

UC Berkeley

UC Berkeley Electronic Theses and Dissertations

Title

Exploring the Factors Controlling the Solution Stability of Metal-oxo Clusters with Computations

Permalink

<https://escholarship.org/uc/item/17b1s0v6>

Author

Stern, Rebecca

Publication Date

2021

Peer reviewed|Thesis/dissertation

Exploring the Factors Controlling the Solution Stability of Metal-oxo Clusters with
Computations

by

Rebecca Stern

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Engineering - Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Kristin Persson, Chair

Professor Jeffrey Neaton

Professor Mark Asta

Summer 2021

Exploring the Factors Controlling the Solution Stability of Metal-oxo Clusters with
Computations

Copyright 2021
by
Rebecca Stern

Abstract

Exploring the Factors Controlling the Solution Stability of Metal-oxo Clusters with Computations

by

Rebecca Stern

Doctor of Philosophy in Engineering - Materials Science and Engineering

University of California, Berkeley

Professor Kristin Persson, Chair

Metal-oxo clusters are discrete molecular metal-oxides that are important for applications in catalysis, medicine, precursors for thin film deposition, flash memory devices, switchable transparent films, and high-resolution nanopatterning, to name a few. There are many factors that control the solution stability of metal-oxo clusters; the internal chemistry of the coordination complex as well as the solution conditions can influence the thermodynamic stability of the species. Currently, there is a lack of understanding surrounding how to best manipulate these factors in order to achieve a specific isomer, geometry, or size of metal-oxo cluster in solution. Therefore, the work presented in this dissertation contains an evaluation of the influence of heteroatoms, caps, ligands, pH, electrochemical potential, metal ion concentration, and counterions on stabilizing metal-oxo clusters. Quantum chemical computations were employed to model tin-based and zirconium-based clusters with varying factors, to determine their hydrolysis Gibbs free energies and electronic structures.

Sn-oxo clusters, specifically of Keggin geometry, have been shown to be an excellent photore-sist candidate for next-generation extreme ultraviolet lithography manufacturing of advanced integrated circuits. I showed how changing the Sn-Keggin heteroatom, caps, and ligands im-pact the stability ordering of the five known Keggin isomers. This Sn-Keggin ion represents the only Keggin ion family thus far, that favors the lower-symmetry isomers. The compu-tational results provide a means to isolate a single isomer to promote a pure and stable material for advanced lithography.

Zr-oxo clusters, specifically the Zr hexamer, has been shown to be a good node for a metal-organic framework (MOF) which is a 3D porous network that can act as a nanoscale carrying device. However the "green" manufacturing of Zr-based MOFs requires that the Zr hexamer stabilize in an aqueous solution without organic ligation, which has yet to be successfully ac-complished. I examined how the pH, electrochemical potential, metal ion concentration, and counterions all influence the aqueous solution stability of Zr(IV) ions clusters and solids. This

study successfully elucidates the magnitude of and reason for the thermodynamic instability of the hypothetical Zr hexamer compared to the ubiquitous Zr tetramer.

The knowledge gained from these computational studies on Sn-oxo and Zr-oxo clusters can expedite experimental syntheses through implementation of the strategic tuning of chemistry and solution conditions.

To Alex

Contents

Contents	ii
List of Figures	iv
List of Tables	vi
1 Introduction	1
2 Tin-Keggin Clusters for Advanced Photoresist Technology	5
2.1 Background	5
2.2 Introduction	8
2.3 Description of Structures	9
2.4 Approach	10
2.5 Results and Discussion	11
2.6 Conclusions	15
2.7 Methodology	16
2.8 Computational Details	17
2.9 Acknowledgements	17
3 Aqueous Hexameric Zirconium Cluster for “Green” Manufacturing of Metal-Organic Frameworks	18
3.1 Background	18
3.2 Introduction	20
3.3 Results and Discussion	22
3.4 Conclusions	32
3.5 Supporting Information	34
3.6 Acknowledgements	42
4 Summary and Outlook	43
Bibliography	46
5 Appendix	58

5.1	Ground state geometries for Sn-Keggin clusters from Chapter 3.	58
5.2	Ground state geometries for Zr clusters from Chapter 4.	109

List of Figures

2.1	Simplified ultraviolet lithography steps for integrated circuit manufacturing. . .	6
2.2	Main difference between ultraviolet and extreme ultraviolet lithography is in step 4 from Figure 2.1, where the wavelength has been decreased from 193nm to 13.5nm to accommodate the smaller mask feature sizes for advanced integrated circuit manufacturing.	7
2.3	Trimer rotation to obtain five Keggin isomers α , β , γ , δ , and ϵ	8
2.4	(a) Uncapped β -NaSn ₁₂ , (b) Single-capped β -NaSn ₁₃ , (c) Uncapped γ -NaSn ₁₂ , (d) Single-capped γ -NaSn ₁₃ , (e) Double-capped γ -NaSn ₁₄ . Purple octahedra: tin. Yellow tetrahedra: sodium. Brown: carbon. White: hydrogen. Green: boron. . .	11
2.5	Four synthesis strategies (I, II, III, IV) and their experimentally observed results (bold-circled isomers). Hydrolysis Gibbs free energies of all relevant isomers are included. Blue= β -NaSn ₁₂ , Yellow= γ -NaSn ₁₂ , Red= β -NaSn ₁₃ , Green= γ -NaSn ₁₃ , Gray= γ -NaSn ₁₄	13
2.6	Uncapped β -CaSn ₁₂ . Purple octahedra: tin. Blue tetrahedra: calcium. Brown: carbon. White: hydrogen.	15
3.1	Simplified graphic of portion of UiO-66 metal-organic framework. Green cubes are the nodes, Zr ₆ O ₄ (OH) ₄ (COO) ₁₂ . Orange lines are linkers, 1,4-benzodicarboxylic acid i.e. BDC. Yellow circle is the tetrahedral cavity. Blue circle is the octahedral cavity.	19
3.2	(a) Ground state geometry of the zirconium(IV) tetranuclear species [Zr ₄ (OH) ₈ (H ₂ O) ₁₆] ⁸⁺ . (b) Ground state geometry of the zirconium(IV) hexanuclear species [Zr ₆ O ₄ (OH) ₄ (H ₂ O) ₂₄] ¹²⁺ . Green polyhedra: zirconium. Red: oxygen. White: hydrogen.	23
3.3	Zirconium Pourbaix diagram at varying [Zr(IV)] concentrations. (a) [Zr(IV)] = 10 ⁻⁴ M, ZrO ²⁺ is between -1.0 ≤ pH ≤ 2.5. (b) [Zr(IV)] = 10 ⁻³ M, {Zr ₂ ⁶⁺ } is at pH = -1.2, {Zr ₄ ⁸⁺ } is between -1.1 ≤ pH ≤ 2.2. (c) [Zr(IV)] = 10 ⁻² M, {Zr ₂ ⁶⁺ } is between -1.7 ≤ pH ≤ -1.5, {Zr ₄ ⁸⁺ } is between -1.4 ≤ pH ≤ 2.1. (d) [Zr(IV)] = 10 ⁻¹ M, {Zr ₂ ⁶⁺ } is between -2.0 ≤ pH ≤ -1.7, {Zr ₄ ⁸⁺ } is between -1.6 ≤ pH ≤ 1.9. Note: Dimer, {Zr ₂ ⁶⁺ } = [Zr ₂ (OH) ₂ (H ₂ O) ₁₂] ⁶⁺ . Tetramer, {Zr ₄ ⁸⁺ } = [Zr ₄ (OH) ₈ (H ₂ O) ₁₆] ⁸⁺ . Hexamer, {Zr ₆ ¹²⁺ } = [Zr ₆ O ₄ (OH) ₄ (H ₂ O) ₂₄] ¹²⁺	24

3.4	Zirconium Pourbaix diagram heat maps at two different concentrations. (a) $[\text{Zr(IV)}] = 10^{-7}$ M showing that the tetramer is 10 meV/atom less stable than ZrO^{2+} . (b) $[\text{Zr(IV)}] = 10^{-3}$ M showing that the tetramer is 1 meV/atom more stable than ZrO^{2+} . Note: Dimer, $\{\text{Zr}_2^{6+}\} = [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. Tetramer, $\{\text{Zr}_4^{8+}\} = [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$	26
3.5	Zirconium Pourbaix diagram heat maps at two different concentrations, with the dimer and the tetramer removed from the cluster dataset, to simulate a scenario where these two species are kinetically inhibited to nucleate. (a) $[\text{Zr(IV)}] = 10^{-3}$ M showing that the hexamer is 9 meV/atom less stable than ZrO^{2+} . (b) $[\text{Zr(IV)}] = 1$ M showing that the hexamer is 1 meV/atom more stable than ZrO^{2+} . Note: Hexamer, $\{\text{Zr}_6^{12+}\} = [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$	27
3.6	Zirconium Pourbaix diagram heat map at $[\text{Zr(IV)}] = 1$ M showing that the hexamer is 9 meV/atom less stable the tetramer. Note: Dimer, $\{\text{Zr}_2^{6+}\} = [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. Tetramer, $\{\text{Zr}_4^{8+}\} = [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. Hexamer, $\{\text{Zr}_6^{12+}\} = [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$	28
3.7	Frontier molecular orbitals for Zr(IV) dimer. (a) Dimer structure. (b) HOMO. (c) LUMO.	29
3.8	Frontier molecular orbitals of the Zr(IV) tetramer. (a) Tetramer structure. (b) HOMO. (c) LUMO.	30
3.9	Frontier molecular orbitals of the Zr(IV) hexamer. (a) Hexamer structure. (b) HOMO. (c) LUMO.	30
3.10	Electrostatic potential map of Zr(IV) tetramer, isosurface level = 0.001. (a) Front view. (b) Side bridging oxygen view. (c) Side top of zirconium view. . . .	31
3.11	Electrostatic potential map of Zr(IV) hexamer, isosurface level = 0.001.	31
3.12	Ground state geometry of the zirconium(IV) mononuclear species $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.	34
3.13	Ground state geometry of the zirconium(IV) dinuclear species $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. (a) front view (b) side view. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.	34
3.14	Frontier molecular orbitals for Zr(IV) monomer. (a) Monomer structure. (b) HOMO. (c) LUMO.	40
3.15	Electrostatic potential map of Zr(IV) monomer, isosurface level = 0.001. (a) Front view. (b) Back view.	41
3.16	Electrostatic potential map of Zr(IV) dimer, isosurface level = 0.001. (a) Bridging view. (b) Side view.	42
4.1	Ground state geometry of the zirconium(IV) hexanuclear peroxide species $[\text{Zr}_6(\text{O}_2)_6(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.	45

List of Tables

2.1	Hydrolysis Gibbs free energies, energy differences, and HOMO-LUMO gaps of uncapped and capped Na-Sn clusters.	12
2.2	Hydrolysis Gibbs free energies, energy differences, and HOMO-LUMO gaps of uncapped and capped Ca-Sn clusters.	15
3.1	Equilibrium Reactions.	25
3.2	Equilibrium Reaction Energies and Constants.	26
3.3	HOMO and LUMO energies and gaps for selected zirconium clusters in eV. . .	29
3.4	Atomic distances and angles for the mononuclear zirconium cluster $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$. . .	34
3.5	Atomic distances and angles for the dinuclear zirconium cluster $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. ^a Zr ions on diagonal. ^b Water O atoms lying in the plane defined by the Zr ions. ^c Water O atoms lying out of the plane defined by the Zr ions.	35
3.6	Atomic distances and angles for the tetranuclear zirconium cluster $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. ^a Zr ions on diagonal. ^b Water O atoms lying in the plane defined by the Zr ions. ^c Water O atoms lying out of the plane defined by the Zr ions.	35
3.7	Atomic distances and angles for the hexanuclear zirconium cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$. ^a Zr ions on diagonal. ^b Short diagonal of distorted square prismatic face. ^c Long diagonal of distorted square prismatic face.	36
3.8	Referencing Values.	38
3.9	Zr(IV) Cluster Hydrolysis Gibbs Free Energies and Pourbaix Formalism Energies. . .	39
3.10	Energy differences between aqueous zirconium species at various $[\text{Zr(IV)}]$ concentrations, with corresponding Pourbaix diagram heat maps.	40

Acknowledgments

Thank you Professor Kristin Persson, for being an exceptional advisor and mentor. I always admired your ability to re-energize my curiosity and focus for a project. Your talent for managing our research family in a kind and proactive way, is what has drawn so many fantastic scientists to our group. I am thankful to have seen our revered community of positive, intelligent, and caring people grow into a large network. Thank you for your financial, academic, and emotional support throughout my time at Berkeley.

Thank you to my dissertation and qualifying committee members, Professor Mark Asta, Professor Jeffrey Neaton, Professor Phil Messersmith, and Dr. Patrick Naulleau, for your helpful guidance and valuable conversations. Thank you to the entire Materials Science and Engineering faculty and staff at UC Berkeley for an exceptional education. Special thanks to Ariana Castro and Catalina Estrada for answering all my questions. Thank you to Professor May Nyman and Dr. Danielle Hutchison for being excellent collaborators!

I would like to thank my financial supporters, without whom I could not have conducted my research; mainly the Center for Sustainable Materials Chemistry (CSMC), the Energy & Biosciences Institute through the EBI-Shell program, the Materials Science and Engineering Department.

Thank you to the three computing centers I used to do my research: (1) The National Energy Research Scientific Computing Center (NERSC) (specifically Cori), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231. (2) The Savio computational cluster resource provided by the Berkeley Research Computing (BRC) program at the University of California, Berkeley (supported by the UC Berkeley Chancellor, Vice Chancellor for Research, and Chief Information Officer). (3) The Molecular Graphics and Computation Facility (MGCF) at the University of California, Berkeley, NIH S10OD023532. Special thanks for Kathy Durkin for all your help with Gaussian!

In the Persson Group, I would first like to thank Alice Muller for being a friend and helpful resource in and out of the office. Thank you to postdoc alumni Dr. Xiaohui Qu, Dr. Joey Montoya, Dr. Arunima Singh, and Dr. Trevor Seguin for teaching me the foundational tools I needed to execute my research. Thank you Dr. Donny Winston for giving me the opportunity to present at the Radtech conference! Thank you to all current postdocs and staff in the Persson Group for helping to answer my questions and teaching me how to approach complex problems. Special thanks to Dr. Ryan Kingsbury, Dr. Shyam Dwaraknath, Dr. Sam Blau, and Dr. Matt Horton for this!

Thank you to my fellow fifth-years, Rachel Woods-Robinson, Julian Self, Eric Sivonxay, Tingzheng Hou, for commiserating and supporting each other. Thank you to my desk mates Dr. Brandon Wood, Ann Rutt, Martin Siron, and to my subgroup mates John Dagdelen, David Mrdjenovich, Handong Ling, Matt McDermott, Caitlin McCandler, Alex Epstein, Evan Spotte-Smith, and to my friends Jordan Burns and Hetal Patel for being an enormous reason I enjoyed coming to work every day.

I really appreciated the friendships of Luke Long, Jonathan Ma, and Isvar Cordova from the Naulleau group. You all helped me feel comfortable transitioning into the world of semiconductor manufacturing!

Thank you to Dr. Aaron Hall, Dr. Whitney Loo, Gumi Sethi, Luis Barroso-Luque, James Chavez Dr. Danny Broberg, and Dr. Tom Angsten for helping with my prep for prelims and quals and for being my friends!

Thank you so much Dr. Yasemin Kutes for being my friend at Pfizer and for taking the time to chat with me about my future job!

Thank you to my Bay Area yoga community whom I miss dearly. You all created my home away from home, and taught me how to use my voice and presence to command a room.

Thank you to my amazing materials science buddies for being my lifelines during this whole experience: Dr. Mallika Bariya, Dr. Rachel Woods-Robinson, Julia Yang, Zhen Lin, and Dr. Clarissa Bhargava (and Miss Faraday).

Thank you to my amazing Rose roommates, Dr. Elizabeth Moore, Dr. Sarah Frank, and Donnie Sproal who made going home feel so safe and fun. And thank you Sarah and Elizabeth for being my favorite grad school role models.

Much thanks to my Francisco roommates for bringing me so much laughter and love. Special love for Ozge Ugurlu, Kristina Chou, Aila Rothweiler, Irem Inal, Sally Karstens, and Sebastian Hummel.

Thank you Sheila and Dick Powell for letting me live with you while I worked at Pfizer and for including me in your community! It was truly one of the best summers.

Thank you to my close friends Kristina Hacker, Kelly Pannikodu, Grace Kim, Corrin Gildea, Daniela Mayer, Oliver Torgersen, and Sarah Collins for your unwavering friendship.

Thank you to my new sister Kat for loving our family.

Thank you very much Dr. Choi, Mrs. Choi, Christopher, and Cosette for your kindness and support.

Thank you grandpa Alain for your kindness. Danke Opa, dass du mir deinen Ingenieurgeist weitergegeben hast. Merci Coco de m'avoir transmis ta passion et ta volonté.

Alex, I am beyond grateful to have you in my life. I have come this far because of your love and support.

Chris and Eric, you are the best brothers I could have asked for. Chris, I admire your calm demeanor. Eric, I admire your sense of adventure.

Mom and Dad, you are the absolute best parents. Thank you both for your unconditional love and support. Dad, thanks for calling me Doctor long before I ever was one. Mom, thanks for teaching me how to have a positive outlook on life.

Chapter 1

Introduction

Metal-oxo clusters are commonly defined as polynuclear species made of metal cations, bonded to O^{2-} and other ligands.[1] These natural and synthetic solution-stable nanoscale clusters are necessary for a myriad of applications such as mineral formation[2–5] and catalysis.[6, 7] Due to the variability of metal-oxo cluster size, geometry, and chemistry, these unique structures have also been strategically synthesized for applications in medicine,[8, 9] thin film manufacturing,[10, 11] technology,[12, 13] and high-resolution nanopatterning,[14, 15] to name a few.

Metal-oxo clusters that have been observed or hypothesized, can be classified into three main categories: (1) Polyoxometalates, (2) non-polyoxometalates *without* H_2O terminal ligands, and (3) non-polyoxometalates *with* H_2O terminal ligands. The first category is polyoxometalates (POMs), which includes d^0 transition metal cations from groups 5 and 6 (Mo^{VI} , W^{VI} , V^V , Nb^V , Ta^V).[16, 17] POMs are well-studied structures that are unique in that they have doubly-bonded oxo terminal ligands, allowing them to be stable in water with ease.[1] The second classification is non-POMs *without* H_2O terminal ligands, exhibiting other stabilizing terminal ligands, often organic in nature. This second class of metal-oxo clusters can be stable in either water or organic solvents, depending on the choice of stabilizing terminal ligands and other stabilizing factors. Examples include open-shell transition metals and post transition metals (Fe^{III} , Cu^{II} , Sn^{IV} , Sb^{III}).[2–4, 18–23] Finally, the third type of metal-oxo cluster is non-POMs *with* H_2O terminal ligands. This includes group 4, group 13, and one open-shell species (Zr^{IV} , Hf^{IV} , Ti^{IV} , Al^{III} , Ga^{III} , Cr^{III}).[24–31] These clusters are stable in water due to their water terminal ligands. These clusters differ from regular POMs in that the water terminal ligands can be removed and replaced with other functional ligands, while maintaining their integral structure. The doubly-bonded oxo terminal ligands that POMs are famous for, do not allow the addition of other functional ligands.

It is known that both internal chemistry and environmental solution conditions can influence the stability of metal-oxo clusters in solution. Factors include metal cation combinations, ligands, pH, electrochemical potential (Eh), concentration of metal ions, and counterions.[32–36] The complexity of all these tunable internal and external factors make progress on stabilizing specific isomers or geometries of metal-oxo clusters often reliant on

trail-and-error. Therefore, quantum chemical computations are a valuable resource to this field of research. Tools like Density Functional Theory (DFT) can be used to model these clusters with varying factors, to determine their governing thermodynamic energy and electronic structure. The knowledge gained from the computations can expedite experimental syntheses through implementation of the strategic tuning of chemistry and solution conditions.

