$

(**9**) $Th_2(OH)_2(H_2O)_8(SeO_4)_2(HSeO_4)_2 \xrightarrow[2H_2O]{4.9/2.1}$ (**11**) $Th_2(H_2O)_{12}(SeO_4)_2(SeO_4)_2$

(**9**) $Th_2(OH)_2(H_2O)_8(SeO_4)_2(HSeO_4)_2 \xrightarrow[2H_2O]{-4.7/16.1}$ (**12**) $Th_2(OH)_2(H_2O)_{10}(SeO_4)_2(HSeO_4)_2$

2 (**18**) $Th(OH)_2(H_2O)_5(SeO_4) \xrightarrow[-2H_2O]{-30.3/-22.2}$ (**20**) $Th_2(OH)_4(H_2O)_8(SeO_4)_2$ (trans) $\xrightarrow{5.8/6.4}$

2 (**18**) $Th(OH)_2(H_2O)_5(SeO_4) \xrightarrow[-2H_2O]{-33.3/-33.9}$ (**21**)$Th_2(OH)_4(H_2O)_8(OSeO_3)_2$ (trans) $\xrightarrow{8.8/18.1}$

(**22**) $Th_2(OH)_4(H_2O)_8(O_2SeO_2)_2 \xrightarrow{0.6/4.4}$ (**23**) $Th_2(OH)_4(H_2O)_8(O_2SeO_2)_2$ (no OH b)

(**25**) $Th(OH)_4(H_2O)_4 \xrightarrow[H_2SeO_4]{-24.3/-28.4}$ (**18**) $Th(OH)_2(H_2O)_5(SeO_4) + H_2O$

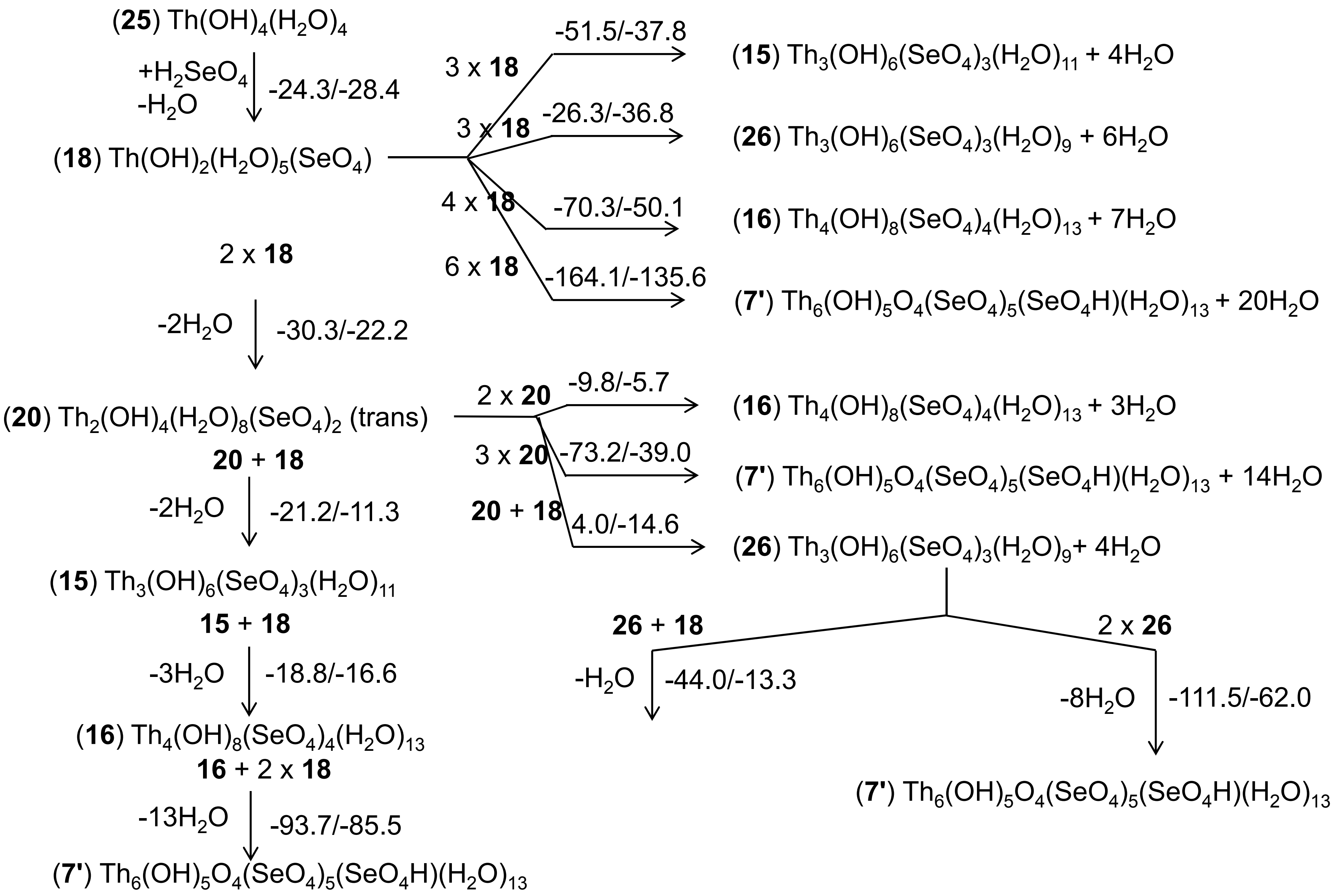
(**25**) $Th(OH)_4(H_2O)_4 \xrightarrow[H_2SeO_4]{-21.8/-22.6}$ (**17**) $Th(OH)_3(H_2O)_5(SeO_3OH)$

(**25**) $Th(OH)_4(H_2O)_4 \xrightarrow[2H_2SeO_4]{-33.1/-48.2}$ (**1'**) $Th(H_2O)_7(SeO_4)_2 + H_2O$

(**25**) $Th(OH)_4(H_2O)_4 \xrightarrow[4H_2SeO_4]{-70.7/-53.7}$ (**4''**) $Th(H_2O)_5(HSeO_4)_4 + 3H_2O$

(**25**) $Th(OH)_4(H_2O)_4 \xrightarrow[4H_2SeO_4]{15.5/34.7}$ (**4'**) $Th(OH)_4(H_2O)(H_2SeO_4)_4 + 3H_2O$

Mechanism: Role of Anions (SeO_4^{2-})



(**25**) $Th(OH)_4(H_2O)_4$

$+H_2SeO_4$, $-H_2O$ ↓ -24.3/-28.4

(**18**) $Th(OH)_2(H_2O)_5(SeO_4)$

3 x **18** → -51.5/-37.8 → (**15**) $Th_3(OH)_6(SeO_4)_3(H_2O)_{11} + 4H_2O$

3 x **18** → -26.3/-36.8 → (**26**) $Th_3(OH)_6(SeO_4)_3(H_2O)_9 + 6H_2O$

4 x **18** → -70.3/-50.1 → (**16**) $Th_4(OH)_8(SeO_4)_4(H_2O)_{13} + 7H_2O$

6 x **18** → -164.1/-135.6 → (**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13} + 20H_2O$

2 x **18**

$-2H_2O$ ↓ -30.3/-22.2

(**20**) $Th_2(OH)_4(H_2O)_8(SeO_4)_2$ (trans)

2 x **20** → -9.8/-5.7 → (**16**) $Th_4(OH)_8(SeO_4)_4(H_2O)_{13} + 3H_2O$

3 x **20** → -73.2/-39.0 → (**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13} + 14H_2O$

20 + **18** → 4.0/-14.6 → (**26**) $Th_3(OH)_6(SeO_4)_3(H_2O)_9 + 4H_2O$

26 + **18**

$-H_2O$ ↓ -44.0/-13.3

2 x **26**

$-8H_2O$ ↓ -111.5/-62.0

(**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13}$

20 + **18**

$-2H_2O$ ↓ -21.2/-11.3

(**15**) $Th_3(OH)_6(SeO_4)_3(H_2O)_{11}$

15 + **18**

$-3H_2O$ ↓ -18.8/-16.6

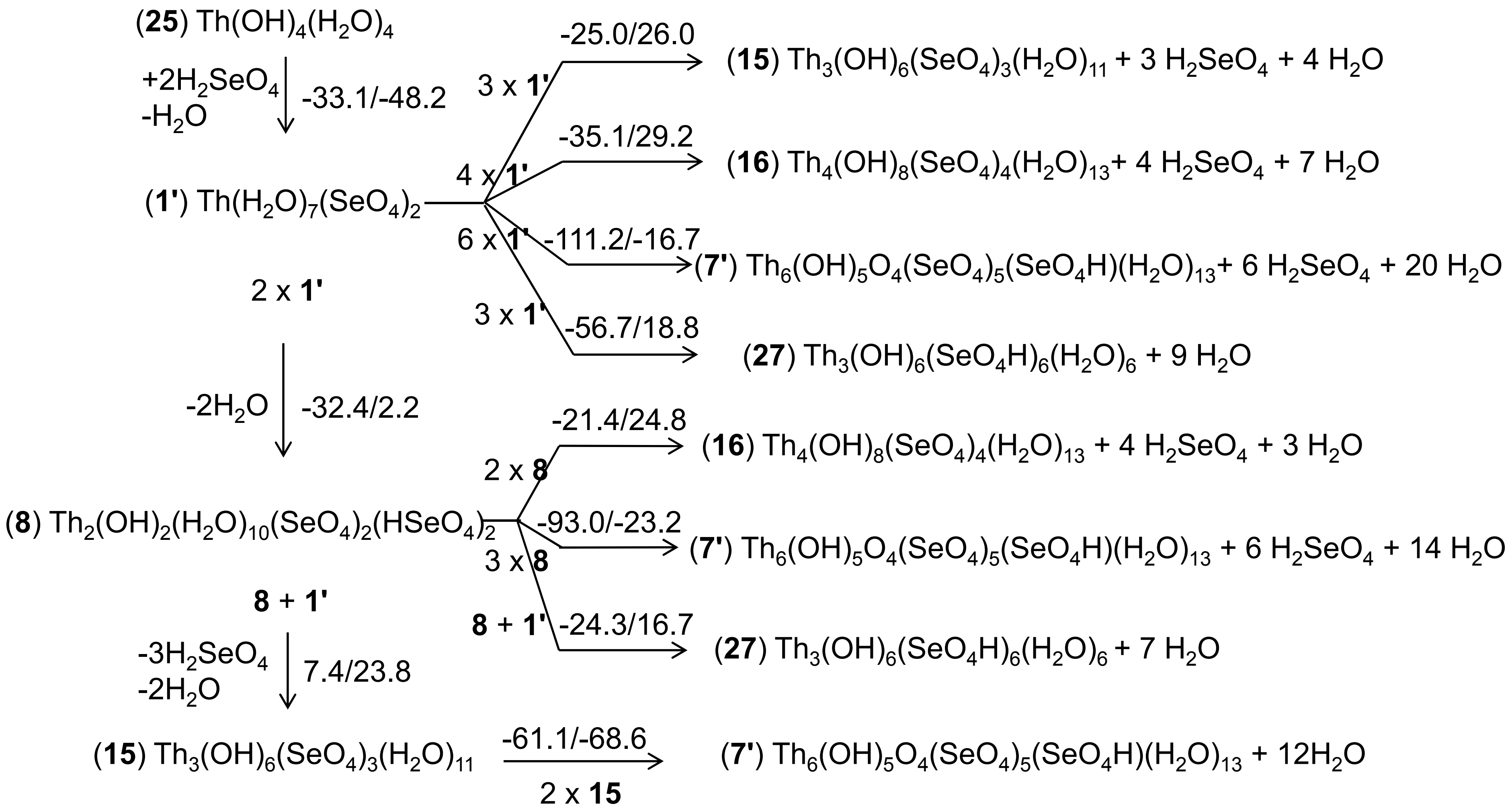
(**16**) $Th_4(OH)_8(SeO_4)_4(H_2O)_{13}$

16 + 2 x **18**

$-13H_2O$ ↓ -93.7/-85.5

(**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13}$

Mechanism: Role of Anions (SeO_4^{2-})



(**25**) $Th(OH)_4(H_2O)_4$

$+2H_2SeO_4$ $-H_2O$ ↓ -33.1/-48.2

(**1'**) $Th(H_2O)_7(SeO_4)_2$

3 x **1'** $\xrightarrow{-25.0/26.0}$ (**15**) $Th_3(OH)_6(SeO_4)_3(H_2O)_{11} + 3\ H_2SeO_4 + 4\ H_2O$

4 x **1'** $\xrightarrow{-35.1/29.2}$ (**16**) $Th_4(OH)_8(SeO_4)_4(H_2O)_{13} + 4\ H_2SeO_4 + 7\ H_2O$