For example, the Keggin geometry observed for many metal-oxo clusters, discussed in detail in Ch. 2, has the formula $[\text{XM}_{12}\text{O}_{40}]^{n-}$ and common POM combinations are when $\text{M} = \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}$ and $\text{X} = \text{P}^{\text{V}}, \text{Si}^{\text{IV}}, \text{Ge}^{\text{IV}}, \text{B}^{\text{III}}$. [1, 19] It has been determined computationally that changing the heteroatom “X” influences which Keggin isomer (α , β , γ , δ , or ϵ) is most stable. [32] Many computational studies have explored POMs extensively. [32–34, 37–55] However, the trends for POMs do not appear to universally describe non-POMs.

For non-POMs *without* H_2O terminal ligands (category 2), additional metal cations can also join the Keggin ion as “capping” agents, further influencing the stability. In this case, the influence of internal chemistry like heteroatoms, caps, and supporting ligands, is apparent but varied across the chemical space, unlike POMs which follow more general trends between metal cations. [32, 48] In some cases, the supporting ligands can be beneficial to cluster’s application, in other cases, it is desirable to limit the ligands to promote the reactivity and functionality of the metal-oxo cluster. For example, understanding the formation of ferrihydrite, a common form of Fe^{3+} in soils and also found in the ferritin protein, (which is in almost all living organisms), is vital for soil geochemistry and intra-cellular iron storage. [2] It is believed that the δ -Fe Keggin ion is a building block in the aqueous formation of ferrihydrite. However, the δ -Fe Keggin ion appears to be an extremely transient species, and only the α -Fe Keggin ion has been successfully stabilized in water with the aid of Bi^{3+} caps and CF_3COO ligands. [3, 4] However, recent computational analyses reveal that the aqueous δ -Fe Keggin cluster is more thermodynamically stable than the α -Fe Keggin cluster. [5] This could imply that the cap and ligand combination of previous experimental studies are promoting the least stable isomer, thus further research could determine improved cap and ligand combinations that could promote the desired isomer, i.e. the δ -Fe Keggin cluster.

For non-POMs *with* H_2O terminal ligands (category 3), environmental conditions such as pH, electrochemical potential (Eh), concentration of metal ion, and counterions are the greatest influencers of the size and geometry of the stable metal-oxo cluster in water. However, the optimal conditions between group 13 and group 4 also appear to be varied. In a different example, additions of supporting ligands hindered the application of a potentially Cr-based Keggin cluster to be used as a water stable node for metal-organic frameworks. [17] Therefore, tuning factors such as caps, counterions, and other solution conditions were exploited. As a result, a mixed Al/Cr-Keggin ion was discovered using a Zn heteroatom, one Zn cap, and only water terminal ligands. A following computational study determined the relative energies of the pure Al-Keggin ion and the pure Cr-Keggin ion, using the same zinc heteroatom and capping combination. [17, 31] The study found that the chromium-based system was energetically more stable than the aluminum version. This led to the success-

ful synthesis of the first open-shell Cr-Keggin cluster without organic ligation.[31] Finally, from all these examples we appreciate the support of computations in understanding and stabilizing non-POM categories 2 and 3.

Chapter 2 explores Sn-Keggin clusters: In POM and non-POM chemistries, it is observed that most systems prefer the more symmetric Keggin isomers: α and ϵ . However, recent research on a Sn-Keggin ion with butyl terminal ligands (category 2), reveals that the species exists as a mixture of β and γ , the isomers with lower symmetry.[20] This is interesting because it means that Sn does not follow traditional trends, which provides an opportunity for exploration. Tin-oxo clusters recently have been proposed as a novel photoresist material for next-generation lithography manufacturing of integrated circuits.[56] For this application, the butyl terminal ligands supporting the solution stability of the Sn-Keggin ion, also act as the necessary active component of the photoresist makeup. However, difficulties in isolating a pure product (e.g. a single isomer over a mixture) make this an ideal challenge for using computational tools to explore the effects of heteroatom, caps, and ligands on promoting a single Sn-Keggin isomer.

Chapter 3 explores Zr-oxo clusters: Zirconium and hafnium metal-oxo clusters are unique in their preference for being an 8-coordinate antiprismatic structure, as opposed to the more commonly observed 6-coordinate octahedral geometry of most metal-oxo building units.[26] These group 4 elements, existing mainly in a 4+ oxidation state, have water terminal ligands that can be replaced with very strong coordination bonds to carboxylates. These auspicious Zr(IV) and Hf(IV) metal-oxo clusters are therefore ideal candidates for nodes in metal-organic frameworks (MOFs). MOFs are 3D porous nanoscale networks made of metal-ion clusters and small organic molecule “linkers”. MOFs can act as nanoscale carrying devices, allowing them to carry drugs for therapeutics or store gases for filtration.[26] Since Zr(IV) and Hf(IV) have similar electronic structure, they have comparable properties. However, hafnium is still 30 times less abundant on earth, and therefore zirconium-oxo clusters will be investigated in this study.[57] Unfortunately, current synthesis of a hexameric Zr-oxo cluster, for MOF applications, uses stabilizing organic ligands to promote stability in a solution containing harmful chemicals.[26] The development of a “green” manufacturing approach for a hexameric Zr-based node is limited by the inability to determine the reasons for the instability of the aqueous hexameric Zr-oxo cluster with only water terminal ligands (category 3). Zirconium in aqueous solution has been observed to form monomers, dimer, tetramers, octamers, and even a 25-unit structure, yet the Zr hexamer has never been stabilized in water. This provides an opportunity to explore this chemical space with computational tools to understand the influence of pH, electrochemical potential (Eh), concentration of metal ions, and counterions in an aqueous solution.

Approach: In both Chapters 2 and 3, density functional theory was used as a computational tool to calculate the relative energies of these species, as factors were systematically altered. Experimental observations were used as a benchmark, and the computational conclusions are used as valuable knowledge to guide any future syntheses. By analyzing the free energy differences between competing cluster and other present species, we open up the possibility to rationally influence cluster stability by tuning the internal chemistry and the

solution environment. For the species stable in water, the stability regions were visualized using Pourbaix analysis in terms of pH and potential with respect to the metal ions and solids.

Chapter 4 presents concluding remarks.

Chapter 2

Tin-Keggin Clusters for Advanced Photoresist Technology

2.1 Background

Extreme Ultraviolet Lithography

Over the years, the feature sizes of microelectronics have gotten smaller and more intricate following advances in materials science and manufacturing technologies. This progress is deemed Moore's Law, which observes that the number of transistors on a dense integrated circuit doubles about every two years.[58] In order to advance into the future of the sub-10nm regime, it is imperative to develop next generation manufacturing techniques. Traditional Edisonian approach for materials discovery, where you synthesize and test a material's properties and performance one material at a time, is time-consuming and expensive. Rather, an in-silico or computational and data driven approach can dramatically accelerate materials discovery and development.[59] Furthermore, collaborations between experimentalists and computational theorists are the key to success.

One of the manufacturing techniques to make the integrated circuit that goes into your computer or other electronic devices is ultraviolet (UV) lithography. Generally, the steps of UV lithography are depicted in Figure 2.1. These steps are a simplified version of the very complex manufacturing process: (1) A thin film is deposited onto a substrate. (2) A photoresist is deposited onto the thin film. (3) A mask is held in the desired pattern above the photoresist. (4) The system is exposed to UV light, and the mask blocks the light in the desired pattern. The UV light hits the photoresist in certain places, which causes a chemical change in the resist to occur. (5) The system is developed which either removes the chemically altered portions of the photoresist (positive tone) or removes the unaltered portions of the resist (negative tone). (6) An etching step removes the exposed thin film, while the photoresist resists the etch, hence the name. (7) Finally, a stripping step removes the original photoresist, leaving behind an intricate pattern which makes up your integrated circuit.[60]

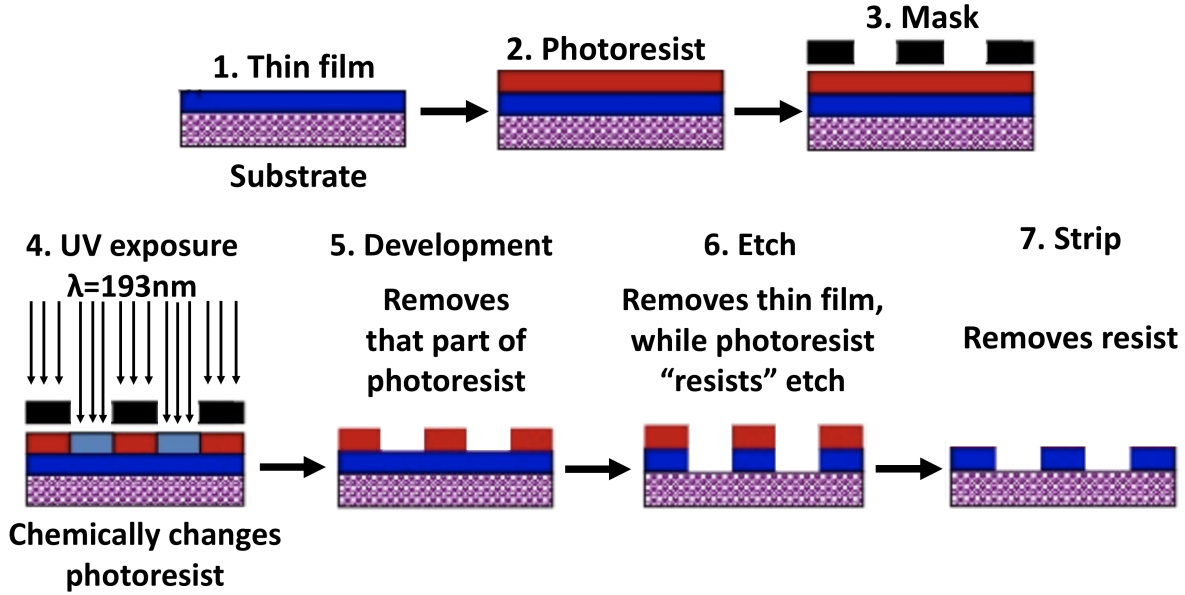


Figure 2.1: Simplified ultraviolet lithography steps for integrated circuit manufacturing.

As chips circuit lines get smaller and smaller, possibilities of having so-called sub-10nm nodes emerge. There have been many efforts to achieve these smaller pattern sizes and the resolution defines how closely features can be packed together. The Rayleigh criterion equation defines the critical dimension, or the minimum feature size, as $k_1 * \lambda / NA$, where λ is the wavelength of light, NA is the numerical aperture of the optics, and the k_1 factor is a coefficient encompassing manufacturing process-related factors. One method to improve the resolution is to increase the numerical aperture with immersion lithography, or printing through water which allows an increased NA lens to be designed and built.[61] Decreasing the k_1 factor also works with chemically amplified resists (CARs), which are polymer based resists with acid-sensitive groups to improve their photosensitivity.[62] Another way to decrease k_1 is by improving the mask, which is needed as the final pattern does not really resemble the mask pattern.[63] Indeed, during illumination the photosensitive resist is activated which sparks a set of reaction-diffusion type of equations which are very non-linear, hence irregular shapes are produced in the pattern. In larger devices, this shape irregularity does not significantly hinder impact, however as devices shrink, precision matters most. Computational lithography is a field of research that uses mathematical algorithms and optimization techniques to determine the exact mask pattern needed to obtain the desired film pattern.[64] Despite progress with these approaches, efforts need to be combined with strategies towards dramatically decreasing the wavelength of light, in order to truly make advances in semiconductor manufacturing.

Extreme ultraviolet (EUV) lithography uses a high energy beam ($\lambda=13.5\text{nm}$), and is the newest technique to sustain Moore's law and create smaller integrated circuit feature sizes

(Figure 2.2).[65] The necessary improvements for EUV lithography to be successful include increasing source power, reducing defects from the mask, and changing the photoresist. A photoresist for EUV lithography must have a high EUV atomic absorption cross section, be made up of small building blocks, and be resistant during the lithographic etching step. The photoresists used for UV lithography are made of acrylic polymers, which are not sufficient for EUV lithography. This is because the polymers have a low EUV atomic absorption cross section, the bulky carbon chains cannot be chemically altered to offer such intricate patterns, and these polymer photoresists are often not completely resistant to the etching step.

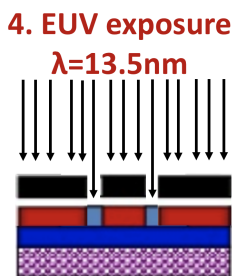


Figure 2.2: Main difference between ultraviolet and extreme ultraviolet lithography is in step 4 from Figure 2.1, where the wavelength has been decreased from 193nm to 13.5nm to accommodate the smaller mask feature sizes for advanced integrated circuit manufacturing.

A material made of an element with a high EUV atomic absorption cross section is needed. Metal-oxo clusters have been proposed as one photoresist solution since metal-containing resists would have a higher EUV absorption, their building blocks are five times smaller compared to the polymers, and they are more durable during the etching step.[66–68] Specifically the most promising novel photoresist material is a sodium-centered tin-Keggin cluster.

The Keggin Geometry

The Keggin cluster was first structurally characterized in 1934 by J.F. Keggin.[69] It contains a heteroatom metal center in a 4-coordinate environment. Surrounding this are four trimer units. Each trimer unit consists of three metals in a 6-coordinate environment. The three octahedra are edge-sharing within the trimer unit. The α -isomer is defined as having its four trimer units connected by corner-sharing between trimers, resulting in T_d symmetry, as shown in Figure 2.3. If one trimer unit is rotated by 60 degrees, the β -isomer is obtained which still exhibits only corner-sharing trimers but with a reduced symmetry of C_{3v} . Continuing this process of successive trimer rotations of 60 degrees, the γ -isomer of C_{2v} symmetry is obtained. Finally, a rotation of a third trimer yields the δ -isomer and a fourth trimer rotation yields the ϵ -isomer, possessing C_{3v} and T_d symmetries, respectively.

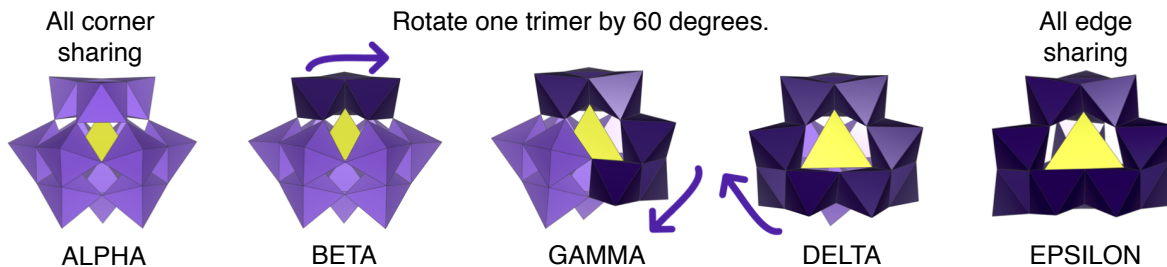


Figure 2.3: Trimer rotation to obtain five Keggin isomers α , β , γ , δ , and ϵ .

In some instances, “caps” can bind to the Keggin structure. This is when additional coordinated-metal ions join the Keggin structure, in either the windows between the trimer units, or directly on top of a trimer unit. In this study, we investigate how changing the heteroatom (Na, Ca) and adding or removing caps and ligands, influence the relative stability of Sn-Keggin clusters, with the intention of isolating a single isomer for use as a pure phase photoresist materials for extreme ultraviolet lithography.

2.2 Introduction

With integrated circuit manufacturers aiming to produce sub-10 nm feature sizes, extreme ultraviolet lithography (EUVL) is perceived as the next developing technology, at a wavelength of only 13.5 nm.[70] The challenges with using polymer-based photoresists for EUVL can be eliminated by using metal-oxo cluster photoresists. Metal-oxo clusters are smaller than the bulky carbon chains in the polymer-based resists, thus preventing pattern collapse. Also, metal-oxo clusters are more durable during the lithographic etching step. Metal-oxo systems previously investigated as potential photoresist materials include hafnium, antimony, and tin clusters.[20, 56, 66, 71, 72] These systems have a high EUV atomic absorption cross-section, needed for proper resist functionality.[73] Each system had their limitations however. Hafnium-based clusters demonstrated 8nm resolution but resulted in background condensation.[66] Antimony-oxo clusters had EUV sensitivity but pattern collapse limited high resolution.[71] The tin-oxo “football” cluster prevented background condensation, but the synthesis was difficult.[56] A capped sodium-centered organotin-oxo Keggin cluster produced high aspect ratio and dense line patterns with helium ion beam lithography, but synthesis of the structure was difficult leading to poor reproducibility and low yields.[20, 72] It is thought that the cleavage of the Sn-C bond of the terminal butyl ligands in this material is the cause of the change in the solubility of this photoresist.[74] In order to evaluate this system in more depth, a simplified synthesis strategy was required to further investigate the possibilities of a sodium center organotin-oxo Keggin cluster as a photoresist for EUV lithography.

Hutchison and coworkers recently discovered a simple one-step synthesis for the Na-Sn

Keggin system that proceeds at room temperature and does not require any filtration or recrystallization.[75] This synthesis strategy successfully made an uncapped Keggin cluster denoted β -NaSn₁₂ i.e. [(BuSn)₁₂(NaO₄)(OCH₃)₁₂(O)₄(OH)₈]¹⁺. However, this synthesis led to a mixture of uncapped β -NaSn₁₂ and uncapped γ -NaSn₁₂ isomers. For fundamental studies on the lithographic mechanisms occurring during exposure to be successful, a pure and stable isomer is desired. Therefore, computational tools were used to investigate this dilemma and unknown cause of mixtures of isomers forming. Since the Keggin geometry has 5 possible isomers, all 5 uncapped NaSn₁₂ isomers α , β , γ , δ , and ϵ , were computationally modeled in this study. The terminal butyl ligands were replaced with methyl ligands to reduce the computational complexity. To evaluate the influence of capping on the prevention of isomerization between uncapped β -NaSn₁₂ and uncapped γ -NaSn₁₂, the experimentally observed capped β -NaSn₁₃ and γ -NaSn₁₃, as well as the most recently synthesized double capped γ -NaSn₁₄ were computationally modeled in this study as well.[21, 75] The advantages of using computational modeling tools is to be able to evaluate the thermodynamic stability of experimental as well as theoretical isomers of a given system. The calculated thermodynamic landscape of the isomers enables comparison of the isomer stability and hence interpretation of experimental results. Ideally, computational results will guide synthesis design, being able to determine the influential factors that drive stability between isomers and predict new structures.

2.3 Description of Structures

Situation I: Mixed β/γ -NaSn₁₂

The one-step synthesis strategy developed by Hutchison et al. occurred at room temperature and did not require any filtration or recrystallization.[75] However, ¹¹⁹Sn-NMR and single-crystal X-ray diffraction showed a mixture of β -NaSn₁₂ and γ -NaSn₁₂. To investigate the isomerization, all five uncapped Na-Sn Keggin isomers (α , β , γ , δ , ϵ) were computationally modeled. They all were given the same formula: [(MeSn)₁₂(NaO₄)(OCH₃)₁₂(O)₄(OH)₈]¹⁺. The β -NaSn₁₂ and γ -NaSn₁₂ clusters are shown in Figure 2.4a and 2.4c, respectively. To decrease the computational cost and complexity of these models, the butyl Sn-terminal ligands were replaced with methyl ligands, a common practice.[23] In this Na-Sn Keggin system, the central heteroatom is sodium. Each trimer unit of the Keggin is comprised of three MeSnO₅ octahedra with a methyl terminal ligand on each tin atom. The three bridging oxygens within each trimer unit (12 total O²⁻) are methoxy ligands. The bridging oxygens between the four trimer units (12 total O²⁻) are oxo or hydroxyl ligands. The overall charge of the structures is determined by the total number of hydroxyl ligands. The location of the hydroxyl ligands impacts the hydrolysis Gibbs free energy and care was taken to obtain the lowest energy conformation. Although the hydrogen location cannot be inferred from the X-ray diffraction data, mass spectrometry identified the overall charge of the structures and bond-valence sum helped guide the hydroxyl ligand placement.

Situation II: Single-capped β -NaSn₁₃

Saha et al. in 2017 produced a single-capped β -NaSn₁₃.^[20] However, authors found impurities of uncapped NaSn₁₂ isomers and Sn₁₂ (i.e. the ‘football’ cluster [(RSn)₁₂O₁₄(OH)₆]²⁺, R=alkyl) co-crystallized with β -NaSn₁₃ in unknown quantities, as determined with electrospray ionization mass spectroscopy (ESI-MS) and ¹¹⁹Sn-NMR. The computationally modeled β -NaSn₁₃ was assigned a formula of [(MeSn)₁₂(NaO₄)(OCH₃)₁₂(O)₈(OH)₄(Sn(H₂O)₂)]¹⁺ which is exactly consistent with the experimental crystal structure determined by ESI-MS.^[75] The cap position and bonding for theoretical α -NaSn₁₃ was modeled after β -NaSn₁₃ since these two isomers exhibit similar symmetries and capping “windows” as compared to γ -NaSn₁₃. The cap on β -NaSn₁₃ and α -NaSn₁₃ is a 6-coordinate tin, with four bonds to the cluster in the tetragonal window. The two terminal ligands are waters. The single-capped β -NaSn₁₃ is shown in Figure 2.4b.

Situation III: Single-capped γ -NaSn₁₃

A different synthesis strategy conducted by Hutchison et al. produced single-capped γ -NaSn₁₃.^[75] However, crystals of both γ -NaSn₁₃ and uncapped β -NaSn₁₂ were isolated from the same closed vial.^[75] This computational study modeled the γ -NaSn₁₃ as [(MeSn)₁₂(NaO₄)(OCH₃)₁₂(O)₆(OH)₆(Sn(Me)(OCH₃))] ¹⁺ as shown in Figure 2.4d. The cap is a 5-coordinate tin, with three bonds to the cluster in one of the pentagonal windows adjacent to the edge sharing trimer units. The two terminal ligands are methyl and methoxy.

Situation IV: Double-capped γ -NaSn₁₄

Zhu et al. recently synthesized the double-capped γ -NaSn₁₄ in 2019.^[21] This synthesis strategy successfully prevented isomerization, yielding pure γ -NaSn₁₄. Two 5-coordinate tin caps are found on the structure, one in each pentagonal window on either side of the edge shared between two trimer units. The terminal ligands are a butyl chain (modeled as methyl) and an oxygen atom from a BO₂(OH) ligand. The two borate ligands provide a bridge between the tin cap and they each replace one methoxy ligand within a trimer unit. The authors believe the borate group stabilizes the cap, which in turn stabilizes the Keggin cluster. This structure is shown in Figure 2.4e.

2.4 Approach

The experimentally isolated clusters were computationally modeled. These consisted of the two uncapped isomers (β -NaSn₁₂, γ -NaSn₁₂), the two single-capped isomers (β -NaSn₁₃, γ -NaSn₁₃), and the one double-capped isomer (γ -NaSn₁₄). Additionally, theoretical clusters (which have never been experimentally isolated) of the Na-Sn system were also modeled. These included three uncapped isomers (α -NaSn₁₂, δ -NaSn₁₂, ϵ -NaSn₁₂), and one single-capped isomer (α -NaSn₁₃), bringing the total number of systems investigated to nine.

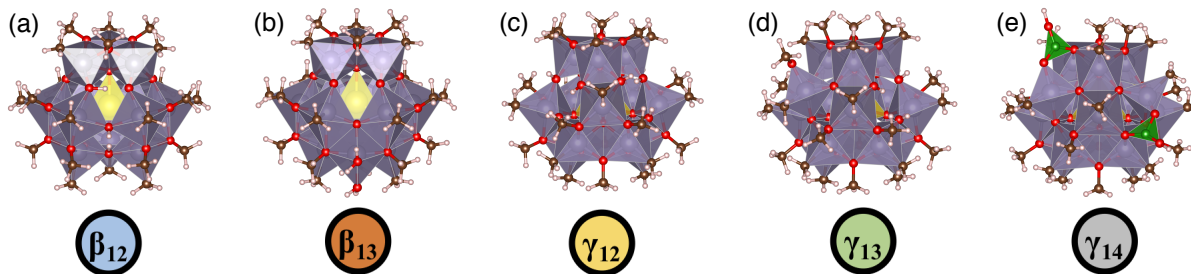


Figure 2.4: (a) Uncapped β -NaSn₁₂, (b) Single-capped β -NaSn₁₃, (c) Uncapped γ -NaSn₁₂, (d) Single-capped γ -NaSn₁₃, (e) Double-capped γ -NaSn₁₄. Purple octahedra: tin. Yellow tetrahedra: sodium. Brown: carbon. White: hydrogen. Green: boron.

We determined the hydrolysis Gibbs free energy (ΔG_{aq}) in solution by using a thermodynamic cycle in which the hydrolysis energy is the sum of the corresponding gas-phase Gibbs free energy (ΔG_{gas}) and the Gibbs free energies of solvation (ΔG_{solv}) as seen in equation 2.1. A thermodynamic cycle is used to reduce errors when calculating the solvation energy and comparing structures of different formula, as described in the Methodology section.[30, 76–78] The gas-phase Gibbs free energy contains a correction term that takes into account the enthalpy, entropy, and temperature of the system when a frequency analysis is conducted. The term “n” is the coefficient of that species. An example of this thermodynamic cycle for β -NaSn₁₂ is shown in Scheme 1 and for β -CaSn₁₂ is shown in Scheme 2. The hydrolysis Gibbs free energy is then determined with equation 2.1.

2.5 Results and Discussion

Influence of Tin capping

The hydrolysis Gibbs free energy in kcal/mol and HOMO-LUMO gap in eV are listed in Table 2.1 for each of the nine Na-centered clusters investigated. The more stable clusters should exhibit a relatively low hydrolysis Gibbs free energy and a relatively large HOMO-LUMO gap. In our case, the stability ordering is evaluated by the hydrolysis Gibbs free energy. The HOMO-LUMO gaps are too close in energy to conclusively determine the isomer stability ordering, but rather used to support the results from the Gibbs free energy.

The uniqueness of the tin-oxo Keggin system is that it prefers the less symmetric isomers, β and γ . To our knowledge, no other Keggin cluster systems have been discovered where the β and γ isomers are the most stable. Traditional polyoxometalates like the W-Keggin and Mo-Keggin clusters prefer the α and β isomers.[32] The Al-Keggin and Sb-Keggin favor the ϵ isomer.[23, 29] And the Cr-Keggin has been recently synthesized as the δ -isomer.[17, 31] A visual guide for the joint results of the four synthesis strategies (bolded values) and the relevant isomer energy differences are shown in Figure 2.5. The hydrolysis Gibbs free energy

Species	Hydrolysis Gibbs Free Energy (kcal/mol)	Energy Differences (kcal/mol)		HOMO-LUMO gap (eV)
ϵ -NaSn ₁₂	386.6	59.2	114.3	5.87
α -NaSn ₁₃	369.7	42.3	97.4	5.17
β -NaSn ₁₃	364.9	37.5	92.6	5.28
γ -NaSn ₁₃	361.2	33.8	88.9	5.80
δ -NaSn ₁₂	347.3	19.9	75.0	6.09
α -NaSn ₁₂	342.7	15.3	70.4	6.20
γ -NaSn ₁₂	337.4	10	65.1	5.91
β -NaSn ₁₂	327.4	0	55.1	6.24
γ -NaSn ₁₄	272.3	-55.1	0	6.04

Table 2.1: Hydrolysis Gibbs free energies, energy differences, and HOMO-LUMO gaps of uncapped and capped Na-Sn clusters.

differences between the uncapped clusters are similar in magnitude to previously reported polyoxometalates.[41, 48] Synthesis strategy I produced a mixture of uncapped β -NaSn₁₂ and γ -NaSn₁₂ clusters, as shown in Figure 2.5. The calculated relative instability of the uncapped α -NaSn₁₂ compared to the uncapped β -NaSn₁₂ and γ -NaSn₁₂ is in accordance with our experimental results, such that it has not been experimentally observed.[75] We hypothesize that the reason γ -NaSn₁₂ is 10 kcal/mol more unstable than β -NaSn₁₂ is due to the electrostatic repulsion from the Sn-Sn edge-sharing distance being 3.26 Å, while the Sn-Sn corner-sharing distance is $\sim$ 3.4-3.5 Å.[75]

Synthesis strategy II performed by Saha et al. in 2017 produced a charge neutral single-capped β -NaSn₁₃. [20] However, authors found impurities of uncapped NaSn₁₂ and Sn₁₂ (i.e. the ‘football’ cluster [(RSn)₁₂O₁₄(OH)₆]²⁺, R=alkyl) co-crystallized with β -NaSn₁₃ in unknown quantities, as determined with ESI-MS and ¹¹⁹Sn-NMR. Results for this situation are shown in Figure 2.5. The computational results performed in this study indicate that single-capped β -NaSn₁₃ is more unstable than uncapped β -NaSn₁₂ by 37.5 kcal/mol and uncapped γ -NaSn₁₂ by 27.5 kcal/mol. One interpretation of these results is that a hydrolysis Gibbs free energy difference of 37.5 kcal/mol between a capped and uncapped system is not sufficient to prevent the respective uncapped system from forming. We also note that it is possible that specific isomers explicitly interact more strongly with the solution, which would not be captured in our mean-field solvation approach.

Synthesis strategy III produced single-capped γ -NaSn₁₃ with the presence of uncapped β -NaSn₁₂. [75] This result is indicated in Figure 2.5; the isomers that are circled in bold are the isomers that were observed with this synthesis strategy. The computational results indicate that single-capped γ -NaSn₁₃ is more unstable than uncapped β -NaSn₁₂ by 33.8 kcal/mol and uncapped γ -NaSn₁₂ by 23.8 kcal/mol. The cap on γ -NaSn₁₃ yields a short Sn-Sn distance of 3.15 Å between the cap and the nearest tin, which might destabilize the single-capped

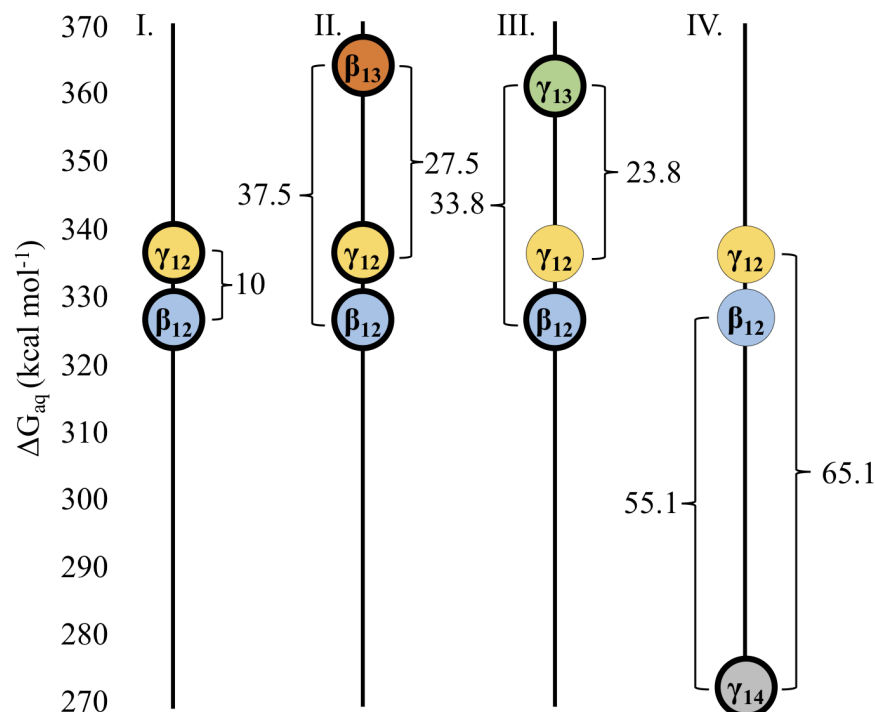


Figure 2.5: Four synthesis strategies (I, II, III, IV) and their experimentally observed results (bold-circled isomers). Hydrolysis Gibbs free energies of all relevant isomers are included. Blue= β -NaSn₁₂, Yellow= γ -NaSn₁₂, Red= β -NaSn₁₃, Green= γ -NaSn₁₃, Gray= γ -NaSn₁₄.

γ -NaSn₁₃ by repulsion, compared to the uncapped γ -NaSn₁₂.^[75] However, the uncapped γ -NaSn₁₂ is not observed. One analysis of these values is that a ΔG_{aq} of 23.8 kcal/mol between a capped and uncapped system is in fact sufficient to prevent the respective uncapped system from forming.

Synthesis strategy IV performed by Zhu et al. in 2019 produced double-capped γ -NaSn₁₄.^[21] The authors were able to use borate ligands to stabilize the two capping butyltin, which in turn prevented isomerization in solution. It is possible that a more symmetric structure with two caps rather than one allows for a more thermodynamically stable state. The computational results performed in this study indicate that double-capped γ -NaSn₁₄ is more stable than uncapped β -NaSn₁₂ by 55.1 kcal/mol and uncapped γ -NaSn₁₂ by 65.1 kcal/mol, as is shown in Figure 2.5. It seems that since this double-capped γ -NaSn₁₄ is more stable than its uncapped counterpart, it dominates in solution. Also, it is possible that since double-capped γ -NaSn₁₄ is 55.1 kcal/mol more stable than β -NaSn₁₂, it prevents uncapped β -NaSn₁₂ from forming.

More structures in the Keggin cluster chemical space of Na-Sn need to be synthesized and computationally modeled to truly determine the influence of capping on the thermodynamic

stability landscape. What is the energy difference that defines the transition point between forming a mixture of uncapped and capped Keggin clusters, and forming a pure phase? For example, in synthesis strategy III, could uncapped β -NaSn₁₂ have been prevented from forming if single-capped γ -NaSn₁₃ had only been 23.8 kcal/mol less stable? Computational tools can be employed to tune the structure of single-capped γ -NaSn₁₃ slightly to see if there is room for improvement. If a variation of the single-capped γ -NaSn₁₃ is determined, new syntheses can be designed to create this system. This would remove the need to double-cap the structure, and thus maintain simplicity of the structure and a promising photoresist material for EUV lithography. It should be noted that these energy differences are specific to the level of theory, including the implicit solvation, employed in the computational investigation.

Influence of Heteroatom: Sodium vs. Calcium

Previous computational studies have investigated how changing the heteroatom can influence the stability of Keggin isomers. For phosphotungstate Keggin ions, a change in isomer stability ordering is seen at the second reduction.[41] In organoantimonate Keggin ions, the central cavity is larger in the β -isomer than the α -isomer.[23] And in general, as the overall charge of the central tetrahedron MO_4^{n-} becomes more positive, the central cavity increases in size[79] and isomerization is less favored for classic POM Keggin ions.[32, 80] Most of the common Keggin structures have a high charge and small ionic radius, e.g. Si^{4+} (0.26 Å) and P^{5+} (0.17 Å).[81] Dissimilarly, sodium and calcium have a low charge and large ionic radius, e.g. Na^+ (0.99 Å) and Ca^{2+} (1.00 Å). Since calcium has a similar size to sodium, it can easily fit in the central cavity of the tin-based Keggin cluster. However, typically calcium prefers a 6-8 coordination, rather than a 4-coordinate tetrahedron.[82] Only one other compound has shown to have a T_d CaO_4 unit, and it required very bulky alkoxide ligands to stabilize it.[83] Nonetheless, we hypothesized that the size and charge of the four-coordinate central heteroatom could influence stability ordering in the Sn-Keggin system, and a calcium heteroatom was investigated.

We computationally modeled calcium centered Keggin structures, once again replacing the butyl ligands with methyl ligands to reduce the complexity of the system. As can be seen in Table 2.2, changing the heteroatom from Na to Ca slightly changed the stability ordering of the five isomers. And the β -isomer always appears most stable which is consistent with experimental observations. Our calculated β -CaSn₁₂ Keggin isomer is shown in Figure 2.6. Our collaborators were able to experimentally develop a one-step synthesis recipe for a new butyltin β -Keggin ion with a calcium heteroatom; $[(\text{BuSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$.[84] This procedure produced a pure phase β -isomer, rather than a mixture of isomers. These computational and experimental results suggests that the slight energy difference increase between the most stable isomer and the second most stable isomer (from 10 kcal/mol to 11.9 kcal/mol) has allowed a single Ca-Keggin isomer to be synthesized, rather than a mixture of isomers. Likely, the β -Keggin ion is more stable than the γ -Keggin ion in both the sodium and calcium cases since the γ -Keggin ion has two edge-sharing trimers with a shorter metal-metal distance between those two Sn centers, which decreases the overall stability of the

cluster.[84] Also, we observe the trend that as the overall charge of the central cavity component becomes more positive, $\{\text{NaO}_4\}^{7-}$ to $\{\text{CaO}_4\}^{6-}$, isomerization is less favored. Here, the shorter and stronger Ca-O bonds, compared to the Na-O bonds, reduces the lability of the molecule.[84]

Species	Hydrolysis Gibbs Free Energy (kcal/mol)	Energy Differences (kcal/mol)	HOMO-LUMO gap (eV)
ϵ -CaSn ₁₂	-297.2	57.5	5.81
δ -CaSn ₁₂	-338.3	16.4	6.01
γ -CaSn ₁₂	-338.6	16.1	5.73
α -CaSn ₁₂	-342.8	11.9	6.20
β -CaSn ₁₂	-354.7	0	6.23

Table 2.2: Hydrolysis Gibbs free energies, energy differences, and HOMO-LUMO gaps of uncapped and capped Ca-Sn clusters.

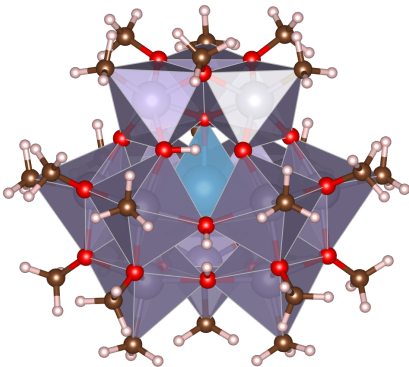


Figure 2.6: Uncapped β -CaSn₁₂. Purple octahedra: tin. Blue tetrahedra: calcium. Brown: carbon. White: hydrogen.

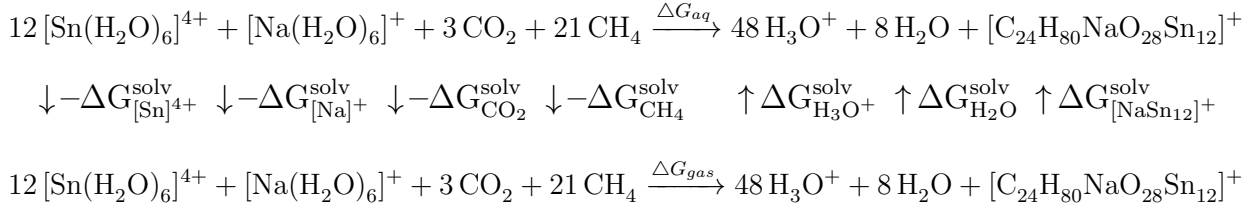
2.6 Conclusions

To build an understanding surrounding the fundamental lithographic mechanisms at play during exposure of a Sn-Keggin photoresist, we explored the tunability of the Sn-Keggin system. Computational results provided vital insight towards understanding the nature of this unique system that favors the lower symmetry Keggin isomers, β and γ . Density functional theory (DFT) was used to obtain the hydrolysis Gibbs free energy and HOMO-LUMO gap, which led to the stability ranking: β -NaSn₁₂ > γ -NaSn₁₂ > α -NaSn₁₂ > δ -NaSn₁₂ > ϵ -NaSn₁₂ for uncapped Na-centered tin Keggin clusters, which was consistent which

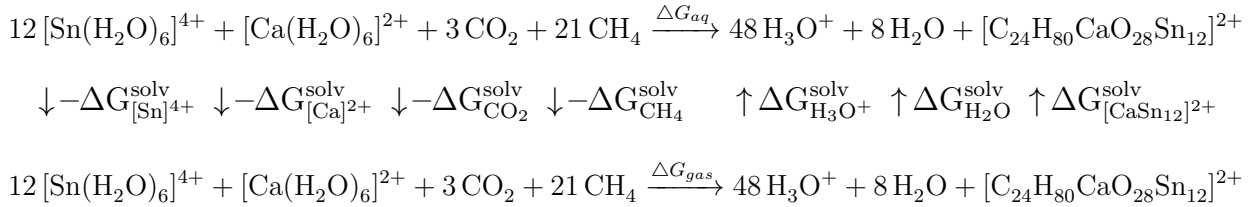
experimental observations. The uncapped NaSn_{12} -isomers were computationally evaluated to be more stable than their respective single-capped analogues. However, the double-capped $\gamma\text{-NaSn}_{14}$ was more stable than either the uncapped or single-capped clusters. Therefore, capping was shown to be a useful tool in exploring the stability landscape of these Keggin clusters to promote a pure and stable material for the next generation EUV lithography photoresists. Another useful strategy was to change the heteroatom from sodium to calcium, which allowed for the $\beta\text{-CaSn}_{12}$ Keggin ion to stabilize as a pure phase, without the need for capping. The successful collaborative accumulation of computational and experimental results, confirmed that the Sn-Keggin clusters represent the only Keggin ion family to this date that favors these lower symmetry isomers. Future work could focus on further probing this Sn-Keggin system's possible capping combinations and further changing the central heteroatom.