6 x **1'** $\xrightarrow{-111.2/-16.7}$ (**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13} + 6\ H_2SeO_4 + 20\ H_2O$

3 x **1'** $\xrightarrow{-56.7/18.8}$ (**27**) $Th_3(OH)_6(SeO_4H)_6(H_2O)_6 + 9\ H_2O$

2 x **1'**

$-2H_2O$ ↓ -32.4/2.2

(**8**) $Th_2(OH)_2(H_2O)_{10}(SeO_4)_2(HSeO_4)_2$

2 x **8** $\xrightarrow{-21.4/24.8}$ (**16**) $Th_4(OH)_8(SeO_4)_4(H_2O)_{13} + 4\ H_2SeO_4 + 3\ H_2O$

3 x **8** $\xrightarrow{-93.0/-23.2}$ (**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13} + 6\ H_2SeO_4 + 14\ H_2O$

8 + **1'** $\xrightarrow{-24.3/16.7}$ (**27**) $Th_3(OH)_6(SeO_4H)_6(H_2O)_6 + 7\ H_2O$

8 + **1'**

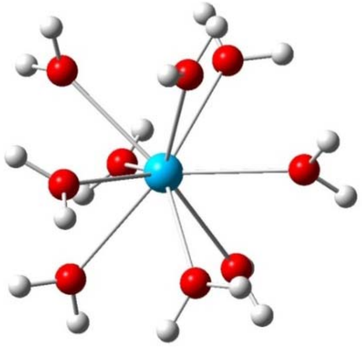
$-3H_2SeO_4$ $-2H_2O$ ↓ 7.4/23.8

(**15**) $Th_3(OH)_6(SeO_4)_3(H_2O)_{11}$ $\xrightarrow[2\ x\ \mathbf{15}]{-61.1/-68.6}$ (**7'**) $Th_6(OH)_5O_4(SeO_4)_5(SeO_4H)(H_2O)_{13} + 12H_2O$

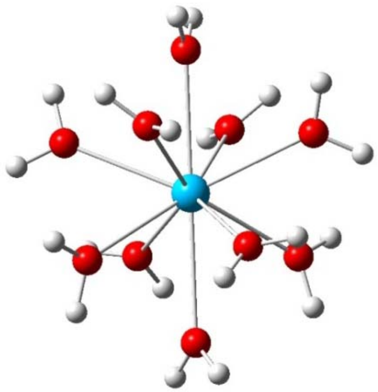
Summary

- Computational methods can predict the properties of thorium oxide clusters.
- CCSD(T) + large basis set (at least triple-ζ) gives good structures and frequencies for small clusters.
- The $Th_6O_8^{8+}$ core structure is an important motif in metal oxide clusters and is closely related to the solid structures.
- One can capture these clusters as they are growing by trapping them with appropriate oxygen donor anions
- DFT provides reasonable structures and the energetics of the isomers can be used to assign the proton positions.
- Spectral predictions are in agreement with experiment and can be used to assign the vibrational (IR and Raman) and nmr spectra. The calculated proton nmr spectra are within 1 ppm of experiment for most assignments.
- The trapping anions play a role in modifying the gas phase acidities and have a large impact on the solution values. The compounds are strong gas phase acids and weak acids in solution.

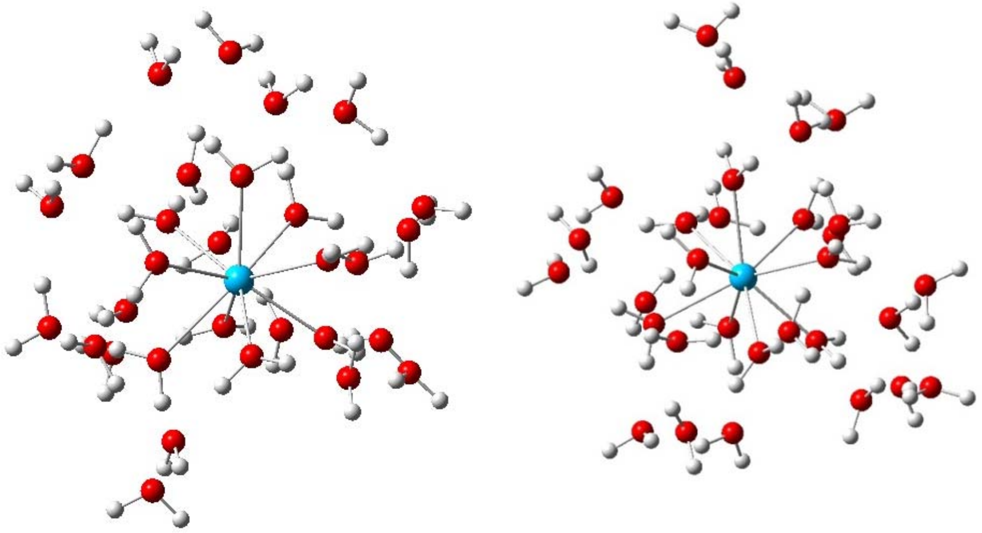
Predicting the Solvation Structure of a +4 Ion



$Th(H_2O)_9^{4+}$
(tricapped
trigonal prism)



$Th(H_2O)_{10}^{4+}$
(bicapped square
antiprism)



$Th(H_2O)_{30}^{4+}$: 2 structures, both with 9 H_2O molecule in the first solvation shell.

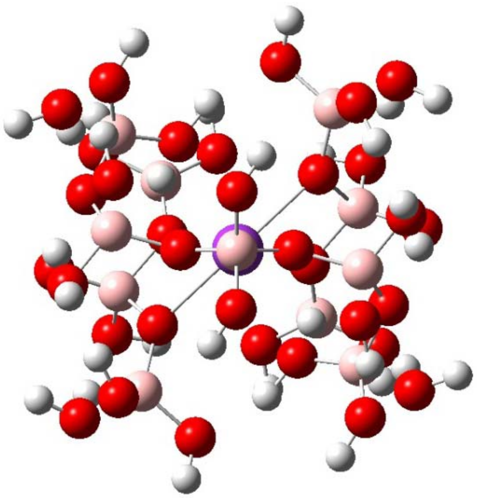
Reaction energies for: $Th(H_2O)_9^{4+} + H_2O \rightarrow Th(H_2O)_{10}^{4+}$.

Method	ΔE_0	ΔH_{298}	ΔG_{298}	
	Gas	Gas	Gas	Solution
B3LYP/TZVP	−22.3	−23.0	−13.1	6.8
MP2/AVDZ	−26.3	−27.0	−17.1	2.8
MP2/AVTZ	−25.7	−26.3	−16.4	3.5

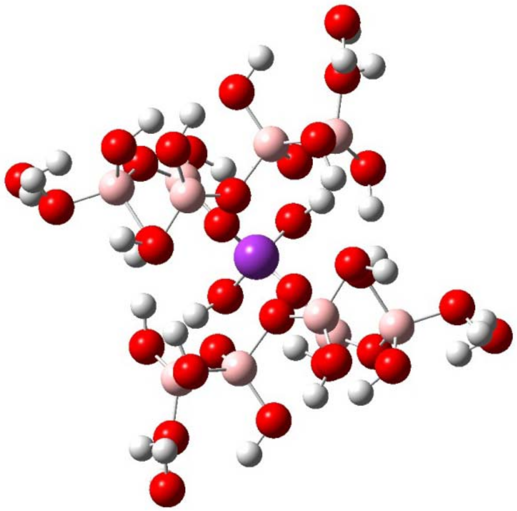
S. Li

HEXS results show 10 H_2O in 1st solvation shell. Do we need a 3rd solvation shell? Do we need anions?

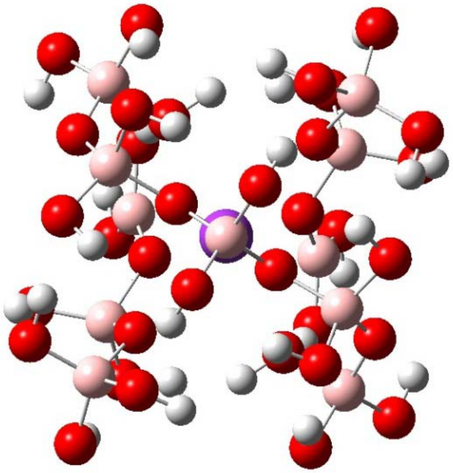
Cf and Cm Compounds



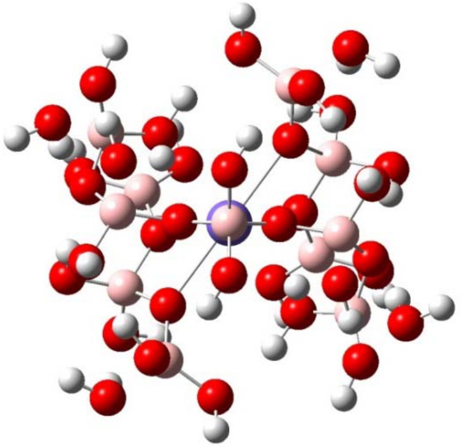
$^{6}\mathrm{CfB}_{11}\mathrm{O}_{34}\mathrm{H}_{32}$



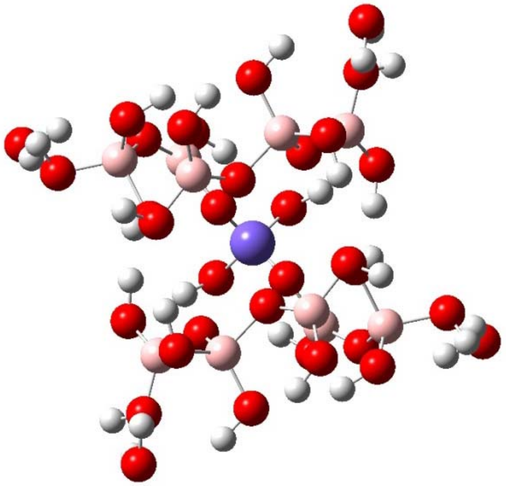
$^{6}\mathrm{CfB}_{11}\mathrm{O}_{34}\mathrm{H}_{30}{}^{-2}$



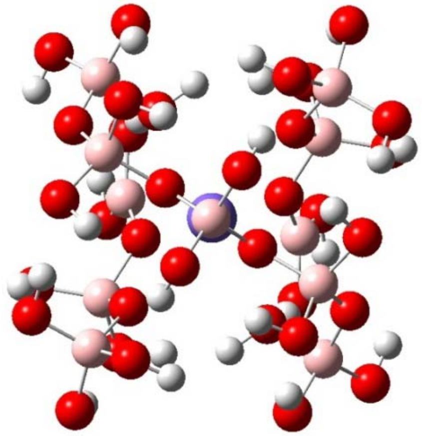
$^{6}\mathrm{CfB}_{11}\mathrm{O}_{34}\mathrm{H}_{26}{}^{-6}$



$^{8}\mathrm{CmB}_{11}\mathrm{O}_{34}\mathrm{H}_{32}$



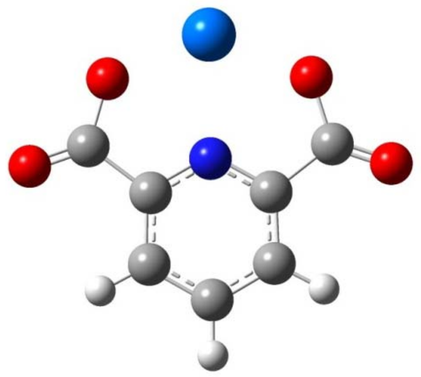
$^{8}\mathrm{CmB}_{11}\mathrm{O}_{34}\mathrm{H}_{30}{}^{-2}$



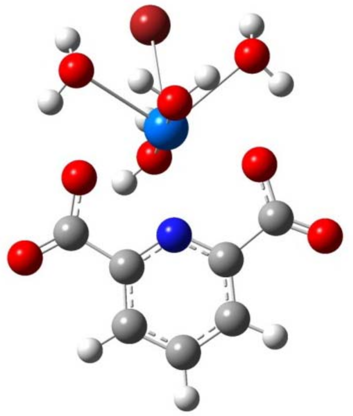
$^{8}\mathrm{CmB}_{11}\mathrm{O}_{34}\mathrm{H}_{26}{}^{-6}$

"Unusual Structure, Bonding, and Properties in a Californium Borate," M. J. Polinski, E. B. Garner, R. Maurice, N. Planas, J. T. Stritzinger, T. G. Parker, J. N. Cross, T. D. Green, E. V. Alekseev, S. M. Van Cleve, W. Depmeier, L. Gagliardi, M. Shatruk, K. L. Knappenberger, G. Liu, S. Skanthakumar, L. Soderholm, D. A. Dixon, and Thomas E. Albrecht-Schmitt, *Nature Chem*., **2014**, 6, 387-392