2.7 Methodology

Scheme 1: Thermodynamic cycle for the uncapped $\beta\text{-NaSn}_{12}$.



Scheme 2: Thermodynamic cycle for the uncapped $\beta\text{-CaSn}_{12}$.



Equation 2.1 for determining the hydrolysis Gibbs free energy.

$$\Delta G_{\text{aq}} = \Delta G_{\text{gas}} + \sum_{i=1}^{N_{\text{products}}} n_i \Delta G_i^{\text{solv}} - \sum_{j=1}^{N_{\text{reactants}}} n_j \Delta G_j^{\text{solv}} \quad (2.1)$$

2.8 Computational Details

Na-Sn Keggin Ions

The geometry of each cluster was first optimized using Gaussian 09 in the gas phase using the B3LYP functional.[85] The basis set 6-31G(d) was used for elements Na, C, H, and O, while the basis set LANL2DZ was used for the element Sn.[86, 87] A subsequent frequency calculation was performed to verify the absence of imaginary vibration modes to confirm that the system is in a stable/metastable state. An effective core potential LANL2DZ was used for Sn. The geometry was further optimized in water using the continuum solvation model SMD.[88] The electronic energy was refined using a B3LYP single point with the basis set 6-311+G(d,p) for elements Na, C, H, and O, and basis set LANL2DZ for Sn.[89] The solvation energy was computed using a B3LYP/6-31G(d) single point with SMD for water ($\epsilon \approx 78.36$).

Ca-Sn Keggin Ions

The geometry of each cluster was first optimized using Gaussian 09 in the gas phase using the B3LYP functional.[85] The basis set 6-31G(d) was used for elements Ca, C, H, and O, while the basis set LANL2DZ was used for the element Sn.[86, 87] A subsequent frequency calculation was performed to verify the absence of imaginary vibration modes to confirm that the system is in a stable/metastable state. An effective core potential LANL2DZ was used for Sn. The geometry was further optimized in water using the continuum solvation model SMD and a solvent accessible surface (SAS).[88] The electronic energy was refined using a B3LYP single point with the basis set 6-311+G(d,p) for elements Ca, C, H, and O, and basis set LANL2DZ for Sn.[89] The solvation energy was computed using a B3LYP/6-31G(d) single point with SMD for water ($\epsilon \approx 78.36$) and a solvent-excluding surface (with a minimum radius for added spheres of 0.20 and an overlap index of 0.89).

2.9 Acknowledgements

The authors gratefully acknowledge the support of the National Science Foundation, Center for Chemical Innovation, grant CHE-1606982. This research used resources of the National Energy Research Scientific Computing Center (NERSC) (specifically Cori), a U.S. Department of Energy Office of Science User Facility located at Lawrence Berkeley National Laboratory, operated under Contract No. DE-AC02-05CH11231.

The work described in this chapter has been published as references [84, 90].

Chapter 3

Aqueous Hexameric Zirconium Cluster for “Green” Manufacturing of Metal-Organic Frameworks

3.1 Background

Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are known as secondary building units, composed of metal-oxo cluster nodes and organic molecule linkers.[91] Through strong covalent bonds formed between the nodes and linkers, a porous 3D network is formed that can act as a storage container that is structurally and energetically sound.[26, 92] The structural diversity encountered in MOF chemistry originates largely from the wide variety of accessible node geometry and linker combinations, allowing for a vast number of applications.[91] MOFs can be used for gas storage or gas separation, for example, certain MOFs can separate CO₂ and other greenhouse gases.[91] Other applications include catalysis, like promoting efficient organic transformations, as well as drug delivery, bio-imaging, and other therapeutics.[26, 91, 92]

Zirconium-Based Metal-Organic Frameworks

Group 4 transition metals titanium, zirconium, and hafnium, all with oxidation state 4+, have been identified to be nodes in MOFs.[93] However, titanium clusters tend to reassemble during MOF synthesis, while zirconium MOFs have a well-established synthesis method.[93] Due to lanthanide contraction, Hf₄⁺ has the same electronic configuration and a nearly identical radius as Zr₄⁺. Therefore, the Hf-MOFs usually show identical structures and properties as their Zr-based counterparts, except for the formula weight.[93] Hafnium MOFs do perform well as gas adsorbents due to the presence of Brønsted acid sites with high

affinity toward adsorbates, however, hafnium MOFs are also lacking in effective synthesis methods.[93] Therefore, zirconium MOFs are the material system investigated in this work.

UiO-66 was the first zirconium-based MOF, and has since become a benchmark for MOFs. A simplified graphic of a portion of UiO-66 is shown in Figure 3.1. The nodes consist of hexameric zirconium clusters i.e. $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{COO})_{12}$. The organic linkers are 1,4-benzodicarboxylic acid i.e. BDC. The UiO-66 MOF has a *fcu* topology, thus providing it with two distinct vacancies; a tetragonal cage and an octahedral cage, both perfect for storing gases or other products.[93] One application includes removal of pharmaceutical and personal care products from wastewater. And one proposed application includes on-board hydrogen storage for fuel cell vehicles.[93] UiO-66 is made by the common solvothermal synthesis.[93]

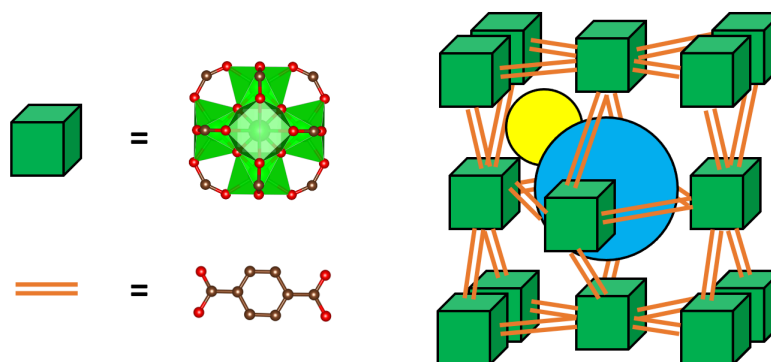


Figure 3.1: Simplified graphic of portion of UiO-66 metal-organic framework. Green cubes are the nodes, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{COO})_{12}$. Orange lines are linkers, 1,4-benzodicarboxylic acid i.e. BDC. Yellow circle is the tetrahedral cavity. Blue circle is the octahedral cavity.

Green Manufacturing of Metal-Organic Frameworks

MOFs can be synthesized following different crystallization procedures, although the most common strategy is a solvothermal synthesis method.[94] In the solvothermal approach, a mixture an organic-ligand-stabilized metal cluster and an organic linker are heated in a high-boiling temperature solvent.[94] However, the most commonly used solvent, dimethylformamide, can decompose at solvothermal temperatures into corrosive products.[94] In order to minimize the use of organic solvents and manufacture at ambient temperature, mechanochemical pathway strategies have been developed such as liquid-assisted grinding. Unfortunately, such methods continue to include complicated reaction steps, use unstable reagents, and produce an amorphous product in low yield.[95–97] Therefore, there is interest in using a “green” alternative synthesis method, where water is used as the solvent instead. The issue here however, is that most metal clusters are not soluble in water without organic ligands.[94] The organic ligands influence the shape of the MOF product but also add to the

complexity of the synthesis which increases the overall cost.[94] Hence, this “green” alternative is not a viable option because it is difficult to identify metal clusters that are naturally stable in water without organic ligands.[94] Regular POMs are not suitable for this application, because although they are easily stable in water without any ligands, their doubly bonded oxo ligand prevents the addition of organic “linkers”.[91] Therefore, it is desirable to have systems that have water-based ligands.

The Zr-MOF UiO-66 has Zr hexamer nodes that are stabilized with organic ligands as $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{COO})_{12}$.[98] For aqueous Zr-based MOF manufacturing to evolve, the challenge is to stabilize the hexanuclear-Zr(IV) node in water without organic ligation. When attempting to make a Zr hexamer stable in aqueous solution, acetate ligands were required for stability, producing $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CH}_3\text{COO})_{12}$.[99] This is not unusual since in Zr(IV) aqueous chemistry, zirconium-oxo clusters predominately hydrolyze and polymerize to the tetranuclear $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ cluster (i.e. $\{\text{Zr}_4^{8+}\}$), dominating at low pH.[100–102] In fact, the desired aqueous hexanuclear $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$ cluster containing only water-based ligands (i.e. $\{\text{Zr}_6^{12+}\}$), remains hypothetical and the reason for its thermodynamic instability is unclear. One method to improve aqueous solution stability of metal-oxo clusters is to add counterion salts to the solution.[94] However, the number of salts should be kept to a minimum; metal nitrates and perchlorates are associated with risks of explosion due to oxidation upon handling, and chloride may induce corrosion.[94] Therefore, tuning other solution conditions such as pH, electrochemical potential, and concentration of the metal ion to promote metal-oxo clusters in water is the ideal “green” solution.[91, 94]

3.2 Introduction

Group 4 metal-oxide clusters comprise a particularly interesting class of materials that are used to build metal organic frameworks (MOFs)[93, 103] for gas storage, catalysis, and drug delivery devices.[26, 93, 104] However, MOFs are often made with solvothermal synthesis methods that involve high temperatures and organic solvents with harmful bi-products.[95]

Therefore, it is highly desirable to develop sustainable MOF manufacturing methods that occur at ambient temperature and in an aqueous environment. Unfortunately, organic ligands are often needed to stabilize the cluster in solution.[3, 4] The drawback is that organic ligands can limit the clusters’ applications due to the hindrance of reactivity or solubility. Therefore, a fundamental challenge is to guide synthesis procedures to promote metal-oxide clusters in an aqueous environment without the crutch of organic ligands. There is still a lack of understanding as to why certain zirconium clusters are favored in aqueous solution.

Aqueous synthesis strategies can be controlled by a number of experimental variables including temperature, metal concentration, pH, electrochemical potential, and counterions. While the effects of temperature and metal concentration are foreseeable and well-understood, the impact of solution characteristics such as pH, electrochemical potential, and counterions can be complex and interdependent depending on the metal cation.[54] This lack of understanding cripples the ability to fully exploit these control knobs to synthesize new

and improved aqueous metal-oxide clusters. This study aims to improve our understanding of the thermodynamic stability relationship between $\{\text{Zr}_4^{8+}\}$ and $\{\text{Zr}_6^{12+}\}$, to not only support the efforts to develop green MOF manufacturing, but to expand the general knowledge of Zr(IV) aqueous solution chemistry.

Computational modeling techniques such as density functional theory (DFT) and molecular dynamics (MD) can be used to explore the stability regimes of hypothesized and novel species. For example, DFT and MD were used to investigate aqueous solution effects in polyoxometalates,[32, 37, 38, 42, 45, 46, 48] group 13 cations,[30, 50, 105] the Fe-Keggin,[5] and in modeling the first open-shell Keggin ion.[17] There have been limited computational studies of group 4 metal-oxide clusters, hitherto all using MD techniques.[106–109] Although MD is useful in optimizing the terminal water ligands of aqueous metal clusters, calculating accurate thermodynamic properties (e.g., hydrolysis Gibbs free energies) requires other techniques. In this respect, DFT enables accurate prediction of hydrolysis Gibbs free energies which can then be used to estimate and compare the aqueous stability of different species.[110–113]

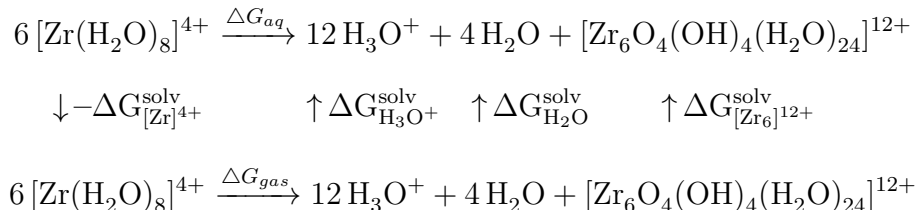
Here, we use DFT to investigate the thermodynamic stability of the hypothetical $\{\text{Zr}_6^{12+}\}$ hexamer in relation to the $\{\text{Zr}_4^{8+}\}$ tetramer and other Zr(IV) aqueous ions and solids. After optimizing the positions of terminal water ligands using DFT, we calculated the hydrolysis Gibbs free energy of ground state cluster geometries and used a Pourbaix formalism[114, 115] developed for the Materials Project[116] to determine equilibrium constants and electrochemical (E-pH) stability regimes of our modeled species. Auxiliary analyses of the electronic structure alongside electrostatic potential maps provided clarity on the thermodynamic landscape governing the competition between the $\{\text{Zr}_4^{8+}\}$ tetramer and the $\{\text{Zr}_6^{12+}\}$ hexamer as well as possible avenues for promoting the synthesis of the hexamer. This study aimed to improve our understanding of the thermodynamic stability relationship between $\{\text{Zr}_4^{8+}\}$ and $\{\text{Zr}_6^{12+}\}$, to not only support the efforts to develop green MOF manufacturing, but to expand the general knowledge of Zr(IV) aqueous solution chemistry.

Computational Details

The geometry of each cluster was first optimized in vacuum using density functional theory (DFT). Calculations were performed with Gaussian 16[117] software using the B3LYP functional.[85] The basis set 6-31+G(d) was used for oxygen and hydrogen, while the basis set 6-31+G(d) and associated effective core potential LANL2DZ was used for zirconium.[86, 87, 118, 119] A subsequent frequency calculation was performed to verify the absence of imaginary vibration modes to confirm that the system was in a stable/meta-stable state. The geometry was further optimized in water using the continuum solvation model COSMO.[120, 121] The electronic energy was refined using a B3LYP single point calculation with the basis set 6-311+G(d,p) for oxygen and hydrogen, and basis set LANL2DZ for zirconium.[89] The solvation energy was computed using a B3LYP/6-31G(d) single point with COSMO ($\epsilon=78.36$ for water) for oxygen and hydrogen, and a B3LYP/LANL2DZ single point for zirconium. GaussSum was used for orbital analysis.[122]

Hydrolysis Gibbs Free Energy

A thermodynamic cycle was used to determine the hydrolysis Gibbs free energy, ΔG_{aq} from computed gas-phase and solvation free energies.[76, 77] An example of the thermodynamic cycle for the Zr(IV) hexamer is shown below (also reproduced as Cycle S3 in the Supporting Information (SI)). The upper reaction is in the aqueous phase and the lower reaction is modeled in vacuum. The cycles for the dimer and tetramer are provided by Cycles S1 and S2 in the SI, respectively. The hydrolysis Gibbs free energy ΔG_{aq} was then determined with equation 3.1 in the SI.



Pourbaix Diagram Formalism

The hydrolysis Gibbs free energies are mapped to the Pourbaix formalism[114, 115] of the Materials Project.[116] The most important aspect of this formalism is that it uses a combination of computed energies for solid states and clusters with experimental Gibbs free energies for monomeric aqueous ions and water, which means that effects such as aqueous ion solvation are inherently accounted for. The equations and referencing scheme to determine the Pourbaix formalism energy $\Delta G_{\text{pourbaix}}$ from the hydrolysis Gibbs free energy ΔG_{aq} are shown in the SI as equations 3.2 through 3.4 and Table 3.8.

Code Availability

The code to plot Pourbaix diagrams is available via pymatgen: https://github.com/materialsproject/pymatgen/blob/master/pymatgen/analysis/pourbaix_diagram.py [110, 114, 115, 123]

3.3 Results and Discussion

Structures

The computed DFT ground state structure of the zirconium tetramer $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ is shown in Figure 3.2a. The tetramer has four Zr^{4+} ions, each 8-coordinate with distorted square antiprism geometry. These four Zr(IV) building units are bonded by double OH^- bridges. Therefore, one Zr^{4+} ion is connected to four OH^- and four H_2O ligands. These four building units form a planar square with respect to the zirconium

ions. The computed bond lengths and angles for the tetranuclear zirconium cluster compare well to EXAFS experimental data and solution phase computational data (see Table 3.6).[106, 124]

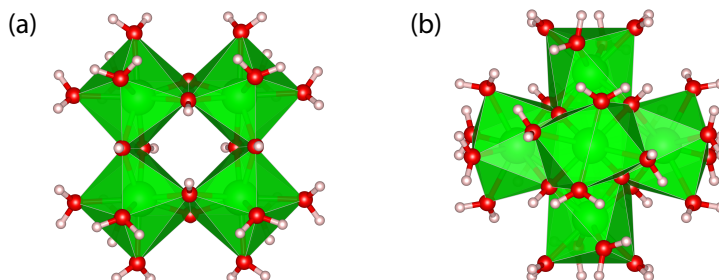


Figure 3.2: (a) Ground state geometry of the zirconium(IV) tetranuclear species $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. (b) Ground state geometry of the zirconium(IV) hexanuclear species $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.

We also report, for the first time, the DFT-relaxed structure for the hypothetical zirconium hexamer $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$ (Figure 3.2b). The hexamer exhibits Zr(IV) building units like the tetramer, being 8-coordinate in a distorted square antiprism fashion. However, the six Zr^{4+} ions are bonded to two O^{2-} , two OH^- and four terminal H_2O ligands each. These six units form a compact structure similar to the hexanuclear acetate complex reported by Hennig *et al.*[99] The computed bond lengths and angles for the hexanuclear zirconium clusters are similar to those of the hexanuclear Zr(IV) acetate complex in aqueous solution of 0.1 M Zr(IV) in 1 M acetic acid at pH 1.5 as reported by Hennig *et al.* (see Table 3.7).[99]

The computed DFT ground state structure of the zirconium monomer $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$ (i.e., $\{\text{Zr}^{4+}\}$) and dimer $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$ (i.e., $\{\text{Zr}_2^{6+}\}$) are depicted in Figures 3.12 and 3.13, respectively. The monomer exhibits a classic square antiprism geometry, with a Zr^{4+} center bound to eight water ligands, while the dimer has a slightly distorted square antiprism geometry, with two 8-coordinate Zr^{4+} ions connected to two OH^- and six H_2O ligands. The monomer and dimer’s bond lengths and angles are listed in Tables 3.4 and 3.5, respectively. These values comparable to experimental and computationally reported results.[107, 124]

Pourbaix Diagrams

The calculated hydrolysis Gibbs free energies ΔG_{aq} of the dimer, tetramer, and hexamer were -6.4, -23.4, and -17.5 kcal/mol, respectively (Table 3.9). At first glance, the low hydrolysis Gibbs free energy of the tetramer indicates that the tetramer is the most stable configuration. But including the cluster free energies (correctly referenced, see Pourbaix Energy Formalism Section of the Supporting Information) on the Zr Pourbaix diagram with respect to other

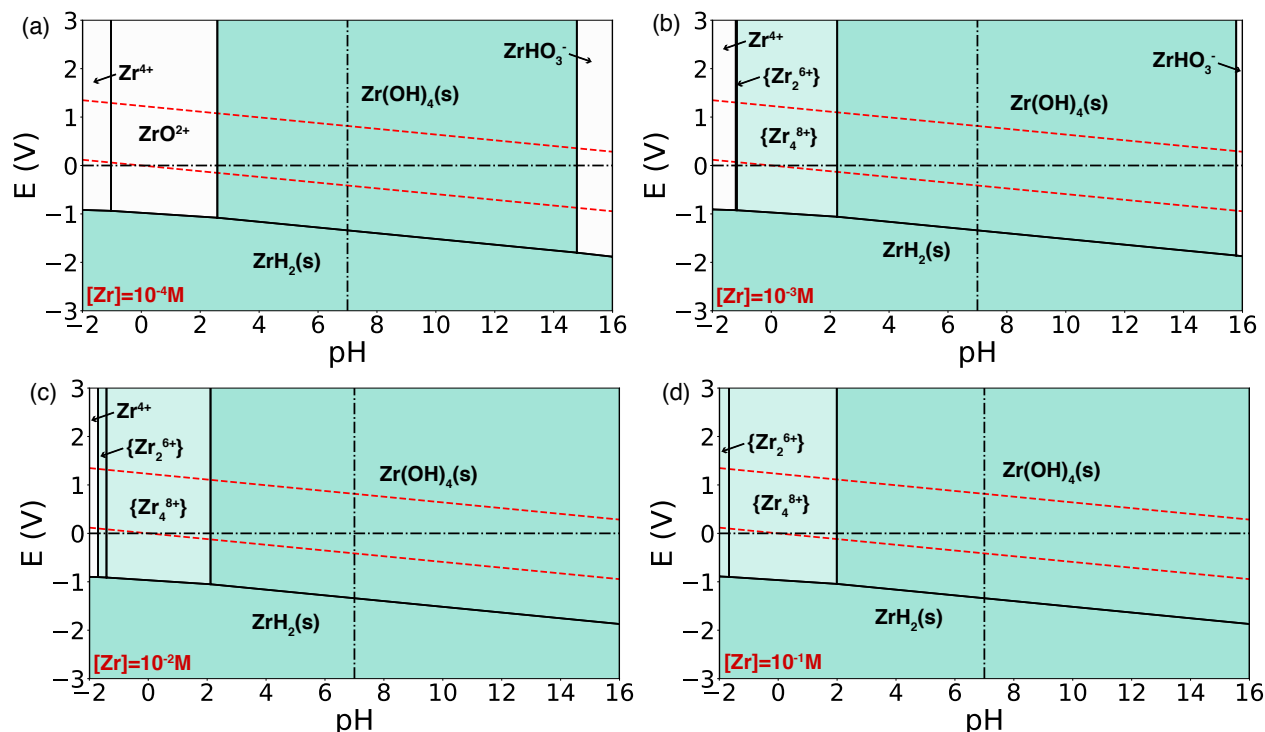


Figure 3.3: Zirconium Pourbaix diagram at varying $[\text{Zr(IV)}]$ concentrations. (a) $[\text{Zr(IV)}] = 10^{-4} \text{ M}$, ZrO^{2+} is between $-1.0 \leq \text{pH} \leq 2.5$. (b) $[\text{Zr(IV)}] = 10^{-3} \text{ M}$, $\{\text{Zr}_2^{6+}\}$ is at $\text{pH} = -1.2$, $\{\text{Zr}_4^{8+}\}$ is between $-1.1 \leq \text{pH} \leq 2.2$. (c) $[\text{Zr(IV)}] = 10^{-2} \text{ M}$, $\{\text{Zr}_2^{6+}\}$ is between $-1.7 \leq \text{pH} \leq -1.5$, $\{\text{Zr}_4^{8+}\}$ is between $-1.4 \leq \text{pH} \leq 2.1$. (d) $[\text{Zr(IV)}] = 10^{-1} \text{ M}$, $\{\text{Zr}_2^{6+}\}$ is between $-2.0 \leq \text{pH} \leq -1.7$, $\{\text{Zr}_4^{8+}\}$ is between $-1.6 \leq \text{pH} \leq 1.9$. **Note:** Dimer, $\{\text{Zr}_2^{6+}\} = [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. Tetramer, $\{\text{Zr}_4^{8+}\} = [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. Hexamer, $\{\text{Zr}_6^{12+}\} = [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$.

aqueous ions and solids (Figure 3.3), allows for a more nuanced understanding that includes the effects of electrochemical potential, pH, and Zr(IV) concentration.

At a zirconium concentration of 10^{-4} M , the aqueous zirconium ion Zr^{4+} and the zirconyl ion ZrO^{2+} are stable at low pH values, as shown in Figure 3.3a. Increasing the concentration to $[\text{Zr(IV)}] = 10^{-3} \text{ M}$, the dimer and tetramer outcompete ZrO^{2+} , as is illustrated in Figure 3.3b. This stability prediction is consistent with experimental observations that Zr(IV) has a strong tendency to hydrolyze and polymerize at $[\text{Zr(IV)}] > 10^{-4} \text{ M}$, at low pH.[99] As the zirconium concentration is increased further to 10^{-2} M and 10^{-1} M , the tetramer develops a broader stability window in the direction of lower pH (Figures 3.3c and 3.3d). This stability prediction is specifically comparable to the experimental results reported by Hennig *et al.*[99] which observes the tetramer at $\text{pH} = 1.5$ when $[\text{Zr(IV)}] = 10^{-1} \text{ M}$.

From our calculated Pourbaix formalism energies $\Delta G_{\text{pourbaix}}$ reported in Table 3.9, we calculated the equilibrium constants (K°) for various reactions between the monomer, ZrO^{2+} ,

Table 3.1: Equilibrium Reactions.

Equilibrium Species	Equilibrium Reaction
(a) Monomer/Tetramer	$4 \text{Zr}^{4+} + 24 \text{H}_2\text{O} = 8 \text{H}^+ + [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$
(b) Dimer/Tetramer	$2 [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+} = 4 \text{H}^+ + 4 \text{H}_2\text{O} + [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$
(c) Monomer/Dimer	$2 \text{Zr}^{4+} + 14 \text{H}_2\text{O} = 2 \text{H}^+ + [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$
(d) ZrO_2^+ /Tetramer	$4 \text{ZrO}^{2+} + 20 \text{H}_2\text{O} = [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$
(e) Monomer/Hexamer	$6 \text{Zr}^{4+} + 32 \text{H}_2\text{O} = 12 \text{H}^+ + [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$
(f) Dimer/Hexamer	$3 [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+} = 6 \text{H}^+ + 10 \text{H}_2\text{O} + [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$
(g) ZrO_2^+ /Hexamer	$6 \text{ZrO}^{2+} + 26 \text{H}_2\text{O} = [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$
(h) Tetramer/Hexamer	$3 [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+} = 8 \text{H}_2\text{O} + 2 [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$
(i) Monomer/ ZrO_2^+	$\text{Zr}^{4+} + \text{H}_2\text{O} = 2 \text{H}^+ + \text{ZrO}^{2+}$

dimer, tetramer, and hexamer, using equations 3.5 through 3.9 in the SI, and reported in Tables 3.1 and 3.2. Our calculated equilibrium constants indicate that the tetramer is the cluster that is most likely to form from either monomers or dimers (Table 3.2). Our calculated $\log(K^\circ)$ value for the equilibrium reaction involving four monomers forming the tetramer is 17.19. And for the reaction describing two dimers joining to form the tetramer, we calculate that $\log(K^\circ) = 7.78$. Lastly, $\log(K^\circ)$ is calculated to be 4.70 for the reaction of two Zr^{4+} to become the dimer. These three large positive calculated $\log(K^\circ)$ values suggest that monomers and dimers readily produce the tetramer in large yields. It has been experimentally observed that the Zr tetramer can also form an octameric cluster made up of two stacked tetramers bridged by hydroxyl ligands.[125] We were unable to simulate this structure; however the experimental $\log(K^\circ)$ value is -0.7, indicating that formation of this species is thermodynamically unfavorable compared to the tetramer.

The ZrO^{2+} species and the tetramer compete for the same stability regime (i.e., same region of potential - pH space) on the Zr Pourbaix diagram. However, a total Zr concentration of 10^{-3} M stabilizes the tetramer over ZrO^{2+} . To illustrate the increasing stability of the tetramer with concentration, in Figures 3.4a and 3.4b we show the stability of the tetramer relative to ZrO^{2+} for $[\text{Zr(IV)}]$ of 10^{-7} M and 10^{-3} M. The energy difference between the tetramer and ZrO^{2+} decreases from 10 meV/atom to -1 meV/atom as the concentration increases, such that the tetramer becomes the stable species at $[\text{Zr(IV)}] = 10^{-3}$ M. Specifically, the total Zr concentration must be greater than 9.4×10^{-4} M in order for the tetramer to be promoted over ZrO^{2+} , as can be calculated by solving equation (d) in Table 3.2 for when the concentration of the two species are equivalent.

Similarly, the ZrO^{2+} species and the hexamer compete for the same stability regime. To better visualize the equilibrium boundary between Zr^{4+} and the hexamer, we removed the dimer and the tetramer from the cluster dataset, to simulate a scenario where the dimer and tetramer are kinetically inhibited from nucleating. Furthermore, the calculated $\log(K^\circ)$ for 3 dimers combining to form the hexamer, $\log(K^\circ) = -1.26$, indicates that this reaction is unlikely. Although we were unable to simulate a trimeric zirconium cluster, a $\log(K^\circ)$

Table 3.2: Equilibrium Reaction Energies and Constants.

Equilibrium Species (Reaction in Table 3.1)	$\Delta G^\circ_{\text{rxn}}$ (kJ/mol)	$\log(K^\circ)$
(a) Monomer/Tetramer	-98.07	$17.19 = \log \frac{[\{\text{Zr}_4^{8+}\}]}{[\text{Zr}^{4+}]^4} - 8\text{pH}$
(b) Dimer/Tetramer	-44.40	$7.78 = \log \frac{[\{\text{Zr}_4^{8+}\}]}{[\{\text{Zr}_2^{6+}\}]^2} - 4\text{pH}$
(c) Monomer/Dimer	-26.83	$4.70 = \log \frac{[\{\text{Zr}_2^{6+}\}]}{[\text{Zr}^{4+}]^2} - 2\text{pH}$
(d) ZrO_2^+ /Tetramer	-51.79	$9.08 = \log \frac{[\{\text{Zr}_4^{8+}\}]}{[\text{ZrO}_2^{2+}]^4}$
(e) Monomer/Hexamer	-73.33	$12.85 = \log \frac{[\{\text{Zr}_6^{12+}\}]}{[\text{Zr}^{4+}]^6} - 12\text{pH}$
(f) Dimer/Hexamer	7.17	$-1.26 = \log \frac{[\{\text{Zr}_6^{12+}\}]}{[\{\text{Zr}_2^{6+}\}]^3} - 6\text{pH}$
(g) ZrO_2^+ /Hexamer	-3.90	$0.68 = \log \frac{[\{\text{Zr}_6^{12+}\}]}{[\text{ZrO}_2^{2+}]^6}$
(h) Tetramer/Hexamer	147.55	$-25.86 = \log \frac{[\{\text{Zr}_6^{12+}\}]}{[\{\text{Zr}_4^{8+}\}]^3}$
(i) Monomer/ ZrO_2^+	-11.57	$2.03 = \log \frac{[\text{ZrO}_2^{2+}]}{[\text{Zr}^{4+}]} - 2\text{pH}$

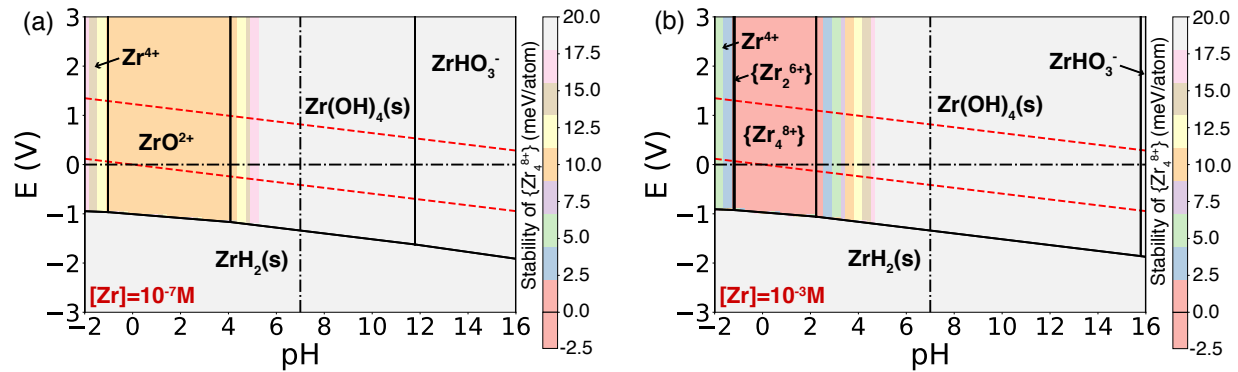


Figure 3.4: Zirconium Pourbaix diagram heat maps at two different concentrations. (a) $[\text{Zr(IV)}] = 10^{-7} \text{ M}$ showing that the tetramer is 10 meV/atom less stable than ZrO_2^+ . (b) $[\text{Zr(IV)}] = 10^{-3} \text{ M}$ showing that the tetramer is 1 meV/atom more stable than ZrO_2^+ . **Note:** Dimer, $\{\text{Zr}_2^{6+}\} = [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. Tetramer, $\{\text{Zr}_4^{8+}\} = [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$.

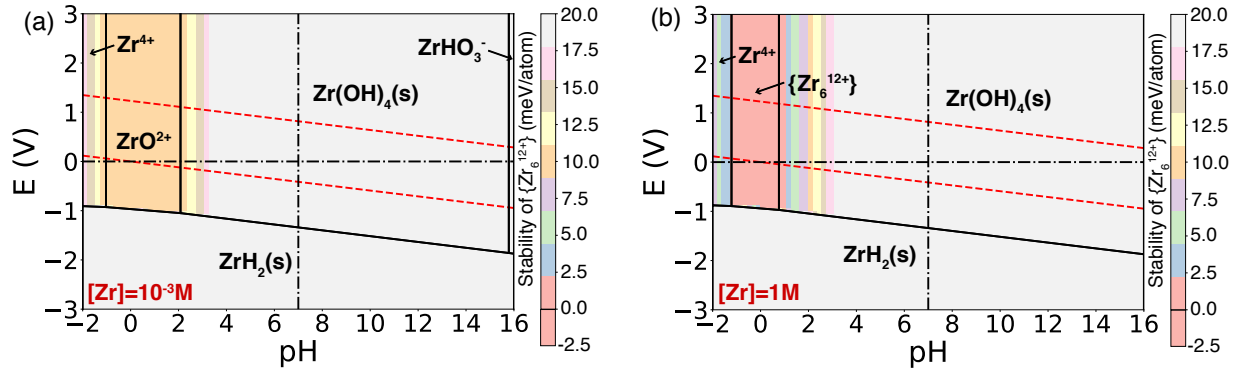


Figure 3.5: Zirconium Pourbaix diagram heat maps at two different concentrations, with the dimer and the tetramer removed from the cluster dataset, to simulate a scenario where these two species are kinetically inhibited to nucleate. **(a)** $[\text{Zr(IV)}] = 10^{-3} \text{ M}$ showing that the hexamer is 9 meV/atom less stable than ZrO^{2+} . **(b)** $[\text{Zr(IV)}] = 1 \text{ M}$ showing that the hexamer is 1 meV/atom more stable than ZrO^{2+} . **Note:** Hexamer, $\{\text{Zr}_6^{12+}\} = [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$.

value of 0.4 has been experimentally reported for three monomers forming a trimer.[126] Therefore, we expect that most likely the building blocks of the hexamer are six monomers since our predicted $\log(K^\circ)$ is 12.85. In this kinetically-limited scenario, we systematically increase the zirconium concentration, and that find an increase in the $[\text{Zr(IV)}]$ from 10^{-3} M to 1 M , decreases the energy difference between the hexamer and ZrO^{2+} from 9 meV/atom to -1 meV/atom, such that the hexamer became the stable species at $[\text{Zr(IV)}] = 1 \text{ M}$, as shown in the heat maps in Figures 3.5a and 3.5b. In fact, the total Zr concentration must be greater than $7.3 \times 10^{-1} \text{ M}$ in order for the hexamer to be promoted over ZrO^{2+} , as can be calculated by solving equation (g) in Table 3.2 for when the concentration of the two species are equivalent.

Finally, the tetramer and the hexamer also compete for the same stability regime, yet an increase in Zr concentration is not able to provide enough thermodynamic driving force for the hexamer to outcompete the tetramer. We find no attainable Zr concentration for which the hexamer is more stable than the tetramer. To this end, the heat map shown in Figure 3.6 at $[\text{Zr(IV)}] = 1 \text{ M}$ looks quite similar to the various heat maps at other Zr concentrations, indicating that an energy difference of about 9 meV/atom between the hexamer and tetramer cannot be overcome by simply changing the concentration of zirconium.

The effects of concentration on the relative stability of species, at the same pH and potential, is ultimately determined by their stoichiometry. ZrO^{2+} requires only 1 zirconium ion to form, whereas $\{\text{Zr}_6^{12+}\}$ requires 6 (see reactions (i) and (e) in Table 3.1). As a result, a three order of magnitude increase in $[\text{Zr(IV)}]$ provides enough thermodynamic driving force for the hexamer to outcompete the zirconyl ion. By comparison, a four order of magnitude

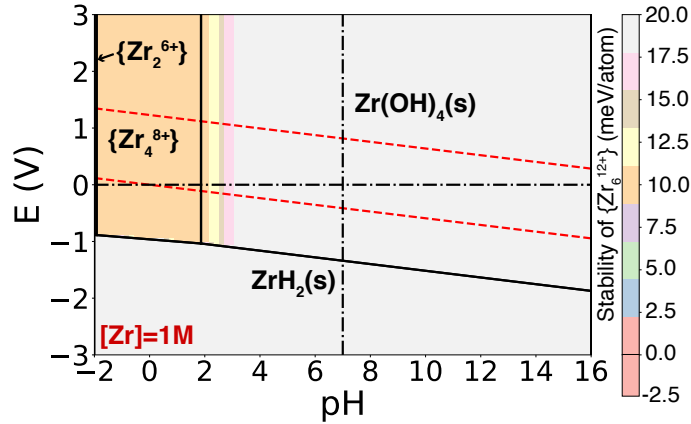


Figure 3.6: Zirconium Pourbaix diagram heat map at $[\text{Zr(IV)}] = 1 \text{ M}$ showing that the hexamer is 9 meV/atom less stable than the tetramer. **Note:** Dimer, $\{\text{Zr}_2^{6+}\} = [\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. Tetramer, $\{\text{Zr}_4^{8+}\} = [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. Hexamer, $\{\text{Zr}_6^{12+}\} = [\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$.

increase in $[\text{Zr(IV)}]$ is needed for the 4:1 ratio of zirconium ions required to form $\{\text{Zr}_4^{8+}\}$ (see reaction (a)). By contrast, for the case of $\{\text{Zr}_4^{8+}\}$ and $\{\text{Zr}_6^{12+}\}$, three tetramers are needed to form two hexamers, and therefore increasing the zirconium concentration has less of an impact on their relative stability. All calculated energy differences for $[\text{Zr(IV)}]$ ranging from 10^{-7} M to 1 M are reported in Table 3.10.

For the hexamer with 90 total atoms and 6 Zr(IV) ions, this 9 meV/atom energy difference at $\text{pH}=0$, $V=0$, and $[\text{Zr(IV)}]=1 \text{ M}$, is $\sim 129 \text{ meV/Zr}$ or $\sim 17.8 \text{ kcal/mol}$. This modeled energy difference is comparable to experimentally-observed energy differences between other metal-oxo cluster polymorphs. For example, a flat- $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{15+}$ Keggin ion is only about $\sim 9 \text{ kcal/mol}$ less stable than an ϵ - $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ Keggin ion, as reported by Wills *et al.*, yet the flat- $\{\text{Al}_{13}\}$ Keggin ion has been synthesized by Wang *et al.*, e.g. using additional zinc in solution.[30, 127] Wills *et al.* further claim that the $[\text{Ga}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ Keggin ion, which has not yet been synthesized, is less stable than the monomeric aqueous specie $[\text{Ga}(\text{OH})_2]^+$ by $\sim 21 \text{ kcal/mol}$, noting that these energy ranges are on the order of counterion interactions.[30, 54] Therefore, we hypothesize that, since the energy difference between the tetramer and hexamer is also on the order of counterion interactions at $\sim 17.8 \text{ kcal/mol}$ at $\text{pH}=0$, $V=0$, and $[\text{Zr(IV)}]=1 \text{ M}$, the Zr(IV) hexamer could be synthesized with proper selection of counterions.