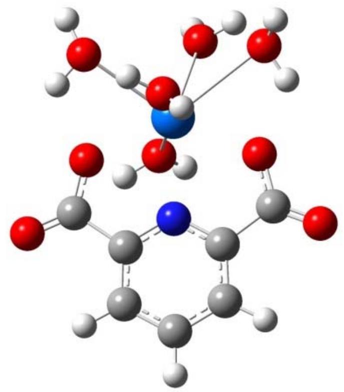
Optimized Pu (III,IV) and Am (III,IV) B3LYP/DZVP2/Stuttgart



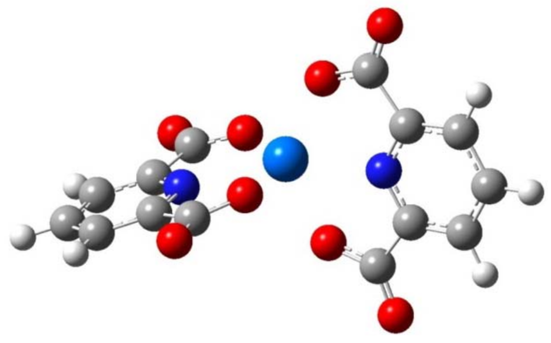
$[\mathrm{M(III)(dipic)}]^{+}$



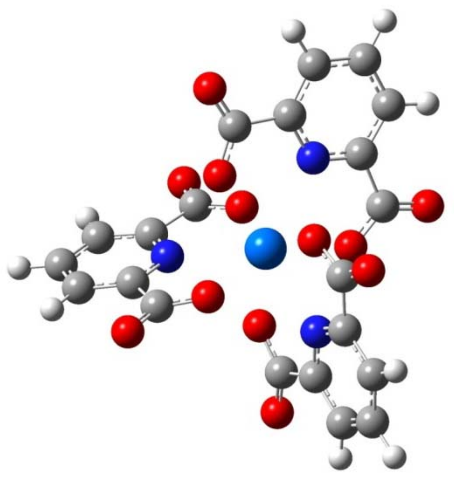
$\mathrm{M(III)(dipic)(H_2O)_4Br}$



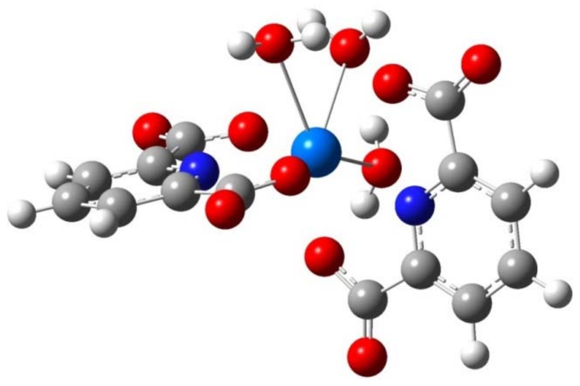
$[\mathrm{M(IV)(dipic)(H_2O)_5}]^{+}$



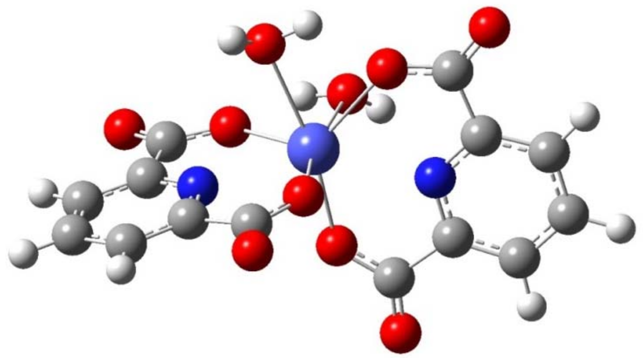
$[\mathrm{M(IV)(dipic)_2}]^{0}$



$[\mathrm{M(IV)(dipic)_3}]^{2-}$



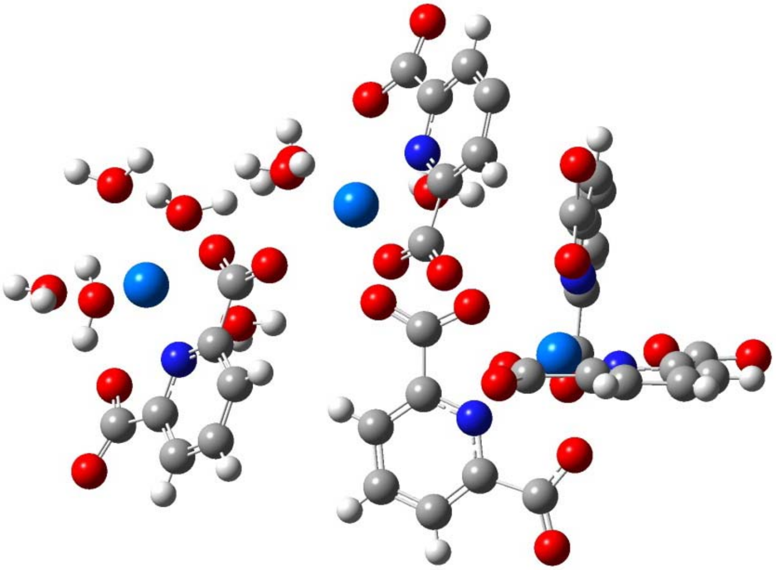
$[\mathrm{Pu(IV)(dipic)_2(H_2O)_3}]^{0}$



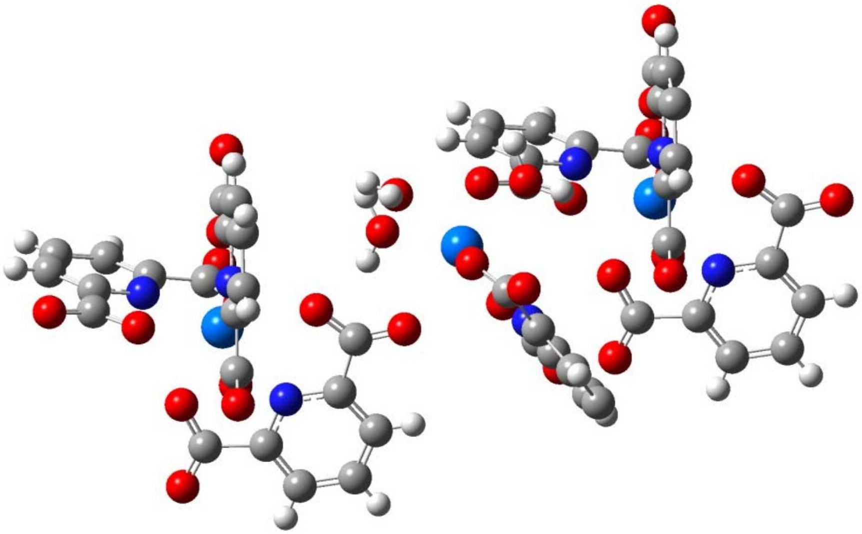
$[\mathrm{Am(IV)(dipic)_2(H_2O)_2}]^{0}$

With T. Albrecht-Schmitt, FSU

Mixed Pu(III,IV)



$[Pu_3(dipic)_5(H_2O)_8]^0$
(Pu(III)(III)(IV)



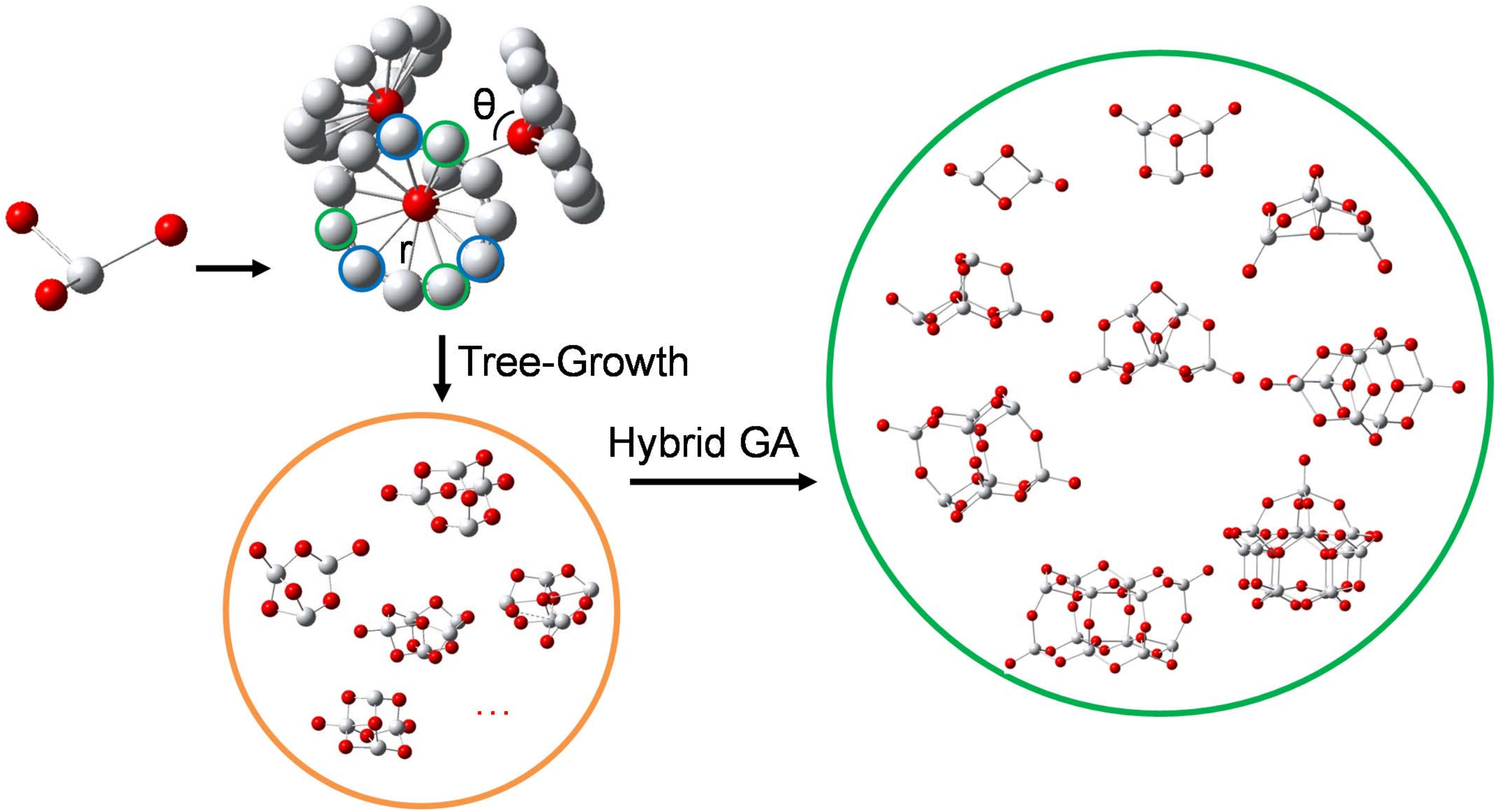
$[Pu_3(dipic)_7(H_2O)_3]^{-3}$
(Pu(IV)(III)(IV)

Structure Building for Synthesis: Tree-Growth-Hybrid Genetic Algorithm-DFT

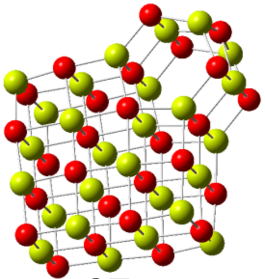
- Expand cluster using tree-growth (TG) algorithm
  - No optimization or relaxation
  - Expand based on expansion pattern (bond length, bond angle, fold, etc.)
  - When used as initial geometry generator of GA, it has low demand for energy evaluator (very coarse pairwise potential can work)
- Hybrid Genetic Algorithm (HGA)
  - Use semi-empirical methods (EAM, PM6, MNDO-D, AM1..) to do relaxation. Efforts to parameterize a suitable force field are saved. Works for many clusters but not all.
- Hybrid Genetic algorithm structures are re-optimized by DFT to verify the results.