Electronic Structure Analysis

To explore the electronic structure and correlate it to the instability of the Zr(IV) hexamer, we calculated the HOMO-LUMO gaps (Table 3.3). We note that for the monomer, dimer, and tetramer, as the size of the cluster increases, the HOMO-LUMO gap decreases, con-

Table 3.3: HOMO and LUMO energies and gaps for selected zirconium clusters in eV.

Species	Formula	HOMO	LUMO	Gap
Monomer	$[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$	-10.92	-4.05	6.87
Hexamer	$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$	-10.37	-3.63	6.74
Dimer	$[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$	-10.21	-3.60	6.62
Tetramer	$[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$	-9.41	-2.97	6.43

sistent with quantum confinement effects.[128] In contrast, the hexamer deviates from this trend. Visualizing the frontier molecular orbitals (FMOs), it is clear that the HOMO of the monomer, dimer, tetramer, and hexamer are all centered on the oxygen atoms (Figures 3.14b, 3.7b, 3.8b, 3.9b, respectively). However, for the hexamer, the fractional contribution to its HOMO is 11% zirconium and 89% oxygen & hydrogen. On the other hand, the dimer’s fractional contribution to its HOMO is 7% zirconium and 93% oxygen & hydrogen, and the tetramer’s fractional contribution to its HOMO is 4% zirconium and 96% oxygen & hydrogen. Therefore, the greater orbital overlap between the Zr and the O & H atoms lowers the hexamer’s HOMO energy below that of the dimer and tetramer.

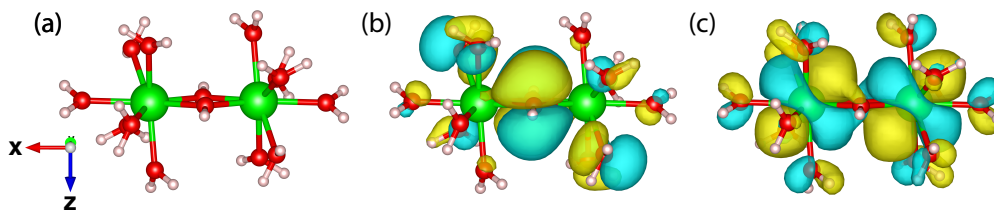


Figure 3.7: Frontier molecular orbitals for Zr(IV) dimer. (a) Dimer structure. (b) HOMO. (c) LUMO.

The LUMO of the monomer is dominated by the Zr d-orbital, following the basic square antiprismatic crystal field splitting (LUMO as d_{z^2} , then d_{xy} and $d_{x^2-y^2}$, then d_{xz} and d_{yz}) (Figure 3.14c). As the clusters grow in size, the complexity of the crystal field splitting increases. The dimer and tetramer’s LUMOs are similar to one another in that the d-orbitals centered on each Zr (d_{xz} and $d_{x^2-y^2}$, respectively) are aligned parallel to one another, but with their phases oriented to minimize overlap (Figures 3.7c and 3.8c, respectively). In contrast, the LUMO for the hexamer is degenerate with its LUMO+1, and the d-orbitals centered on each Zr ($d_{x^2-y^2}$ type) are aligned perpendicular for neighboring Zr such that there is more orbital overlap (Figure 3.9c). For the hexamer, we calculate the fractional contribution to its LUMO to be 94% zirconium and 6% oxygen & hydrogen. On the other hand, the dimer’s fractional contribution to its LUMO is 93% zirconium and 7% oxygen & hydrogen, and the tetramer’s fractional contribution to its LUMO is 96% zirconium and 4% oxygen & hydrogen. The hexamer and dimer are similar in their LUMO fractional contributions,

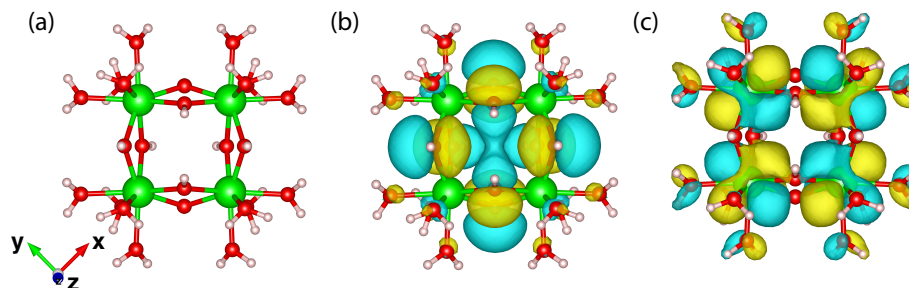


Figure 3.8: Frontier molecular orbitals of the Zr(IV) tetramer. (a) Tetramer structure. (b) HOMO. (c) LUMO.

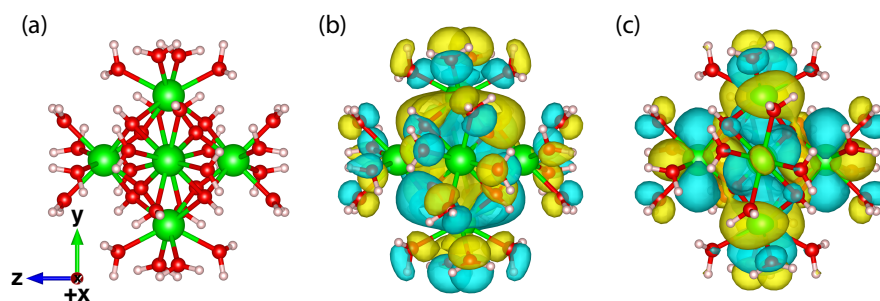


Figure 3.9: Frontier molecular orbitals of the Zr(IV) hexamer. (a) Hexamer structure. (b) HOMO. (c) LUMO.

hence their similar LUMO energies. The slightly larger orbital overlap between the Zr and the O & H atoms in the hexamer’s LUMO compared to that of the tetramer, is reflected in the hexamer’s lower LUMO energy.

Electrostatic Potential (ESP) Maps

As noted above, the difference in hydrolysis Gibbs free energy between the Zr tetramer and hexamer is on the order of counterion effects. Since we did not explicitly include counterions in this study, we generated electrostatic potential (ESP) maps to show the charge distribution in the modeled clusters as a way of estimating how counterions might affect Zr cluster stability. The regions of dense blue (more positive) charge can guide computational placement of counteranions, potentially improving the stability of the cationic Zr(IV) clusters in solution.

At first glance, the ESP map of the tetramer (Figure 3.10a) has many blue regions, but noting the location of Cl^- counteranions observed in the literature,[100–102] we know that the counterions wrap along the perimeter of the tetramer. Therefore, we rotate the tetramer

to face the side (Figures 3.10b and 3.10c). Examining the alternation of blue regions from the right of the bridging oxygen (Figure 3.10b) to the left of the bridging oxygen (image not shown) as you rotate the tetramer, we observe four deep blue locations at the bridging oxygen location. Additionally, when viewing the tetramer from the side with the top of a Zr ion at the center (Figure 3.10c), we count four deep blue locations at a diagonal on top of the Zr ion. The eight total highly positive charged regions are situated along the perimeter of the tetramer, allowing eight e.g. Cl^- counteranions to reside, thus neutralizing the overall charge of the $\{\text{Zr}_4^{8+}\}$ tetramer.

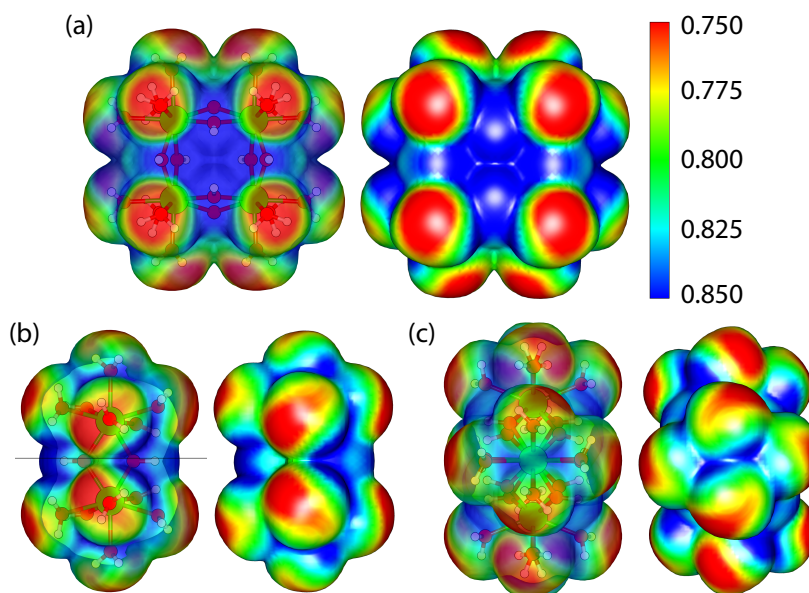


Figure 3.10: Electrostatic potential map of Zr(IV) tetramer, isosurface level = 0.001. (a) Front view. (b) Side bridging oxygen view. (c) Side top of zirconium view.

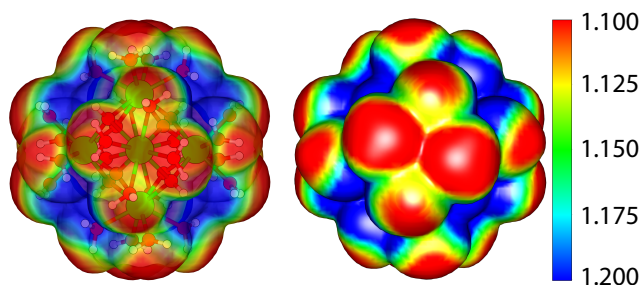


Figure 3.11: Electrostatic potential map of Zr(IV) hexamer, isosurface level = 0.001.

Inspecting the ESP map of the hexamer, we again observe eight very dark blue regions; four seen in Figure 3.11 and four mirroring these four in the back of the hexamer. Assuming that the site availability limits the $\{\text{Zr}_6^{12+}\}$ hexamer to eight total Cl^- counteranions, it can only reduce its charge to 4+. Hence, although the energy difference between the tetramer and the hexamer is on the order of counterion interactions, the hexamer may be unable to improve its competitiveness through counterion interactions, as compared with the tetramer. We note that the experimentally synthesized Zr(IV) hexamer nodes used to form the UiO-66 family of MOFs, require syntheses with sulfate counterions and glycine ligands,[129] or acetic acid ligands/modulators,[95, 99, 130] or dimethylformamide (DMF) and HCl solutions.[131] These higher-charged counterions and/or bulky ligands may be required in order to favor the geometry of the hexamer over that of the tetramer.

From the monomer’s ESP map in Figure 3.15, we note four regions of deep blue intensity at the posterior triangular faces. We hypothesize that four counteranions, such as Cl^- , could occupy these sites and neutralize the $\{\text{Zr}^{4+}\}$ monomer. In the ESP map of the dimer, it appears there are four dark blue regions around the bridging hydroxyl ligands (Figure 3.16). If the $\{\text{Zr}_2^{6+}\}$ dimer can only accommodate four Cl^- counteranions, its overall 6+ charge would be lowered to 2+.

In summary, the first-principles calculated structural characteristics and stability trends we obtain for the aqueous Zr(IV) dimer, tetramer, and hexamer match experimental observations in three main ways. First, the dimer $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$ exhibits small stability windows in Eh-pH diagrams and is often overpowered by the tetramer. Second, the tetramer $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$ is shown as the predominant cluster in an aqueous environment at low pH and relatively low concentrations of Zr. Third, the hexamer $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$ could not be stabilized at any concentration of Zr or pH, albeit neglecting any potential stabilizing effects of counterions or bulky supporting ligands.

3.4 Conclusions

To improve our understanding of aqueous zirconium chemistry and advance more sustainable synthesis strategies for functional metal-oxide clusters, we used density functional theory to investigate the thermodynamic stability of known as well as hypothetical Zr clusters (tetramer and hexamer, respectively). We analyzed Zr Pourbaix diagrams to show that the tetramer is more stable than the hexamer for all reasonable pH and potential values, in alignment with experimental observations. However, Gibbs free energies of the hexamer relative to the tetramer (9 meV/atom or ~ 17.8 kcal/mol at pH=0, V=0, and $[\text{Zr(IV)}]=1$ M) were found to be within the range of counterion effects. An electronic structure analysis revealed that while the monomer, dimer and tetramer HOMO-LUMO gaps follow quantum confinement trends, the hexamer does not. We find that the HOMO the hexamer exhibits more orbital overlap between Zr and O & H atoms as compared to the dimer or tetramer, which decreases the energy of the HOMO, and allows for a larger HOMO-LUMO gap. Finally, maps of the electrostatic potential around each cluster showed that both the tetramer and

the hexamer exhibit eight regions of high positive charge that could provide favorable binding sites for negative counteranions. Eight monovalent counterions could neutralize the tetramer but would leave the hexamer with an overall 4+ charge.

Our thermodynamic analysis suggests that although aqueous synthesis of a Zr hexamer with only water-based ligands is challenging, formation of the Zr hexamer by means of counterions or ligation may be possible. Fruitful areas for future research on this topic include an investigation of such counterion effects, and an exploration of the similarities and differences between the system studied here and aqueous hafnium clusters, which have a similar chemistry to zirconium.[24, 25, 57, 93] We hope the approach demonstrated herein will contribute to simpler and more sustainable synthesis strategies for MOFs.

3.5 Supporting Information

Structures

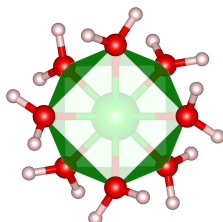


Figure 3.12: Ground state geometry of the zirconium(IV) mononuclear species $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.

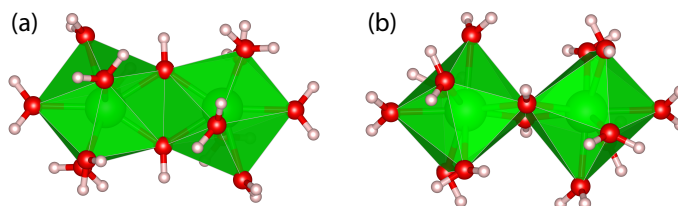


Figure 3.13: Ground state geometry of the zirconium(IV) dinuclear species $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. (a) front view (b) side view. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.

Tables of Bond Lengths and Angles

Table 3.4: Atomic distances and angles for the mononuclear zirconium cluster $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$.

	Distance (Å)
Zr-O _{H2O}	2.21
	Angle (degrees)
O _{H2O} -Zr-O _{H2O}	73, 78, 114

Table 3.5: Atomic distances and angles for the dinuclear zirconium cluster $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$. ^aZr ions on diagonal. ^bWater O atoms lying in the plane defined by the Zr ions. ^cWater O atoms lying out of the plane defined by the Zr ions.

	Distance (Å)
Zr-Zr	3.59
Zr-O _{OH}	2.13, 2.16
Zr-O _{H2O}	2.22, 2.26, 2.29
	Angle (degrees)
Zr-O _{OH} -Zr	114
O _{OH} -Zr-O _{OH}	66
O _{OH} -Zr-O _{H2O} ^b	74
O _{OH} -Zr-O _{H2O} ^c	76, 78, 80, 82
O _{H2O} ^b -Zr-O _{H2O} ^c	71, 76

Table 3.6: Atomic distances and angles for the tetranuclear zirconium cluster $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$. ^aZr ions on diagonal. ^bWater O atoms lying in the plane defined by the Zr ions. ^cWater O atoms lying out of the plane defined by the Zr ions.

	Distance (Å)
Zr-Zr	3.60
Zr-Zr ^a	5.09
Zr-O _{OH}	2.15, 2.16
Zr-O _{H2O}	2.27, 2.33
	Angle (degrees)
Zr-Zr-Zr	90
Zr-O _{OH} -Zr	113, 114
O _{OH} -Zr-O _{OH}	66
O _{OH} -Zr-O _{H2O} ^b	77, 95
O _{OH} -Zr-O _{H2O} ^c	74
O _{H2O} ^b -Zr-O _{H2O} ^c	72, 75

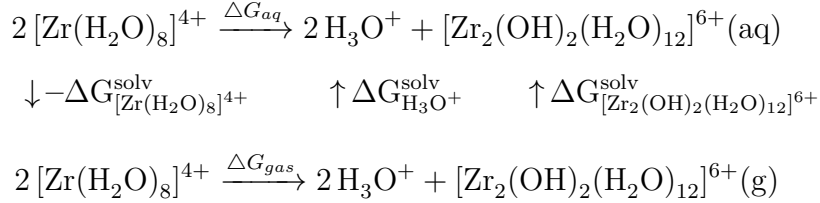
Table 3.7: Atomic distances and angles for the hexanuclear zirconium cluster $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$. ^aZr ions on diagonal. ^bShort diagonal of distorted square prismatic face. ^cLong diagonal of distorted square prismatic face.

	Distance (Å)
Zr-Zr	3.61
Zr-Zr ^a	5.10
Zr-O _{OH}	2.31
Zr-O _{H2O}	2.24, 2.30
Zr-O	2.12
	Angle (degrees)
Zr-Zr-Zr	60
Zr-O _{OH} -Zr	103
Zr-O-Zr	117
O _{OH} -Zr-O _{OH}	122
O _{OH} -Zr-O _{H2O}	79
O _{H2O} -Zr-O _{H2O}	71, 72
O _{H2O} ^b -Zr-O _{H2O} ^b	91
O _{H2O} ^c -Zr-O _{H2O} ^c	126
O-Zr-O	92
O-Zr-O _{OH}	70
O-Zr-O _{H2O}	77, 103

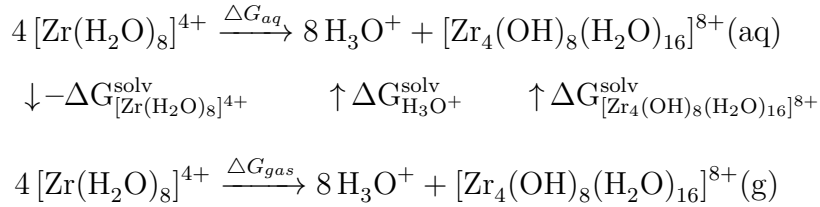
Hydrolysis Gibbs Free Energy

A thermodynamic cycle is used to determine the hydrolysis Gibbs free energy.

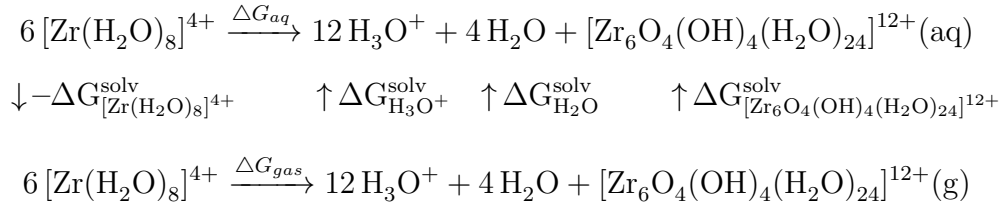
Cycle S1: Thermodynamic cycle for the Zr(IV) dimer.



Cycle S2: Thermodynamic cycle for the Zr(IV) tetramer.



Cycle S3: Thermodynamic cycle for the Zr(IV) hexamer.