"Tree Growth – Hybrid Genetic Algorithm for Predicting the Structure of Small $(TiO_2)_n$, n = 2 – 13, Nanoclusters," M. Chen and D A. Dixon *J. Chem. Theory Comp.* **2013**, *9*, 3189–3200

Tree Growth + HGA for TiO_2 nanoclusters

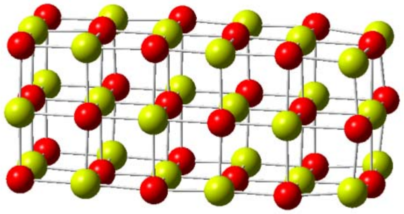


- TG: Two-body Morse-like potential
- HGA: PM6
- post-HGA: B3LYP/DZVP2 – benchmarked against CCSD(T)/correlation-consistent basis sets/CBS



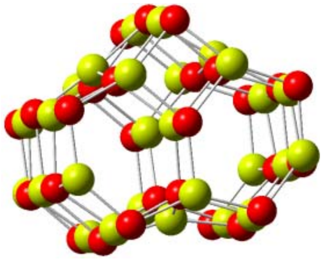
27a

0



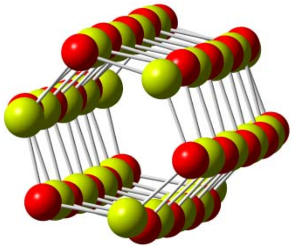
27b

8.7



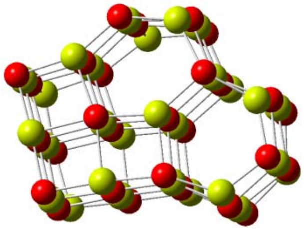
27c

40.2



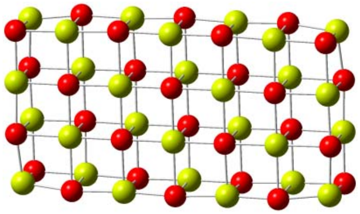
27d

44.4



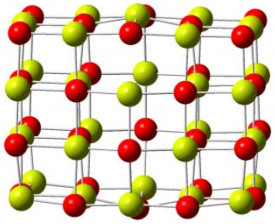
28a

0



28b

17.1



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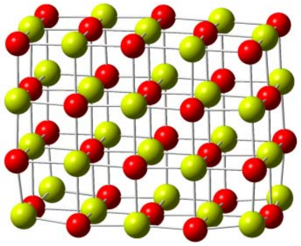

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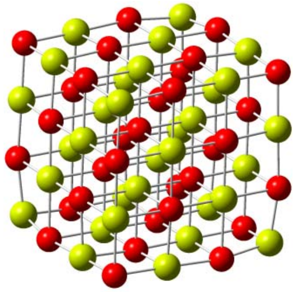
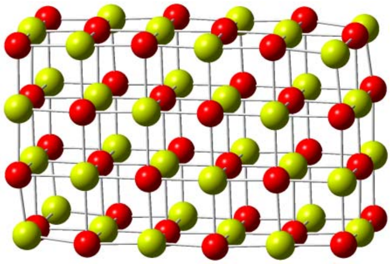
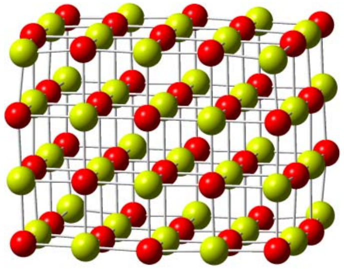


32a



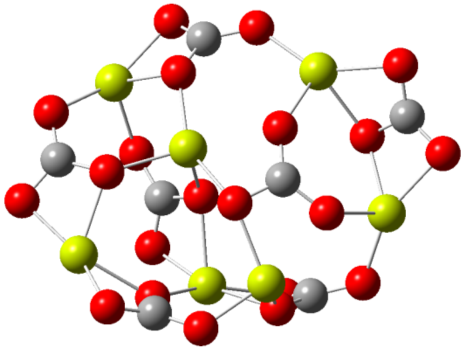
36a



40a

(MgO)$_n$
Clusters
ΔE,
kcal/mol
B3LYP/
DZVP

$(MgCO_3)_n$ Energies in kcal/mol



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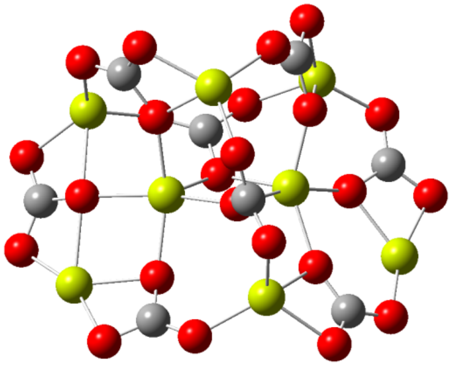

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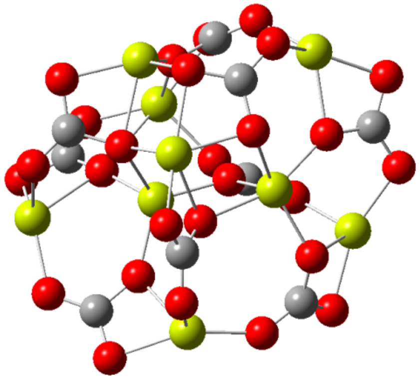

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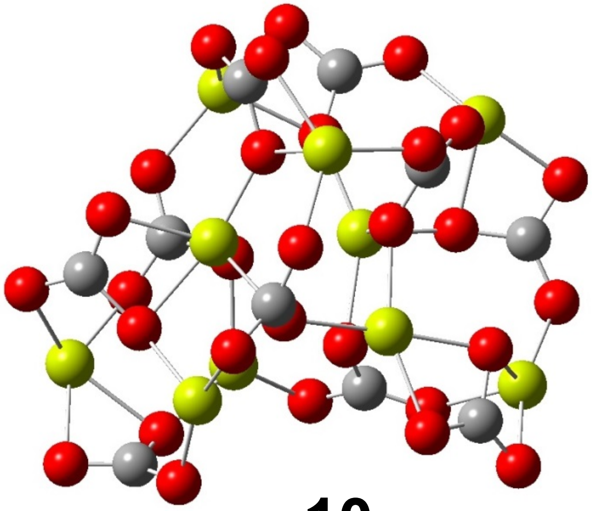
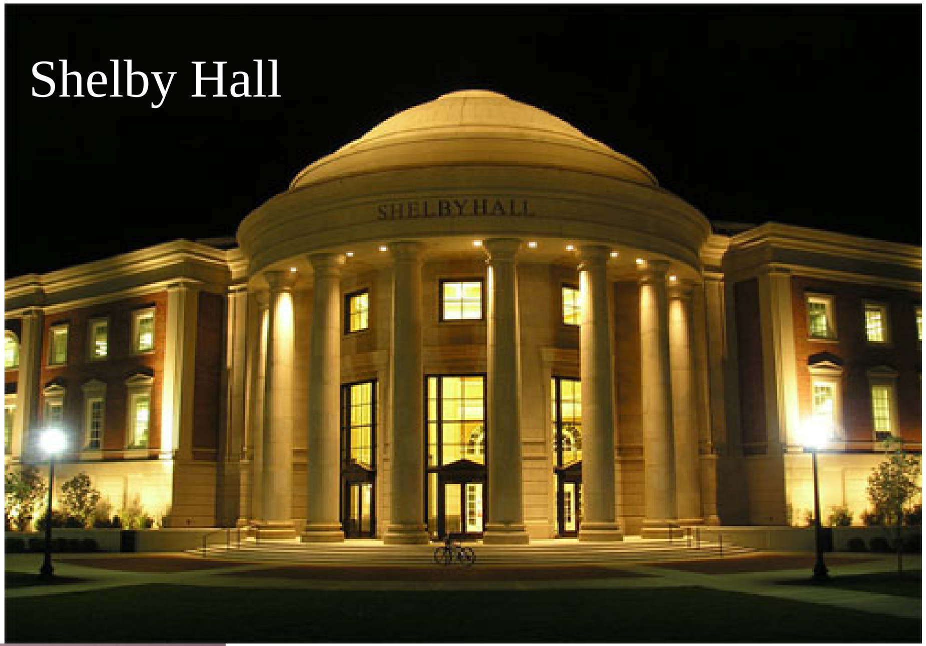


10



Shelby Hall

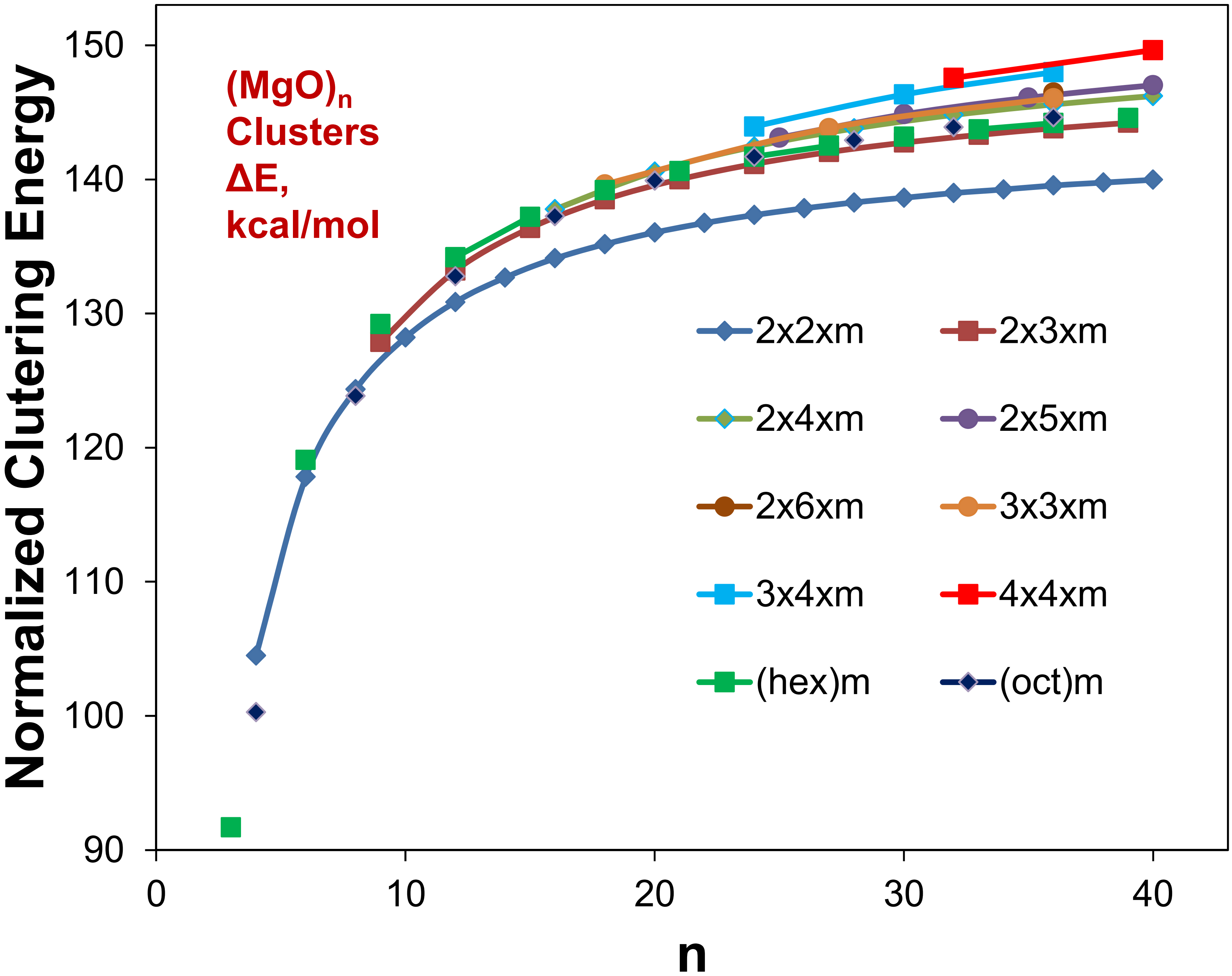
Roll Tide

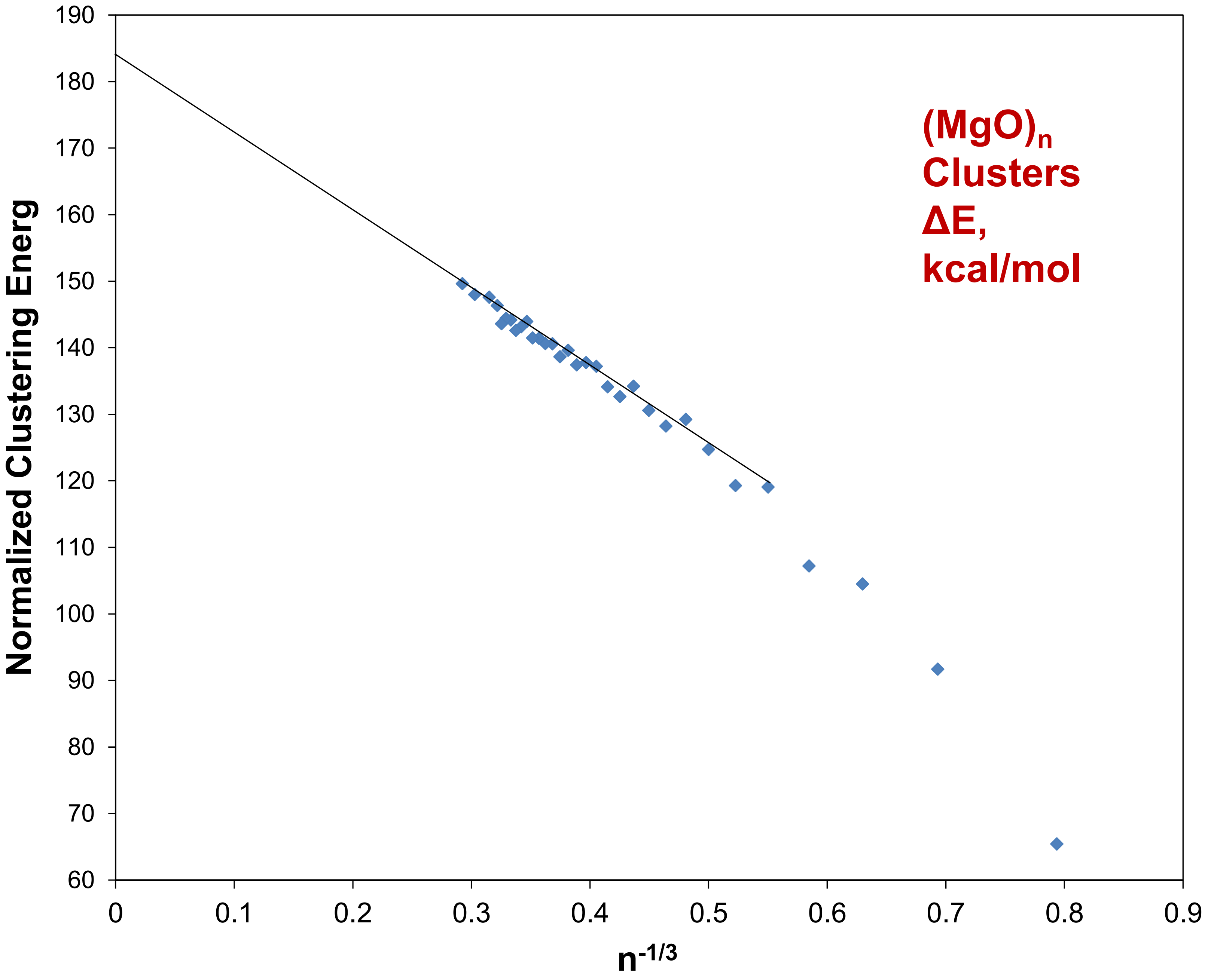
ALABAMA

CRIMSON TIDE

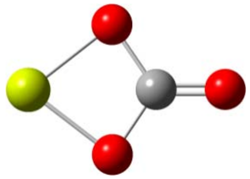
Benchmarks for the Normalized Clustering Energies in kcal/mol for $(MgO)_n$, n = 1 - 9.

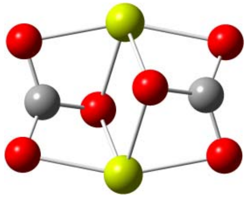
n	CCSD(T)/D	CCSD(T)/T	CCSD(T)/Q	CCSD(T)/ CBS(DTQ)	B3LYP/DZVP
2	57.6	62.6	64.0	64.9	65.4
3	86.8	89.9	90.6	91.1	91.7
4	103.0	104.3	104.7	104.9	104.5
5	105.9	107.1	107.3	107.3	107.2
6	118.9	119.5	119.5	119.5	119.1
7	119.4	119.8	119.7	119.7	119.3
8	125.2	125.4	125.2	125.1	124.7
9	130.4	130.1			129.2


(MgO)$_n$
Clusters
ΔE,
kcal/mol
Normalized Clutering Energy
n
90
100
110
120
130
140
150
0
10
20
30
40
2x2xm
2x3xm
2x4xm
2x5xm
2x6xm
3x3xm
3x4xm
4x4xm
(hex)m
(oct)m


(MgO)$_n$
Clusters
ΔE,
kcal/mol
Normalized Clustering Energ
n$^{-1/3}$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

$(MgCO_3)_n$
ΔH(0), kcal/mol
B3LYP/DZVP


1a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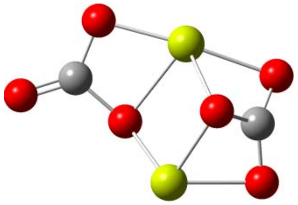
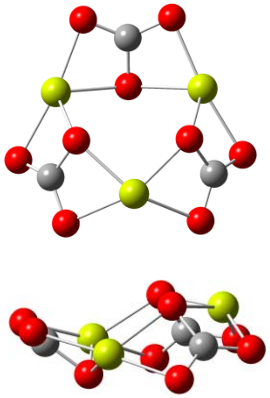

2b, 9.0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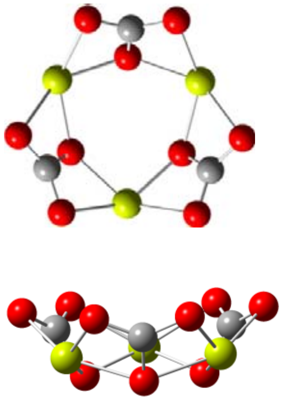
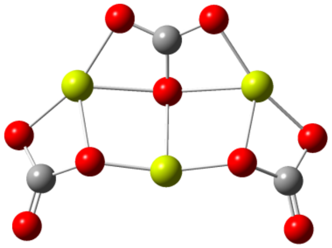
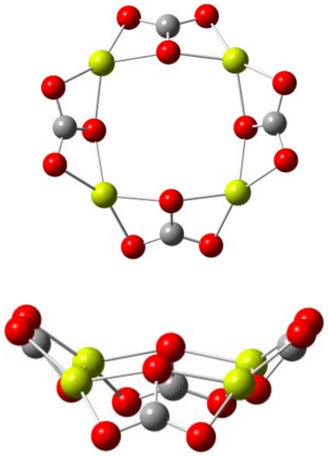

3b, 12.2


3c, 28.2

top

side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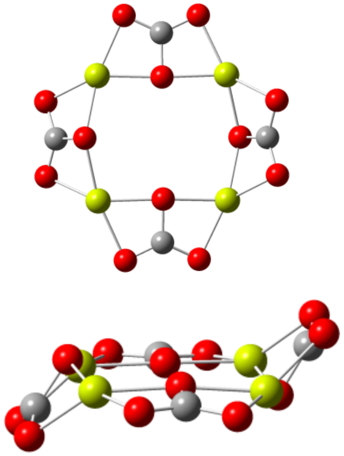
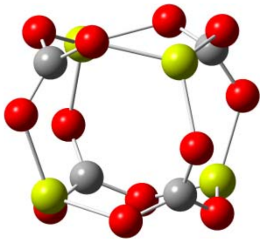

4b, 7.7


4c, 34.0

top

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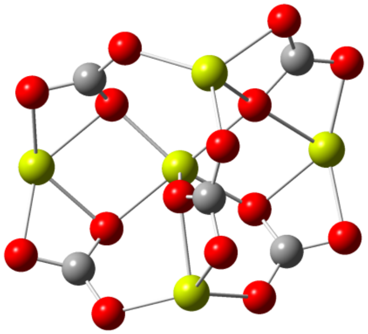

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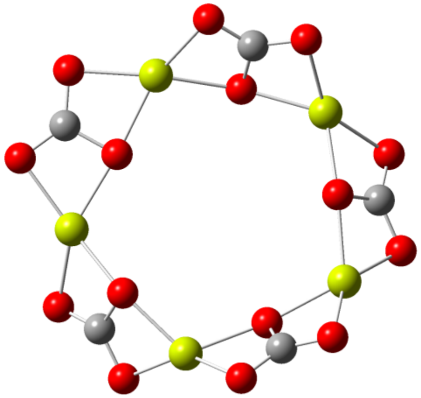

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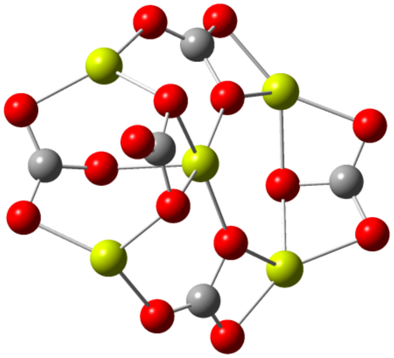

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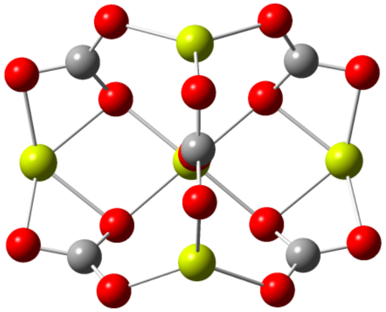

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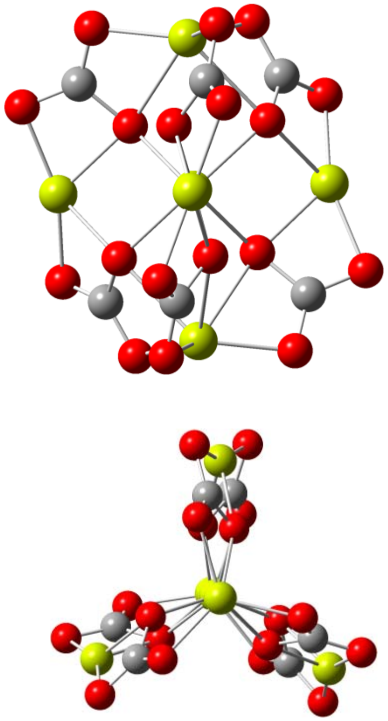
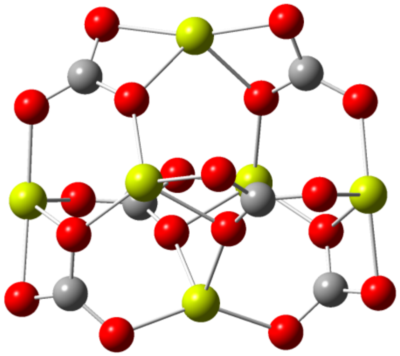
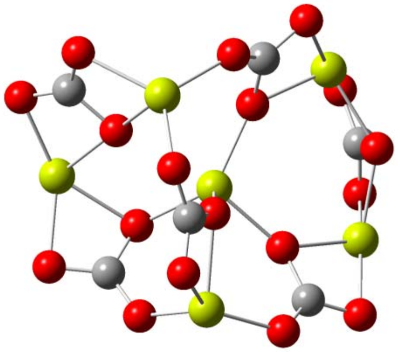