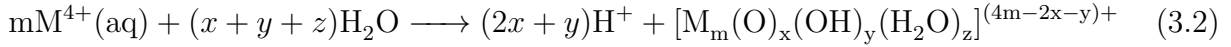


The hydrolysis Gibbs free energy is then determined with equation 3.1 and reported in Table 3.9.

$$\Delta G_{\text{aq}} = \Delta G_{\text{gas}} + \sum_{i=1}^{N_{\text{products}}} n_i \Delta G_i^{\text{solv}} - \sum_{j=1}^{N_{\text{reactants}}} n_j \Delta G_j^{\text{solv}} \quad (3.1)$$

Pourbaix Energy Formalism

To integrate the hydrolysis Gibbs free energies into the Persson Pourbaix formalism, a reaction is written with respect to the monomeric aqueous ions, equation 3.2. The corresponding Pourbaix formalism energy G_{pourbaix} is then calculated by equation 3.3 using the coefficients determined from 3.2.



$$\Delta G_{\text{pourbaix}} = \Delta G_{\text{aq}} + m \cdot \mu_{M^{4+}}^{\text{ref}} + (x + y + z) \cdot \mu_{H_2O}^{\text{ref}} + (2x + y) \cdot \mu_{H^+}^{\text{ref}} \quad (3.3)$$

A zirconium reference species M^{4+} from the Materials Project Database was required, however Zr^{4+} was not yet included. Therefore, an experimental standard Gibbs free energy ΔG° was found for the ion Zr^{4+} and the solid ZrO_2 from Pourbaix’s atlas[132]. The solid ZrO_2 already has a VASP energy in the Materials Project Database, for which we must maintain the energy difference between the ion and the solid, as explained by equation 3.4. This referencing method was also used to add $HZrO_3^-$, ZrO^{2+} , and $Zr(OH)_4(s)$ to the zirconium Pourbaix diagram in order to reproduce the Zr Pourbaix diagram from Pourbaix’s atlas.

$$\mu^{\text{ref}} = [\Delta G^{\text{expt}} - \Delta G_{ZrO_2(s)}^{\text{expt}}] + \mu_{ZrO_2(s)}^{\text{ref}} \quad (3.4)$$

Table 3.8: Referencing Values.

Species	Energy	Reference
H_2O	$\mu^{\text{ref}} = -2.46 \text{ eV}/H_2O$	Materials Project[116]
H^+	$\mu^{\text{ref}} = 0 \text{ eV}/H^+$	Materials Project[116]
$ZrO_2(s)$	$\Delta G^{\text{expt}} = -10.740 \text{ eV}/ZrO_2$	Pourbaix[132]
$ZrO_2(s)$	$\mu^{\text{ref}} = -10.809 \text{ eV}/ZrO_2$	Materials Project[116]
Zr^{4+}	$\Delta G^{\text{expt}} = -6.157 \text{ eV}/Zr^{4+}$	Pourbaix[132]
Zr^{4+}	$\mu^{\text{ref}} = -6.226 \text{ eV}/Zr^{4+}$	eq. 3.4
ZrO^{2+}	$\Delta G^{\text{expt}} = -8.737 \text{ eV}/ZrO^{2+}$	Pourbaix[132]
ZrO^{2+}	$\mu^{\text{ref}} = -8.806 \text{ eV}/ZrO^{2+}$	eq. 3.4
$HZrO_3^-$	$\Delta G^{\text{expt}} = -12.475 \text{ eV}/HZrO_3^-$	Pourbaix[132]
$HZrO_3^-$	$\mu^{\text{ref}} = -12.544 \text{ eV}/HZrO_3^-$	eq. 3.4
$Zr(OH)_4(s)$	$\Delta G^{\text{expt}} = -16.043 \text{ eV}/Zr(OH)_4$	Pourbaix[132]
$Zr(OH)_4(s)$	$\mu^{\text{ref}} = -16.112 \text{ eV}/Zr(OH)_4$	eq. 3.4

Table 3.9: Zr(IV) Cluster Hydrolysis Gibbs Free Energies and Pourbaix Formalism Energies.

Species	Cycle	ΔG_{aq} (kcal/mol)	ΔG_{aq} (eV)	m	x	y	z	$\Delta G_{pourbaix}$ (eV)	$\Delta G_{pourbaix}$ (kJ/mol)
$[Zr_2(OH)_2(H_2O)_{12}]^{6+}$	S1	-6.4	-0.278	2	0	2	12	-47.171	-4551.2
$[Zr_4(OH)_8(H_2O)_{16}]^{8+}$	S2	-23.4	-1.016	4	0	8	16	-84.961	-8197.4
$[Zr_6O_4(OH)_4(H_2O)_{24}]^{12+}$	S3	-17.5	-0.760	6	4	4	24	-116.837	-11273.1

Equilibrium Constants

For an given reaction, a reaction quotient Q can be written. For example, for equation 3.2, the reaction quotient is given by equation 3.5, as the concentration of the products over the concentration of the reactants. The change in Gibbs free energy of the reaction at a specific temperature and concentration values is given by equation 3.6, where R is the ideal gas constant $8.314 \text{ Joule mol}^{-1} \text{ K}^{-1}$ and T is room temperature 298.15 K .

$$Q = \frac{[[M_m(O)_x(OH)_y(H_2O)_z]^{(4m-2x-y)+}][H^+]^{(2x+y)}}{[M^{4+}]^m} \quad (3.5)$$

$$\Delta G_{rxn} = \Delta G_{rxn}^o + RT \ln(Q) \quad (3.6)$$

The change in Gibbs free energy for a reaction at equilibrium and standard state is shown in equation 3.7.

$$\Delta G_{rxn}^o = -RT \ln(K^o) \quad (3.7)$$

If the reaction is at an equilibrium, $\Delta G_{rxn} = 0$, and combining equations 3.6 and 3.7 shows that $Q = K^o$, i.e. the equilibrium constant. A reaction with a large and positive $\log(K^o)$ value indicates that there is a higher concentration of products than reactants.

$$K^o = \exp\left(\frac{-\Delta G_{rxn}^o}{RT}\right) = \frac{[[M_m(O)_x(OH)_y(H_2O)_z]^{(4m-2x-y)+}][H^+]^{(2x+y)}}{[M^{4+}]^m} \quad (3.8)$$

Finally, the $\log(K^o)$ exemplifies how the concentration ratios and equilibrium pH boundary between the species are related (eq. 3.9).

$$\log(K^o) = \log\left(\frac{[[M_m(O)_x(OH)_y(H_2O)_z]^{(4m-2x-y)+}]}{[M^{4+}]^m}\right) - (2x+y)pH \quad (3.9)$$

Table 3.10: Energy differences between aqueous zirconium species at various $[\text{Zr(IV)}]$ concentrations, with corresponding Pourbaix diagram heat maps.

Concentration Zr(IV) (M)	$\Delta G = \{\text{Zr}_4^{8+}\} - \text{ZrO}^{2+}$ (meV/atom)	$\Delta G = \{\text{Zr}_6^{12+}\} - \text{ZrO}^{2+}$ (meV/atom)	$\Delta G = \{\text{Zr}_6^{12+}\} - \{\text{Zr}_4^{8+}\}$ (meV/atom)
10^{-7}	10 (Fig. 3a)	22	11
10^{-6}	7	19	11
10^{-5}	5	15	10
10^{-4}	2	12	10
10^{-3}	-1 (Fig. 3b)	9 (Fig. 4a)	10
10^{-2}		6	9
10^{-1}		2	9
1		-1 (Fig. 4b)	9 (Fig. 5)

Frontier Molecular Orbitals

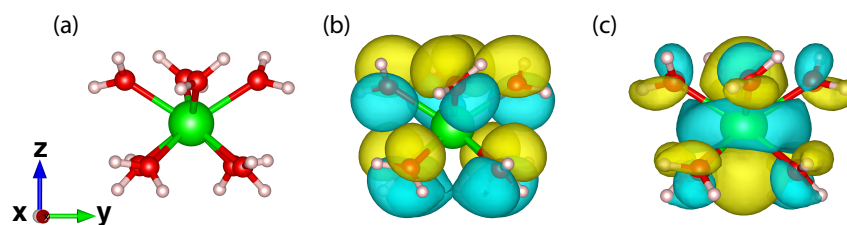


Figure 3.14: Frontier molecular orbitals for Zr(IV) monomer. (a) Monomer structure. (b) HOMO. (c) LUMO.

Electrostatic Potential Maps

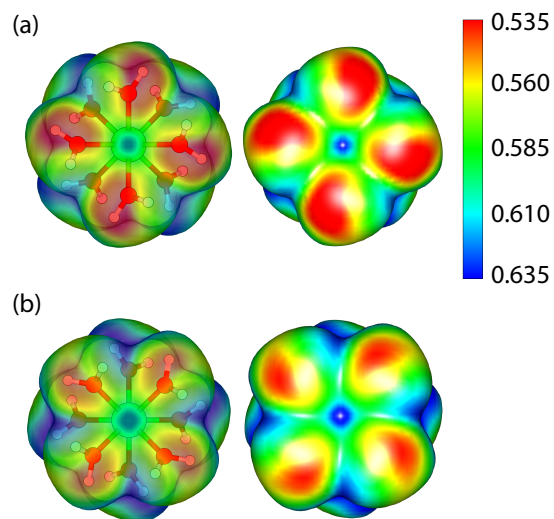


Figure 3.15: Electrostatic potential map of Zr(IV) monomer, isosurface level = 0.001. (a) Front view. (b) Back view.

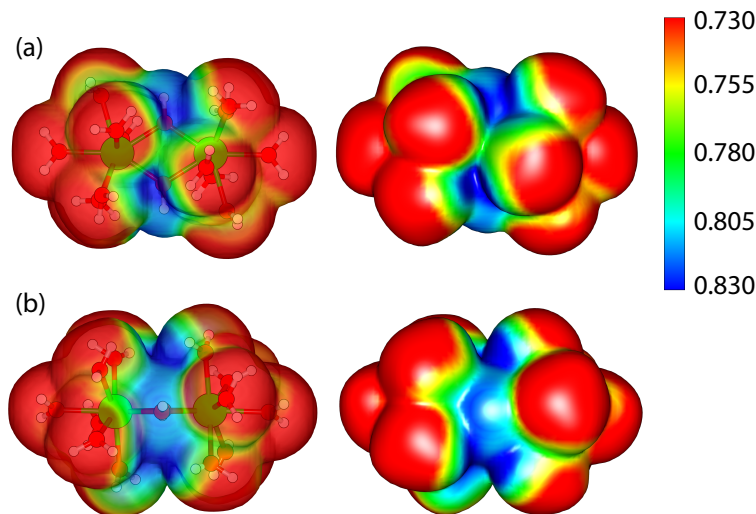


Figure 3.16: Electrostatic potential map of Zr(IV) dimer, isosurface level = 0.001. (a) Bridging view. (b) Side view.

3.6 Acknowledgements

The authors gratefully acknowledge the support of the Energy & Biosciences Institute through the EBI-Shell program. This research used the Savio computational cluster resource provided by the Berkeley Research Computing (BRC) program at the University of California, Berkeley (supported by the UC Berkeley Chancellor, Vice Chancellor for Research, and Chief Information Officer). This research also benefited from NIH S10OD023532 the Molecular Graphics and Computation Facility (MGCF) at the University of California, Berkeley.

The work described in this chapter has been submitted as a manuscript: R.D. Stern, R.S. Kingsbury, K.A. Persson. Aqueous stability of zirconium clusters, including the Zr(IV) hexanuclear hydrolysis complex $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$, from density functional theory. 2021.

Chapter 4

Summary and Outlook

Extreme ultraviolet lithography (EUVL) is the newest technique to keep up with Moore’s law to create smaller integrated circuit feature sizes. However, novel photoresist materials must be used for EUVL in order to withstand the high energy beam. Metal-oxo clusters have been identified as one photoresist solution, and specifically a recently proposed promising material is a sodium-centered tin-Keggin cluster. However, the synthesis product is a mixture of the β -NaSn₁₂ and the γ -NaSn₁₂, rather than a pure isomer, which limits the fundamental understanding of the lithographic mechanisms at play during exposure. The investigation described in this dissertation included computational modeling to determine the ground state energy of all five uncapped isomers in this Na-Sn Keggin system. Density functional theory (DFT) was used to obtain the hydrolysis Gibbs free energy and HOMO-LUMO gap of these clusters, which validated that β -NaSn₁₂ and γ -NaSn₁₂ are the most stable isomers for NaSn₁₂-Keggin ions. Additionally, computations were employed to evaluate the influence of capping (the inclusion of one or two tin atoms in this case), on the stability ordering of the NaSn₁₃-Keggin isomers. It was found that the single-capped isomers were computationally evaluated to be less stable than their respective uncapped isomer analogues. However, the double-capped γ -NaSn₁₄ was more stable than either the uncapped or single-capped clusters. Since the double-capped γ -NaSn₁₄ also required additional borate ligands, a simpler approach to obtaining a pure isomer was discovered, e.g. changing the Sn-Keggin heteroatom from sodium to calcium. This allowed the β -CaSn₁₂ Keggin ion to stabilize as a pure phase, without the need for capping. The collaboration between computations and experiments successfully confirmed that the Sn-Keggin clusters represent the only Keggin ion family so far that favors these lower symmetry isomers. Future work could focus on further probing this Sn-Keggin system’s possible capping combinations and additionally changing the central heteroatom, in order to continue improving the next-generation EUVL photoresists.

To move towards building universal guidelines for non-POMs *without* H₂O terminal ligands (category 2, as described in the Introduction), quantum chemical calculations can be used to elucidate Sn-Keggin design guidelines for promoting the δ -Fe Keggin isomer, an elusive open-shell structure, and a known building block of the mineral ferrihydrite. Electrostatic potential maps can be used to aid in cap placement, and emergent trends are

rationalized by examining distortions and electronic structure. We anticipate that either transition metal caps or s-block caps will bring the field closer to isolating the δ -Fe Keggin over the α -Fe Keggin. If similarities are found regarding how heteroatom, caps, and ligands can be exploited to promote a specific isomer in different systems, we will be able to improve design rules for Keggin clusters to aid in the discovery of new metal-oxo clusters.

Metal-oxo clusters also play a crucial role in the synthesis of metal-organic frameworks (MOFs); these 3D porous networks have vast applications from gas storage and separation to catalysis and drug delivery. One MOF with many such applications is the UiO-66 metal-organic framework series, which is constructed of hexanuclear $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{CO}_2)_{12}]$ cluster nodes and linear carboxylate linkers. Unfortunately, these Zr-based MOF cluster nodes cannot currently be manufactured in a sustainable way, motivating a search for “green” alternative synthesis methods. Stabilizing the hexanuclear Zr(IV) cluster (i.e., the hexamer, $\{\text{Zr}_6^{12+}\}$) without the use of organic ligation would enable the use of environmentally-friendly solvents such as water. The Zr(IV) tetranuclear cluster (i.e., the tetramer, $\{\text{Zr}_4^{8+}\}$) can be stabilized in solution with or without organic ligands, yet the hexamer has yet to be synthesized without supporting ligands. The reasons why certain zirconium clusters are favored in aqueous solution over others are not well understood. The work presented here successfully reports the relative thermodynamic instability of the hypothetical hexamer $\{\text{Zr}_6^{12+}\}$ compared to the ubiquitous $\{\text{Zr}_4^{8+}\}$ tetramer. Density functional theory calculations were performed to obtain the hydrolysis Gibbs free energy of these species and used to construct Zr Pourbaix diagrams that illustrate the effects of electrical potential, pH, and Zr(IV) concentration. It was found that the aqueous $\{\text{Zr}_6^{12+}\}$ hexamer is about ~ 17.8 kcal/mol less stable than the aqueous $\{\text{Zr}_4^{8+}\}$ tetramer, which is an energy difference on the order of counterion interactions. Electronic structure analyses were used to explore trends in the HOMO-LUMO gap, frontier molecular orbitals, and electrostatic potential distribution of these clusters. The evidence suggests that the aqueous $\{\text{Zr}_6^{12+}\}$ hexamer may be promoted with more strategic syntheses incorporating minimal ligands and counterions.

To expand the knowledge of Group IV clusters like zirconium and hafnium ions, alternative ligands such as peroxide can be explored. It was recently shown that Zr(IV) and Hf(IV) clusters can be stabilized in mildly acidic aqueous solutions with peroxide O_2^{2-} and oxalate $(\text{C}_2\text{O}_4)^{2-}$ ligands, and tetramethyl ammonia $\text{N}(\text{CH}_3)_4^+$ and alkali (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) counterions.[25] The authors hypothesized that the presence of both peroxide and oxalate ligands alters the solution speciation of Zr and Hf, and the counterions promote solubility and crystallization of the clusters, such that new polynuclear topologies are possible. The authors believe these factors can aid with differentiating Zr/Hf chemistry, to expand the realm of patterned thin films and MOFs.

I believe that bridging peroxide ligands provide a strategic route towards stabilizing a ring-shaped Zr hexamer structure. However, I argue that the oxalate terminal ligands can be replaced with water terminal ligands. Figure 4.1 illustrates my preliminary result of a computationally optimized circular Zr-hexamer $[\text{Zr}_6(\text{O}_2)_6(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$, i.e. $\{\text{Zr}_6^{12+}\}$. This Zr-hexamer ring has highly symmetric peroxide and hydroxide bridging ligands, as well as water terminal ligands. The same computational methods were used as reported in Chapter

3. This result shows that there is opportunity to synthesize the same geometry (circular Zr hexamer), but with less bulky terminal ligands (water instead of oxalate), promoting clean and sustainable aqueous solution manufacturing for future applications.

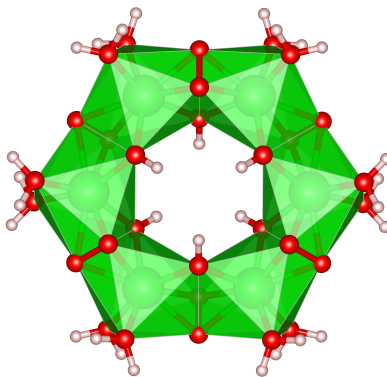


Figure 4.1: Ground state geometry of the zirconium(IV) hexanuclear peroxide species $[\text{Zr}_6(\text{O}_2)_6-(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$. Green polyhedra: zirconium. Red: oxygen. White: hydrogen.

In conclusion, the factors that influence the solution stability of metal-oxo clusters are complex and variable. However, through analyses of clusters from different groups across the periodic table, it has been shown that a computational approach can provide valuable insights into how metal-oxo clusters can be tuned and optimized for stability. The studies presented in this dissertation aim to improve computer chip manufacturing as well as metal-organic framework assembly. The anticipated future studies will help to expand the knowledge surrounding the general trends of metal-oxo clusters, with the possibility of synthesizing novel Fe-oxo and Zr/Hf-oxo cluster systems.

Bibliography

- [1] May Nyman. "Polyoxometalates and Other Metal-Oxo Clusters in Nature". In: *Encyclopedia of Geochemistry*. Ed. by Peter Bobrowsky and Brian Marker. Encyclopedia of earth sciences series. Cham: Springer International Publishing, 2016, pp. 1–5. ISBN: 978-3-319-12127-7. DOI: 10.1007/978-3-319-39193-9_43-1.
- [2] Omid Sadeghi, Lev N Zakharov, and May Nyman. "Crystal growth. Aqueous formation and manipulation of the iron-oxo Keggin ion." In: *Science* 347.6228 (Mar. 2015), pp. 1359–1362. DOI: 10.1126/science.aaa4620.
- [3] Omid Sadeghi et al. "Chemical stabilization and electrochemical destabilization of the iron keggion ion in water." In: *Inorganic Chemistry* 55.21 (Nov. 2016), pp. 11078–11088. DOI: 10.1021/acs.inorgchem.6b01694.
- [4] Omid Sadeghi et al. "The role of Bi^{3+} in promoting and stabilizing iron oxo clusters in strong acid." In: *Angewandte Chemie* 57.21 (May 2018), pp. 6247–6250. DOI: 10.1002/anie.201802915.
- [5] Bidisa Das. "Theoretical Study of Small Iron-Oxyhydroxide Clusters and Formation of Ferrihydrite." In: *The Journal of Physical Chemistry. A* 122.2 (Jan. 2018), pp. 652–661. DOI: 10.1021/acs.jpca.7b09470.
- [6] Qiushi Yin et al. "A fast soluble carbon-free molecular water oxidation catalyst based on abundant metals." In: *Science* 328.5976 (Apr. 2010), pp. 342–345. DOI: 10.1126/science.1185372.
- [7] Marta Blasco-Ahicart et al. "Polyoxometalate electrocatalysts based on earth-abundant metals for efficient water oxidation in acidic media." In: *Nature Chemistry* 10.1 (2018), pp. 24–30. ISSN: 1755-4330. DOI: 10.1038/nchem.2874.
- [8] Jeffrey T. Rhule et al. "Polyoxometalates in Medicine". In: *Chemical Reviews* 98.1 (Feb. 1998), pp. 327–358. ISSN: 0009-2665. DOI: 10.1021/cr960396q.
- [9] In Su Lee et al. "Selective precipitation of prions by polyoxometalate complexes." In: *Journal of the American Chemical Society* 127.40 (Oct. 2005), pp. 13802–13803. DOI: 10.1021/ja055219y.
- [10] J. T. Anderson et al. "Solution-Processed HfSO_x and ZrSO_x Inorganic Thin-Film Dielectrics and Nanolaminates". In: *Advanced Functional Materials* 17.13 (Sept. 2007), pp. 2117–2124. ISSN: 1616301X. DOI: 10.1002/adfm.200601135.