top

side

6a

6b, 2.1

6c, 5.5

Normalized Clustering Energies (NCEs) and Heats of Formation in kcal/mol

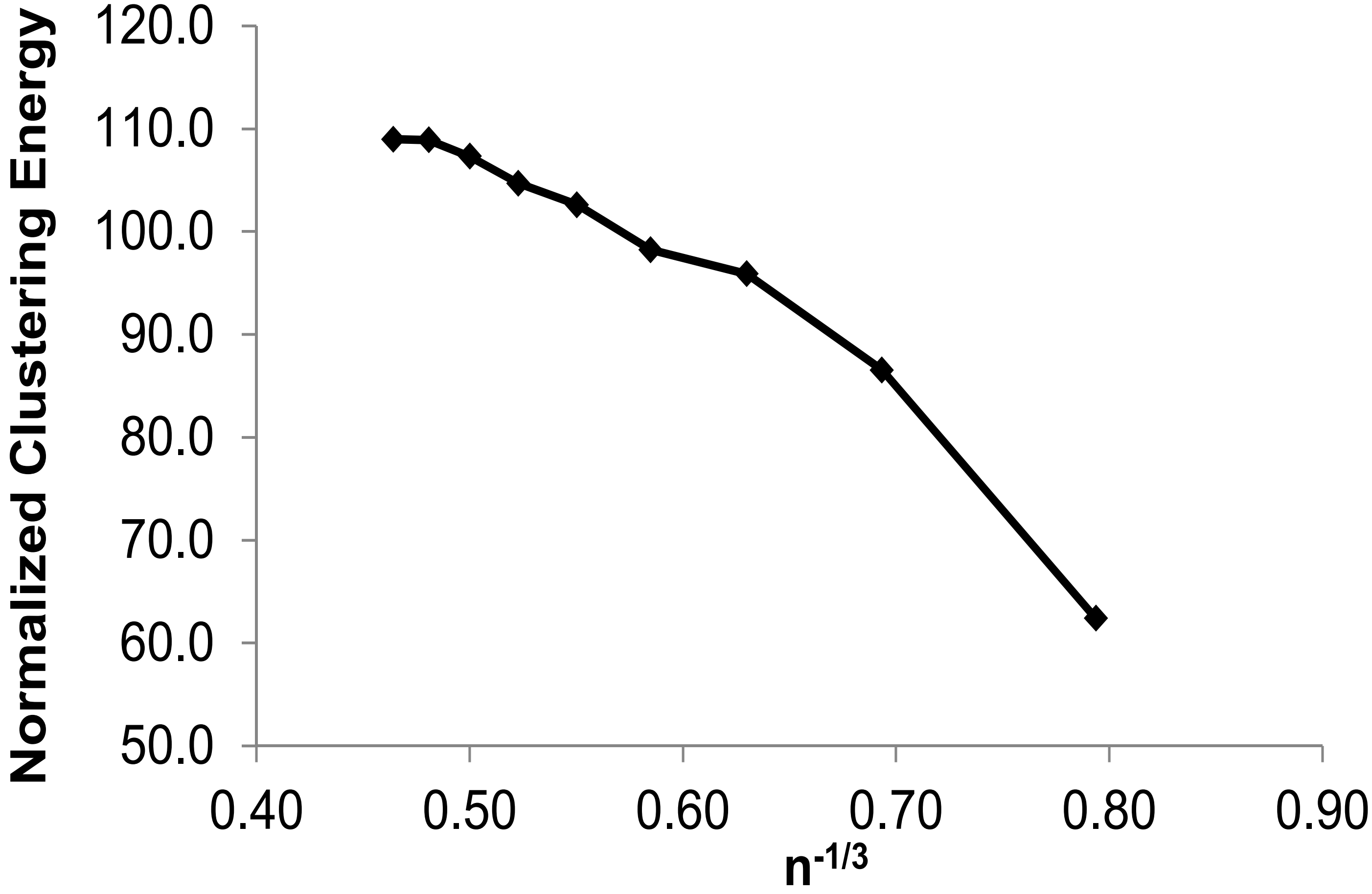
n	NCE $(MgCO_3)_n$	$\Delta H_f(g,298)$ $(MgCO_3)_n$
1	0	-111.8*
2	62.4	-348.4
3	86.5	-595.0
4	95.9	-830.7
5	98.2	-1050.1
6	102.6	-1286.4
7	105.7	-1522.5
8	107.3	-1752.8
9	108.9	-1986.2
10	110.1	-2219.0
11	110.9	-2449.7
12	111.9	-2684.4
Expt sol	153.9	

* FPD value

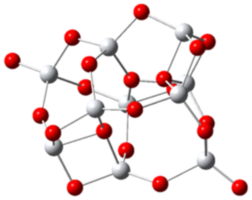
Reaction Energy (kcal/mol) for $(MgCO_3)_n \rightarrow (MgO)n + nCO_2$

n	ΔE $(MgCO_3)_n$	$\Delta E/n$ $(MgCO_3)_n$
1	52.2	52.2
2	98.3	49.1
3	141.1	47.0
4	174.3	43.6
5	216.2	43.2
6	214.3	35.7
7	270.6	38.7
8	281.0	35.1
9	286.8	31.9
10	340.5	34.1
11	357.4	32.5
12	358.0	29.8
Expt solid		27.9

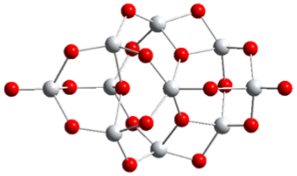
$(MgCO_3)_n$ Energies in kcal/mol



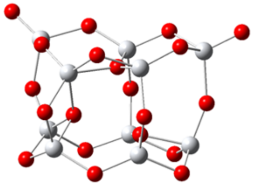
TiO_2 Nanoclusters



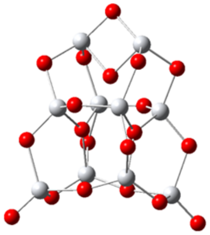
10a C_1 0



10b C_s 0.1



10c C_1 1.4



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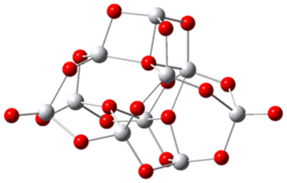
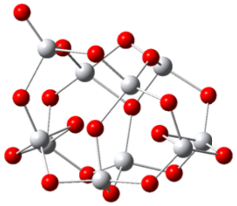
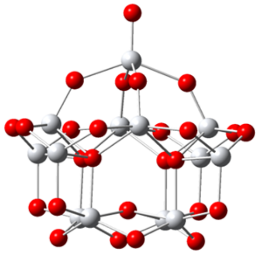


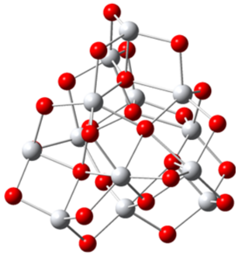
10e C_1 5.0



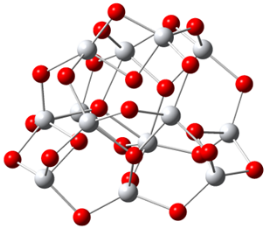
10f C_1 7.9



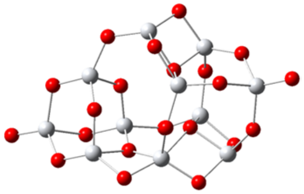
13a C_i 0



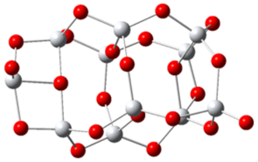
13b $C_1$8.4



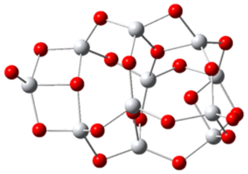
13c C_1 9.9



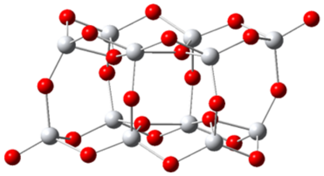
11a C_1 0



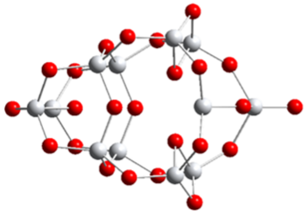
11b C_1 2.5



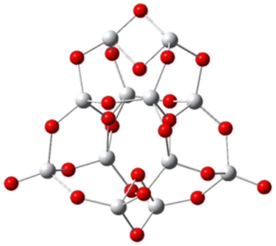
11c C_1 3.4



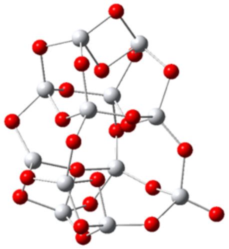
12a C_i 0



12b C_s 4.8

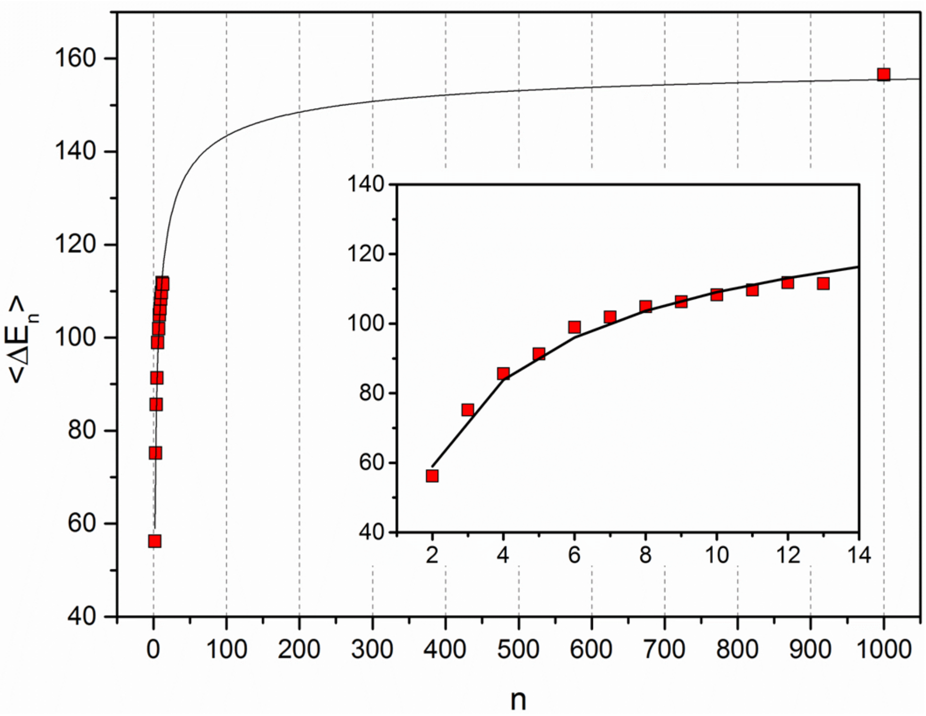


12c C_2 7.8



12d C_1 8.9

TiO_2 Nanoclusters



- The experimental value $\langle \Delta E_\infty \rangle$ for bulk rutile is 156.5 kcal/mol
- $\langle \Delta E_{30} \rangle$ ~130 kcal/mol, 84% of bulk value,
- $\langle \Delta E_{50} \rangle$ ~140 kcal/mol, 90% of bulk value,
- $\langle \Delta E_{250} \rangle$ ~150 kcal/mol, 96% of bulk value.
- Convergence of $\langle \Delta E_n \rangle$ to bulk value suggests that the core structural unit in bulk TiO_2, e.g., 6-coordinate Ti, has energetics comparable to the values for the smaller clusters.
- At n =13, the structure is not yet large enough to contain a hexacoordinate Ti.

Dissociation reactions

$$(TiO_2)_n \rightarrow (TiO_2) + (TiO_2)_{n-1}$$

n	ΔE(kcal/mol)
2	112.4
3	113.4
4	116.8
5	114.0
6	137.6
7	119.0
8	125.7
9	118.2
10	126.3
11	123.5
12	134.8
13	107.5

- For n = 12, ΔE ~ 86% of bulk.
- For n = 13, ΔE is the smallest.
- $(TiO_2)_{12}$ cluster is stable and the $(TiO_2)_{13}$ cluster is less stable due to the loss of a Ti=O bond for n =13 without forming a hexacoordinate Ti.

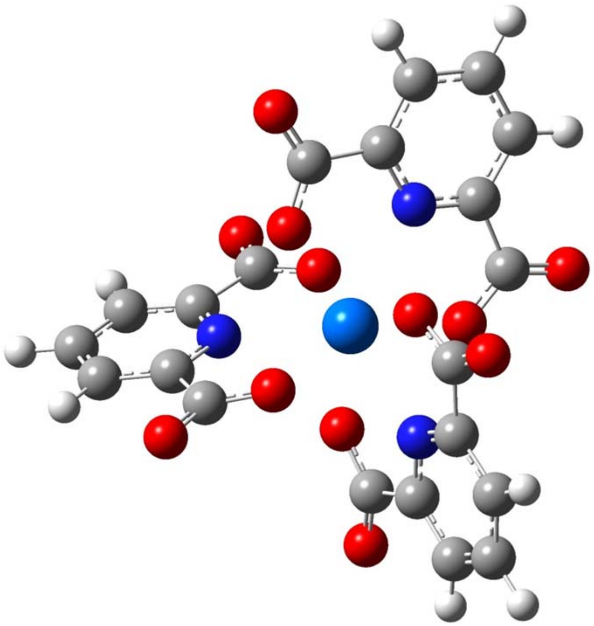
Clustering Energies & Heats of Formation

Cluster	Symmetry	Normalized Clustering Energies (kcal/mol)	Differential Clustering Energies (kcal/mol)	ΔH_f (kcal/mol)
Th_2O_4	C_{2h}	-46.6	-93.2 (1→2)	-310.8
Th_3O_6	C_s	-61.9	-92.5 (2→3)	-512.1
Th_4O_8	A_2	-75.8	-117.5 (3→4)	-738.4
Th_5O_{10}	C_s	-85.7	-125.3 (4→5)	-972.5
Th_6O_{12}	C_1	-110.8	-125.6 (5→6)	-1206.9

Normalized Th – H_2O Physisorption Energies (kcal/mol)

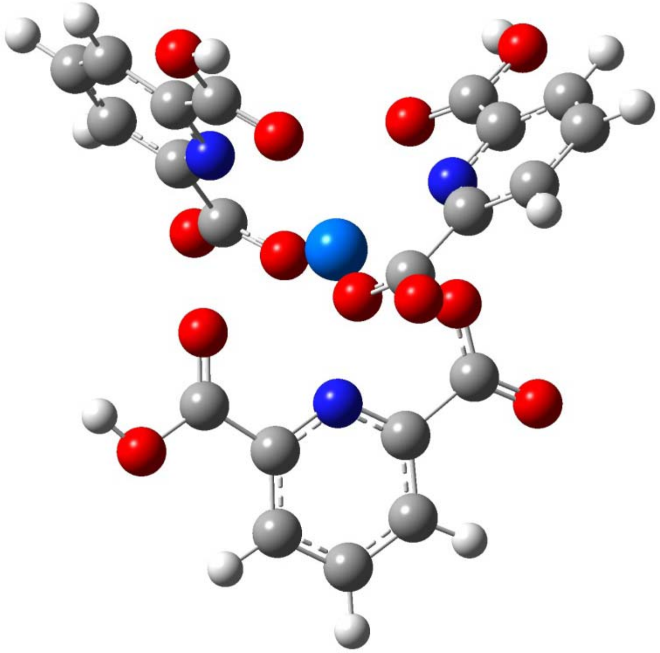
Cluster	ΔE (S)	ΔE(T)	Cluster	ΔE (S)	ΔE(T)
ThO_2 (C_{2v}) + H_2O	-20.5	-16.2	Th_5O_{10} (C_{4v}) + H_2O	-18.8	-18.4
Th_2O_4 (C_{2v}) + H_2O	-17.5	-15.1	Th_5O_{10} + $2H_2O$	-18.8	-18.5
Th_2O_4 + $2H_2O$	-17.5	-17.7	Th_5O_{10} + $3H_2O$	-18.8	-18.1
Th_3O_6 (C_1) + H_2O	-14.5	-23.8	Th_5O_{10} + $4H_2O$	-18.8	-18.2
Th_3O_6 + $2H_2O$	-16.4	-17.2	Th_5O_{10} + $5H_2O$	-15.0	-9.0
Th_3O_6 + $3H_2O$	-16.4	-15.0	Th_6O_{12} (C_1) + H_2O	-18.2	-16.7
Th_4O_8 (A_2) + H_2O	-18.2	-18.4	Th_6O_{12} + $2H_2O$	-18.0	-13.7
Th_4O_8 + $2H_2O$	-18.0	-15.3	Th_6O_{12} + $3H_2O$	-17.8	
Th_4O_8 + $3H_2O$	-18.0	-19.3	Th_6O_{12} + $4H_2O$	-18.3	
Th_4O_8 + $4H_2O$	-18.0	-11.1	Th_6O_{12} + $5H_2O$	-20.7	

$[M(dipic)_3]^{3-}$ for M(III), M = Pu, Am, Cm, and Cf



$[M(dipic)_3]^{3-}$	M(oxid)	M(Mulliken)	NBO	M(spin)	M 5f	M 6d	M 7s	M 7p
Pu	3 (f^5)	1.64	1.44	5.03	5.22	0.77	0.17	0.36
Am	3 (f^6)	1.49	1.54	6.02	6.11	0.77	0.18	0.36
Cm	3 (f^7)	1.29	1.46	6.95	6.95	0.93	0.13	0.48
Cf	3 (f^9)	1.37	1.52	4.93	9.08	0.77	0.46	0.13

$[M(dipicH)_3]^0$ for M(III), M = Pu, Am, Cm, and Cf



$[M(dipicH)_3]^0$	M(oxid)	M(Mulliken)	M(NBO)	M(spin)	M 5f	M 6d	M 7s	M 7p
Pu	3 (f^5)	1.60	1.43	5.04	5.27	0.75	0.16	0.33
Am	3 (f^6)	1.50	1.55	6.05	6.17	0.75	0.18	0.33
Cm	3 (f^7)	1.29	1.45	6.93	6.94	0.95	0.13	0.47
Cf	3 (f^9)	1.39	1.54	4.91	9.12	0.75	0.44	0.12

Functional	f^{occ}	Spin pop	NBO charge	Mulliken charge	Pop 7s	Pop 5f	Pop 6d	Pop 7p
$^{6}CfB_{11}O_{34}H_{32}$								
B3LYP	f^9	4.91	1.85	1.51	0.08	9.11	0.65	0.29
PW91	f^9	4.80	1.70	1.27	0.08	9.24	0.67	0.29
$^{8}CmB_{11}O_{34}H_{32}$								
B3LYP	f^7	7.02	1.82	1.43	0.08	7.07	0.70	0.29
PW91	f^7	7.06	1.72	1.17	0.08	7.09	0.76	0.30

Functional	f^{occ}	Spin pop	NBO charge	Mulliken charge	Pop 7s	Pop 5f	Pop 6d	Pop 7p
$^{6}CfB_{11}O_{34}H_{30}^{-2}$								
B3LYP	f^9	4.91	1.81	1.46	0.09	9.10	0.65	0.32
PW91	f^9	4.80	1.65	1.20	0.09	9.24	0.67	0.32
$^{8}CmB_{11}O_{34}H_{30}^{-2}$								
B3LYP	f^7	7.02	1.79	1.38	0.09	7.06	0.70	0.32
PW91	f^7	7.07	1.68	1.12	0.08	7.08	0.76	0.33

Functional	f^{occ}	Spin pop	NBO charge	Mulliken charge	Pop 7s	Pop 5f	Pop 6d	Pop 7p
$^{6}CfB_{11}O_{34}H_{26}^{-6}$								
B3LYP	f^9	4.90	1.92	1.48	0.07	9.12	0.60	0.26
PW91	f^9	4.76	1.74	1.22	0.07	9.28	0.61	0.27
$^{8}CmB_{11}O_{34}H_{32}^{-6}$								
B3LYP	f^7	7.04	1.89	1.41	0.07	7.04	0.68	0.26
PW91	f^7	7.09	1.78	1.15	0.07	7.06	0.74	0.28

Pu and Am Results

compound	Pu(oxid)	Pu(Mull)	Pu(NBO)	Pu(spin)	Pu 5f	Pu 6d	Pu 7s	Pu 7p
$[Pu(dipic)]^{+}$	3 (f^5)	1.70	2.21	5.04	5.17	0.54	0.06	0.04
$[Pu(dipic)(H_2O)_5]^{+}$	3 (f^5)	1.79	1.68	5.05	5.26	0.64	0.13	0.25
$Pu(dipic)(H_2O)_4Br$	3 (f^5)	1.48	1.38	5.07	5.27	0.79	0.17	0.32
$[Pu(dipic)_3]^{3-}$[a]	3 (f^5)	1.64	1.44	5.03	5.22	0.77	0.17	0.36
$[Pu(dipic)_2(H_2O)_3]^{0}$	4 (f^4)	1.80	1.35	4.15	4.90	1.01	0.17	0.40
$[Pu(dipic)_3]^{2-}$	4 (f^4)	1.79	1.25	4.14	4.90	1.05	0.18	0.45
$[Pu(dipic)_2]$	4 (f^4)	1.79	1.93	4.12	4.75	0.93	0.13	0.23

[a] $[Pu(dipic)_3]^{3-}$ (Pu(III)) is 59.6 kcal/mol higher in energy than $[Pu(dipic)_3]^{2-}$ (Pu(IV))

compound	Am(oxid)	Am(Mull)	Am(NBO)	Am(spin)	Am 5f	Am 6d	Am 7s	Am 7p
$[Am(dipic)]^{+}$	3 (f^6)	1.60	2.15	6.15	6.27	0.50	0.07	0.04
$[Am(dipic)(H_2O)_5]^{+}$	3 (f^6)	1.71	1.74	6.06	6.18	0.64	0.15	0.26
$Am(dipic)(H_2O)_4Br$	3 (f^6)	1.40	1.46	6.07	6.18	0.79	0.19	0.32
$[Am(dipic)_3]^{3-}$[a]	3 (f^6)	1.49	1.54	6.02	6.11	0.77	0.18	0.36
$[Am(dipic)_3]^{2-}$	4 (f^5)	1.63	1.51	5.27	5.77	1.01	0.20	0.44
$[Am(dipic)_2]$	4 (f^5)	1.73	1.96	5.33	5.78	0.89	0.13	0.22
$[Am(dipic)_2(H_2O)_2]^{0}$[b]	4 (f^5)	1.80	1.68	5.32	5.81	0.93	0.18	0.35

[a] $[Am(dipic)_3]^{3-}$(Am(III)) is 33.1 kcal/mol higher in energy than $[Am(dipic)_3]^{2-}$ (Am(IV))

[b] For M = Am $[Am(dipic)_2(H_2O)_2]^{0}$ was optimized instead of $[Am(dipic)_2(H_2O)_3]^{0}$

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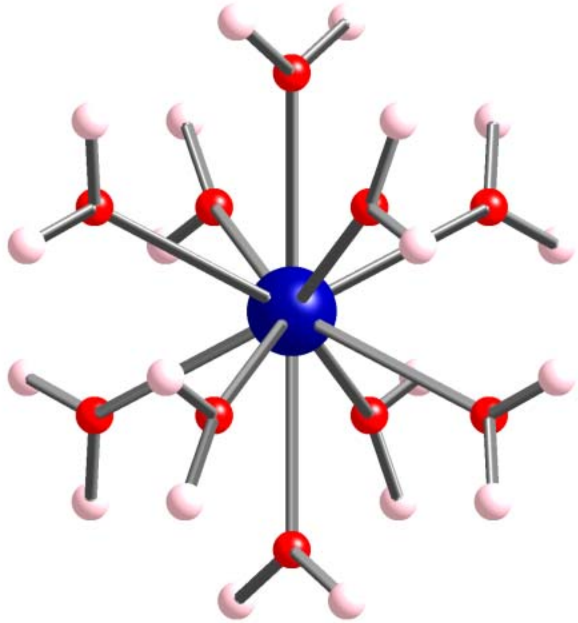
2011

Thorium hydrolysis and condensation

- Aqueous chemistry limited to tetravalent state
- Largest and softest of M(IV)
- Substantial literature but very little of it is backed by structural chemistry
- No f-electrons – good for theory
- Spectroscopically silent
- Species play crucial role in understanding solution chemistry – known to cause discrepancies in thermodynamic data
- Very little known about structural chemistry – composition largely unknown

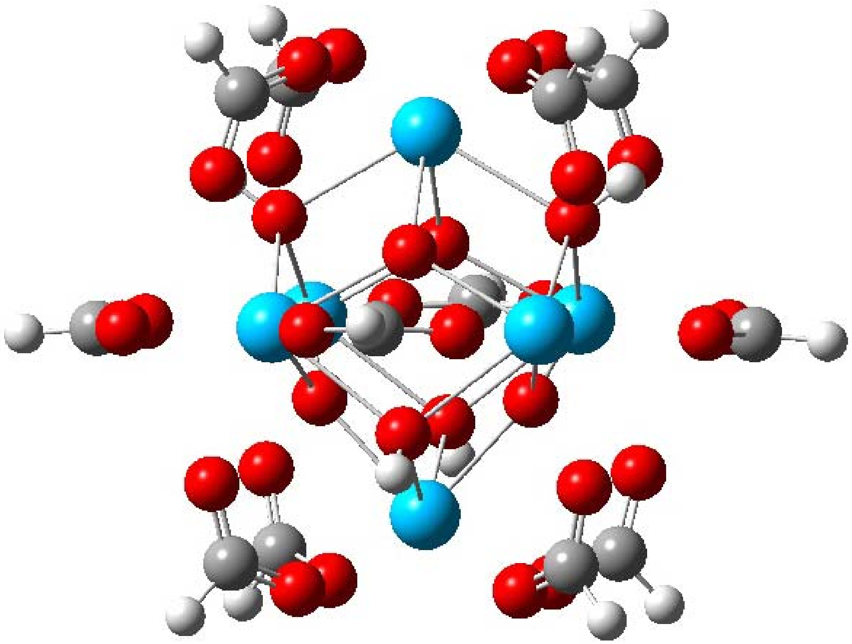


$[Th(H_2O)_{10}]Br_4$

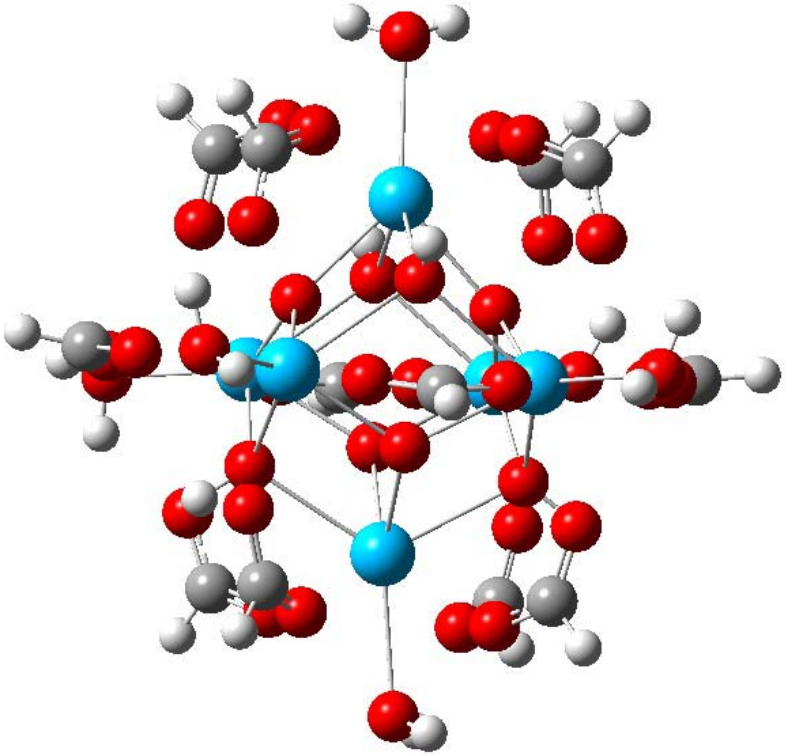
Wilson et al., Angew. Chem, 2007, 46, 8043

Thorium hydrolysis and condensation

The lowest energy formate structures



$Th_6(OH)_4O_4(HCOO)_{12}$ (**A**)

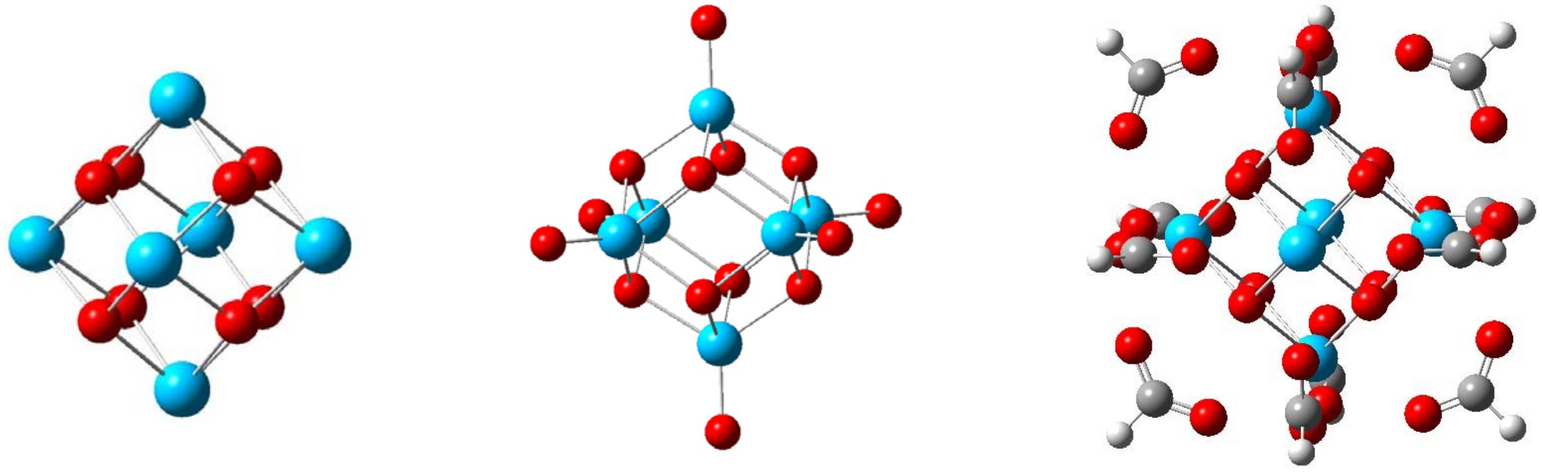


$Th_6(OH)_4O_4(H_2O)_6(HCOO)_{12}$ (**A**)

“Thorium(IV) molecular clusters with a hexanuclear core,” K. E. Knope, R. E. Wilson, M. Vasiliu, D. A. Dixon, and L. Soderholm, *Inorg. Chem*., **2011**, *50*, 9696-9704

Comparison of average calculated bond (SVWN5) distances (Å)

Distance	$Th_6O_8^{8+}$	$Th_6O_8O_6^{4-}$	$Th_6O_8(HCOO)_{12}^{4-}$	$Th_6(OH)_4O_4(H_2O)_6(HCOO)_{12}$	$Th_6(OH)_4O_4(HCOO)_{12}$	$Th_6(OH)_4O_4O_6$
Th- μ_3-O	2.306	2.355	2.280	2.287	2.274	2.329
Th - μ_3-OH				2.493	2.476	2.559
Th=O		2.016				1.891
Th-Th (edge)	3.826	3.783	3.721	3.911	3.896	3.932
Th-Th(vertex)	5.411	5.349	5.262	5.529	5.510	5.561



Structure of $Th_6O_8^{8+}$ core remains remarkably the same

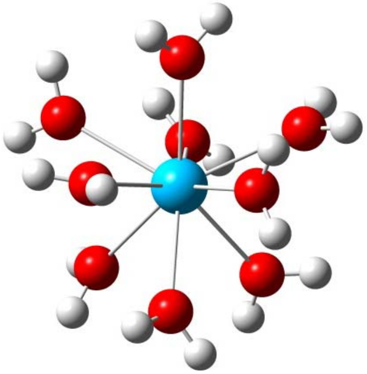
Role of Solvent Shells on Reactivity?

$Th(H_2O)_9^{+4} \rightarrow Th(OH)(H_2O)_8^{+3} + H^+$

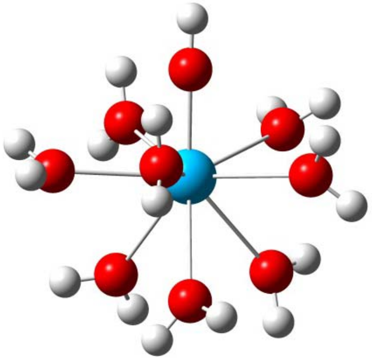
ΔG_{gas} = -43.1 kcal/mol, pK_a = -17.6 (too acidic)

$Th(OH)(H_2O)_8^{+3} \rightarrow Th(OH)_2(H_2O)_7^{+2} + H^+$

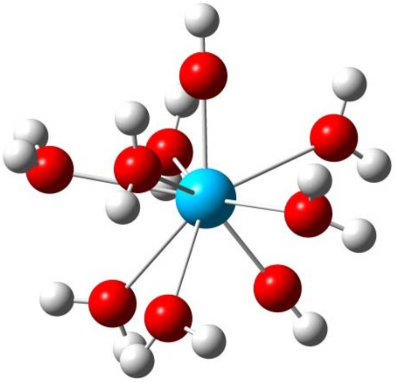
ΔG_{gas} = 59.5 kcal/mol, pK_a = -5.4 (too acidic)



$Th(H_2O)_9^{+4}$



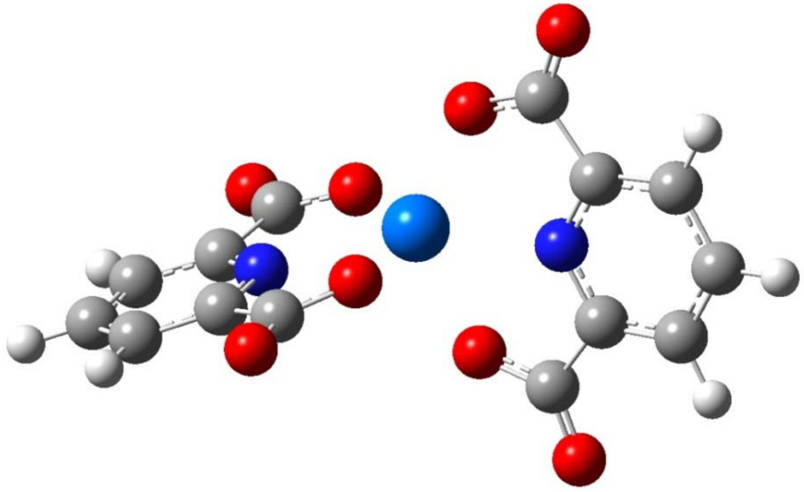
$Th(OH)(H_2O)_8^{+3}$



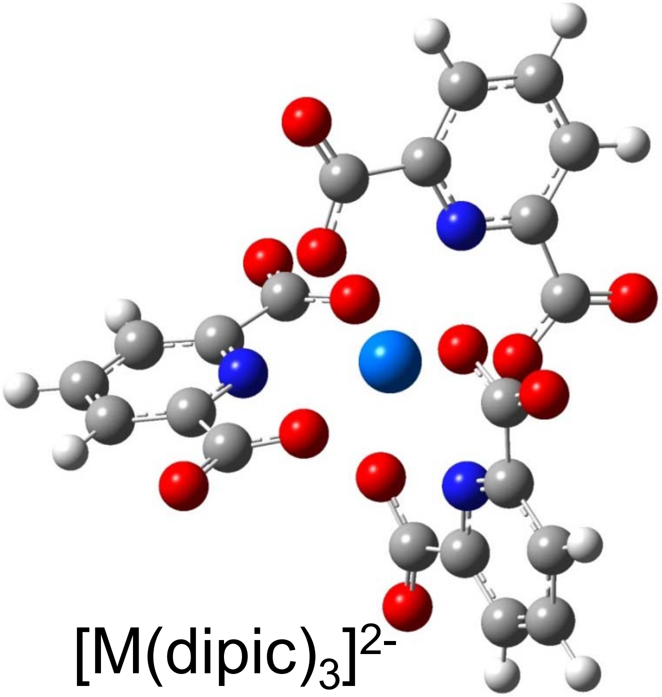
$Th(OH)_2(H_2O)_7^{+2}$

- How many solvent shells needed for acidity?
- Are explicit anions required?
- Are the anions involved in proton transfer reactions?

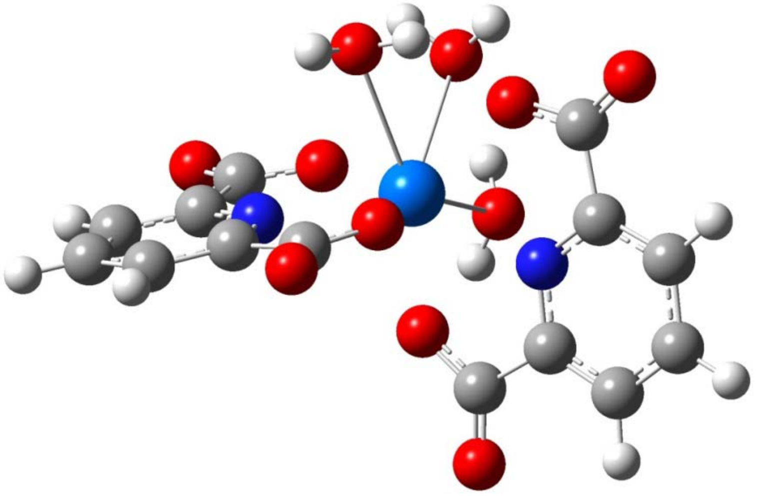
Optimized Pu (+4) and Am (+4) at B3LYP/DZVP2/Stuttgart



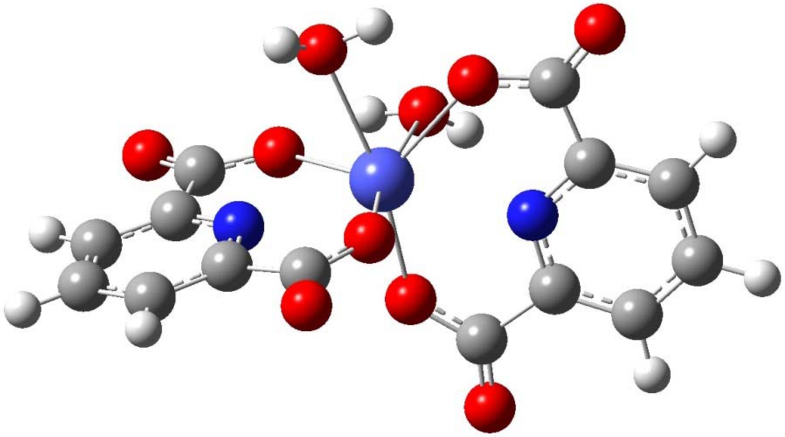
$[M(dipic)_2]^0$



$[M(dipic)_3]^{2-}$



$[Pu(dipic)_2(H_2O)_3]^0$



$[Am(dipic)_2(H_2O)_2]^0$