- [11] David A Marsh et al. “Ln polyoxocations: yttrium oxide solution speciation & solution deposited thin films.” In: *Dalton Transactions* 46.3 (Jan. 2017), pp. 947–955. DOI: 10.1039/c6dt03733j.
- [12] Anna Llordés et al. “Tunable near-infrared and visible-light transmittance in nano-crystal-in-glass composites.” In: *Nature* 500.7462 (Aug. 2013), pp. 323–326. DOI: 10.1038/nature12398.
- [13] Christoph Busche et al. “Design and fabrication of memory devices based on nanoscale polyoxometalate clusters.” In: *Nature* 515.7528 (Nov. 2014), pp. 545–549. DOI: 10.1038/nature13951.
- [14] Richard P Oleksak et al. “Chemical and structural investigation of high-resolution patterning with HafSO(x).” In: *ACS Applied Materials & Interfaces* 6.4 (Feb. 2014), pp. 2917–2921. DOI: 10.1021/am405463u.
- [15] Sonia Castellanos Ortega et al. “Ti, Zr, and Hf-based molecular hybrid materials as EUV photoresists”. In: *Extreme Ultraviolet (EUV) Lithography IX*. Ed. by Nelson M. Felix and Kenneth A. Goldberg. SPIE, Mar. 2018, p. 6. ISBN: 9781510616585. DOI: 10.1117/12.2297167.
- [16] May Nyman. “Polyoxoniobate chemistry in the 21st century.” In: *Dalton Transactions* 40.32 (Aug. 2011), pp. 8049–8058. DOI: 10.1039/c1dt10435g.
- [17] Wei Wang et al. “Crystallizing elusive chromium polycations”. In: *Chem* 1.6 (Dec. 2016), pp. 887–901. ISSN: 24519294. DOI: 10.1016/j.chempr.2016.11.006.
- [18] Avi Bino et al. “Synthesis and Structure of [Fe₁₃ O₄ F₂₄ (OMe)₁₂]⁵⁻: The First Open-Shell Keggin Ion”. In: *Journal of the American Chemical Society* 124.17 (May 2002), pp. 4578–4579. ISSN: 0002-7863. DOI: 10.1021/ja025590a.
- [19] Aleksandar Kondinski and Kirill Yu Monakhov. “Breaking the Gordian Knot in the Structural Chemistry of Polyoxometalates: Copper(II)-Oxo/Hydroxo Clusters.” In: *Chemistry - A European Journal* 23.33 (June 2017), pp. 7841–7852. DOI: 10.1002/chem.201605876.
- [20] Sumit Saha et al. “Alkyltin keggins clusters templated by sodium.” In: *Angewandte Chemie* 56.34 (Aug. 2017), pp. 10140–10144. DOI: 10.1002/anie.201701703.
- [21] Yu Zhu et al. “Stabilizing γ -Alkyltin-Oxo Keggin Ions by Borate Functionalization.” In: *Inorganic Chemistry* 58.7 (Apr. 2019), pp. 4534–4539. DOI: 10.1021/acs.inorgchem.9b00093.
- [22] Viswanathan Baskar et al. “Reverse-Keggin ions: polycondensation of antimonate ligands give inorganic cryptand.” In: *Journal of the American Chemical Society* 129.11 (Mar. 2007), pp. 3042–3043. DOI: 10.1021/ja068214p.

- [23] Fu-Qiang Zhang et al. “On the origin of the inverted stability order of the reverse-Keggin $[(\text{MnO}_4)(\text{CH}_3)_{12}\text{Sb}_{12}\text{O}_{24}]^{6-}$: a DFT study of alpha, beta, gamma, delta, and epsilon isomers.” In: *Inorganic Chemistry* 49.12 (June 2010), pp. 5472–5481. DOI: 10.1021/ic100343t.
- [24] James A Sommers et al. “Peroxide-Promoted Disassembly Reassembly of Zr-Polyoxocations.” In: *Journal of the American Chemical Society* 141.42 (Oct. 2019), pp. 16894–16902. DOI: 10.1021/jacs.9b08627.
- [25] Karoly Kozma, Lev N. Zakharov, and May Nyman. “Counteraction-controlled nuclearity of Zr/Hf peroxo-oxalates”. In: *Crystal growth & design* (Aug. 2020). ISSN: 1528-7483. DOI: 10.1021/acs.cgd.0c00713.
- [26] Liang Feng et al. “Metal-Organic Frameworks Based on Group 3 and 4 Metals.” In: *Advanced Materials* (Sept. 2020), e2004414. DOI: 10.1002/adma.202004414.
- [27] Sara Goberna-Ferrón et al. “Amphoteric aqueous hafnium cluster chemistry.” In: *Angewandte Chemie* 55.21 (May 2016), pp. 6221–6224. DOI: 10.1002/anie.201601134.
- [28] Pedro I Molina et al. “Aqueous Bismuth Titanium-Oxo Sulfate Cluster Speciation and Crystallization.” In: *Angewandte Chemie* 56.51 (Dec. 2017), pp. 16277–16281. DOI: 10.1002/anie.201709539.
- [29] Christopher R Armstrong, William H Casey, and Alexandra Navrotsky. “Energetics of Al Keggin cluster compounds.” In: *Proceedings of the National Academy of Sciences of the United States of America* 108.36 (Sept. 2011), pp. 14775–14779. DOI: 10.1073/pnas.1111243108.
- [30] Lindsay A Wills et al. “Group additivity-Pourbaix diagrams advocate thermodynamically stable nanoscale clusters in aqueous environments.” In: *Nat Commun* 8 (June 2017), p. 15852. DOI: 10.1038/ncomms15852.
- [31] Wei Wang et al. “Reaction Pathway to the Only Open-Shell Transition-Metal Keggin Ion without Organic Ligation”. In: *European journal of inorganic chemistry* 2018.42 (Nov. 2018), pp. 4638–4642. ISSN: 14341948. DOI: 10.1002/ejic.201801087.
- [32] Xavier López et al. “Electronic Properties of Polyoxometalates: A DFT Study of α / β - $[\text{XM}_{12}\text{O}_{40}]^{n-}$ Relative Stability (M = W, Mo and X a Main Group Element)”. In: *Journal of the American Chemical Society* 123.39 (Oct. 2001), pp. 9571–9576. ISSN: 0002-7863. DOI: 10.1021/ja010768z.
- [33] Xavier López, Jorge A Fernández, and Josep M Poblet. “Redox properties of polyoxometalates: new insights on the anion charge effect.” In: *Dalton Transactions* 9 (Mar. 2006), pp. 1162–1167. DOI: 10.1039/b507599h.
- [34] Alain Chaumont and Georges Wipff. “Ion aggregation in concentrated aqueous and methanol solutions of polyoxometallates Keggin anions: the effect of counterions investigated by molecular dynamics simulations.” In: *Physical Chemistry Chemical Physics* 10.46 (Dec. 2008), pp. 6940–6953. DOI: 10.1039/b810440a.

- [35] Blandine Courcot and Adam J Bridgeman. "Modeling the interactions between polyoxometalates and their environment." In: *Journal of Computational Chemistry* 32.15 (Nov. 2011), pp. 3143–3153. DOI: 10.1002/jcc.21894.
- [36] Yu-Jie Wang et al. "Capped Polyoxometalate Pillars between Metal-Organic Layers for Transferring a Supramolecular Structure into a Covalent 3D Framework." In: *Inorganic Chemistry* 57.3 (Feb. 2018), pp. 1342–1349. DOI: 10.1021/acs.inorgchem.7b02754.
- [37] J.M. Maestre et al. "Electronic Structure of the Highly Reduced Polyoxoanion $\text{PMo}_{12}\text{O}_{40}(\text{VO})_2^{5-}$: A DFT Study". In: *Inorganic Chemistry* 37 (June 1998).
- [38] Xavier López, Carles Bo, and Josep M Poblet. "Electronic properties of polyoxometalates: electron and proton affinity of mixed-addenda Keggin and Wells-Dawson anions." In: *Journal of the American Chemical Society* 124.42 (Oct. 2002), pp. 12574–12582. DOI: 10.1021/ja020407z.
- [39] Joan Miquel Maestre et al. "A DFT Study of the Electronic Spectrum of the α -Keggin Anion $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ ". In: *Inorganic Chemistry* 41.7 (Apr. 2002), pp. 1883–1888. ISSN: 0020-1669. DOI: 10.1021/ic0110676.
- [40] Josep M. Poblet, Xavier López, and Carles Bo. "Ab initio and DFT modelling of complex materials: towards the understanding of electronic and magnetic properties of polyoxometalates". In: *Chem. Soc. Rev.* 32.5 (2003), pp. 297–308. ISSN: 0306-0012. DOI: 10.1039/{B109928K}.
- [41] Xavier López and Josep M Poblet. "DFT study on the five isomers of $\text{PW}_{12}\text{O}_{40}^{3-}$: relative stabilization upon reduction." In: *Inorganic Chemistry* 43.22 (Nov. 2004), pp. 6863–6865. DOI: 10.1021/ic049119p.
- [42] Xavier López et al. "Are the solvent effects critical in the modeling of polyoxoanions?" In: *Journal of Computational Chemistry* 25.12 (Sept. 2004), pp. 1542–1549. DOI: 10.1002/jcc.20083.
- [43] Xavier López et al. "Highly Reduced Polyoxometalates: Ab Initio and DFT Study of $[\text{PMo}_8\text{V}_4\text{O}_{40}(\text{VO})_4]^{5-}$ ". In: *Journal of Chemical Theory and Computation* 1.5 (Sept. 2005), pp. 856–861. DOI: 10.1021/ct050040z.
- [44] Xavier López et al. "Polyoxometalates in solution: Molecular dynamics simulations on the α - $\text{PW}_{12}\text{O}_{40}^{3-}$ Keggin anion in aqueous media." In: *The Journal of Physical Chemistry. A* 109.6 (Feb. 2005), pp. 1216–1222. DOI: 10.1021/jp046862u.
- [45] Jorge A. Fernández, Xavier López, and Josep M. Poblet. "A DFT study on the effect of metal, anion charge, heteroatom and structure upon the relative basicities of polyoxoanions". In: *Journal of Molecular Catalysis A: Chemical* 262.1-2 (Feb. 2007), pp. 236–242. ISSN: 13811169. DOI: 10.1016/j.molcata.2006.08.065.
- [46] Xavier López et al. "Current trends in the computational modelling of polyoxometalates". In: *Theoretical chemistry accounts* 128.4-6 (Mar. 2011), pp. 393–404. ISSN: 1432-881X. DOI: 10.1007/s00214-010-0820-9.

- [47] Davide Ravelli et al. “Predicting the UV spectrum of polyoxometalates by TD-DFT.” In: *Journal of Computational Chemistry* 32.14 (Nov. 2011), pp. 2983–2987. DOI: 10.1002/jcc.21879.
- [48] Xavier López et al. “Structure, properties and reactivity of polyoxometalates: a theoretical perspective.” In: *Chemical Society Reviews* 41.22 (Nov. 2012), pp. 7537–7571. DOI: 10.1039/c2cs35168d.
- [49] Alain Chaumont and Georges Wipff. “Do Keggin anions repulse each other in solution? The effect of solvent, counterions and ion representation investigated by free energy (PMF) simulations”. In: *Comptes Rendus Chimie* 15.2-3 (Feb. 2012), pp. 107–117. ISSN: 16310748. DOI: 10.1016/j.crci.2011.07.001.
- [50] C. André Ohlin, James R. Rustad, and William H. Casey. “The energetics of isomerisation in Keggin-series aluminate cations”. In: *Dalton Trans.* 43.39 (2014), pp. 14533–14536. ISSN: 1477-9226. DOI: 10.1039/{C4DT01763C}.
- [51] Francisca Clavería-Cádiz, Ramiro Arratia-Pérez, and Desmond MacLeod-Carey. “Density functional study on Keggin heteropolyanions containing fifth period main group heteroatoms”. In: *Polyhedron* 117 (Oct. 2016), pp. 478–486. ISSN: 02775387. DOI: 10.1016/j.poly.2016.06.035.
- [52] Xavier López. “Effect of protonation, composition and isomerism on the redox properties and electron (de)localization of classical polyoxometalates”. In: *Physical Sciences Reviews* 2.11 (Nov. 2017). ISSN: 2365-6581. DOI: 10.1515/psr-2017-0137.
- [53] Alena Kremleva et al. “Quantum chemical modeling of tri-Mn-substituted W-based Keggin polyoxoanions”. In: *Electrochimica acta* 231 (Mar. 2017), pp. 659–669. ISSN: 00134686. DOI: 10.1016/j.electacta.2017.02.046.
- [54] Dylan Sures et al. “Alkali-Driven Disassembly and Reassembly of Molecular Niobium Oxide in Water.” In: *J Am Chem Soc* 140.34 (Aug. 2018), pp. 10803–10813. DOI: 10.1021/jacs.8b05015.
- [55] Nadiia I. Gumerova and Annette Rompel. “Synthesis, structures and applications of electron-rich polyoxometalates”. In: *Nature Reviews Chemistry* 2.2 (Feb. 2018), p. 0112. ISSN: 2397-3358. DOI: 10.1038/s41570-018-0112.
- [56] Brian Cardineau et al. “EUV resists based on tin-oxo clusters”. In: *Advances in Patterning Materials and Processes XXXI*. Ed. by Thomas I. Wallow and Christoph K. Hohle. Vol. 9051. SPIE Proceedings. SPIE, Apr. 2014, 90511B. DOI: 10.1117/12.2046536.
- [57] James A Sommers et al. “Differentiating Zr/HfIV Aqueous Polyoxocation Chemistry with Peroxide Ligation.” In: *Inorganic Chemistry* 60.3 (Feb. 2021), pp. 1631–1640. DOI: 10.1021/acs.inorgchem.0c03128.
- [58] John Daintith. *A Dictionary of Physics*. 6th ed. Oxford University Press, 2009, pp. i–624. ISBN: 9780191726798.

- [59] Gerbrand Ceder and Kristin A. Persson. “The Stuff of Dreams”. In: *Scientific American* 309.6 (Dec. 2013).
- [60] *Lithography Process Overview*. Integrated Micro Materials <https://imicromaterials.com/technical/lithography-process-overview>.
- [61] Burn J. Lin. “Immersion lithography and its impact on semiconductor manufacturing”. In: *Journal of Micro/Nanolithography, MEMS, and MOEMS* 3.3 (July 2004), p. 377. ISSN: 1932-5150. DOI: 10.1117/1.1756917.
- [62] Hiroshi Ito. “Chemically amplified resists: past, present, and future”. In: *Advances in Resist Technology and Processing XVI*. Ed. by Will Conley. Vol. 3678. SPIE Proceedings. SPIE, June 1999, p. 2. DOI: 10.1117/12.350143.
- [63] Lars W. Liebmann. “Mask challenges in high-resolution lithography”. In: *Single Frequency Semiconductor Lasers*. Ed. by Jens Buus. SPIE, Aug. 2017, p. 5. ISBN: 9780819405357. DOI: 10.1117/12.2284085.
- [64] J. Fung Chen et al. “Development of a computational lithography roadmap”. In: *Optical Microlithography XXI*. Vol. 6924. SPIE Proceedings. SPIE, Mar. 2008, p. 69241C. DOI: 10.1117/12.773060.
- [65] Harry J. Levinson. “Extreme ultraviolet lithographypath to manufacturing”. In: *Journal of Micro/Nanolithography, MEMS, and MOEMS* 8.4 (Oct. 2009), p. 041501. ISSN: 1932-5150. DOI: 10.1117/1.3273965.
- [66] Ryan T. Frederick et al. “Surface characterization of tin-based inorganic EUV resists”. In: *Advances in Patterning Materials and Processes XXXV*. Ed. by Christoph K. Hohle and Roel Gronheid. SPIE, Mar. 2018, p. 6. ISBN: 9781510616646. DOI: 10.1117/12.2297484.
- [67] Richard P. Oleksak et al. “Evaluation of Thermal and Radiation Induced Chemistries of Metal Oxo-Hydroxo Clusters for Next-Generation Nanoscale Inorganic Resists”. In: *ACS Applied Nano Materials* 1.9 (Sept. 2018), pp. 4548–4556. ISSN: 2574-0970. DOI: 10.1021/acsanm.8b00865.
- [68] Christopher K. Ober et al. “The challenges of highly sensitive EUV photoresists”. In: *Journal of Photopolymer Science and Technology* 31.2 (June 2018), pp. 261–265. ISSN: 0914-9244. DOI: 10.2494/photopolymer.31.261.
- [69] J. F. Keggin. “Structure of the Molecule of 12-Phosphotungstic Acid”. In: *Nature* 131.3321 (June 1933), pp. 908–909. ISSN: 0028-0836. DOI: 10.1038/131908b0.
- [70] Nassir Mojarad, Jens Gobrecht, and Yasin Ekinici. “Beyond EUV lithography: a comparative study of efficient photoresists’ performance.” In: *Scientific Reports* 5 (Mar. 2015), p. 9235. DOI: 10.1038/srep09235.

- [71] James Passarelli et al. “High-sensitivity molecular organometallic resist for EUV (MORE)”. In: *Advances in Patterning Materials and Processes XXXII*. Ed. by Thomas I. Wallow and Christoph K. Hohle. Vol. 9425. SPIE Proceedings. SPIE, Mar. 2015, 94250T. DOI: 10.1117/12.2086599.
- [72] Mengjun Li et al. “Novel Sn-based photoresist for high aspect ratio patterning”. In: *Advances in Patterning Materials and Processes XXXV*. Ed. by Christoph K. Hohle and Roel Gronheid. SPIE, Mar. 2018, p. 19. ISBN: 9781510616646. DOI: 10.1117/12.2297440.
- [73] Kristina D Closser et al. “The importance of inner-shell electronic structure for enhancing the EUV absorption of photoresist materials.” In: *The Journal of Chemical Physics* 146.16 (Apr. 2017), p. 164106. DOI: 10.1063/1.4981815.
- [74] Meredith C. Sharps et al. “Organotin Carboxylate Reagents for Nanopatterning: Chemical Transformations during Direct-Write Electron Beam Processes”. In: *Chemistry of Materials* (June 2019). ISSN: 0897-4756. DOI: 10.1021/acs.chemmater.9b01440.
- [75] Danielle C Hutchison et al. “Alkyltin clusters: the less symmetric Keggin isomers.” In: *Dalton Transactions* 29 (July 2018), pp. 9804–9813. DOI: 10.1039/c8dt01950a.
- [76] Rodrigo Casasnovas et al. “Theoretical p K a calculations with continuum model solvents, alternative protocols to thermodynamic cycles”. In: *International journal of quantum chemistry* 114.20 (Oct. 2014), pp. 1350–1363. ISSN: 00207608. DOI: 10.1002/qua.24699.
- [77] Eric J Sundstrom et al. “Computational and experimental study of the mechanism of hydrogen generation from water by a molecular molybdenum-oxo electrocatalyst.” In: *Journal of the American Chemical Society* 134.11 (Mar. 2012), pp. 5233–5242. DOI: 10.1021/ja210949r.
- [78] Lei Zhang et al. “Energetic trends in monomer building blocks for uranyl peroxide clusters.” In: *Inorganic Chemistry* 58.1 (Jan. 2019), pp. 439–445. DOI: 10.1021/acs.inorgchem.8b02661.
- [79] Fu-Qiang Zhang et al. “Structural and electronic properties of hetero-transition-metal Keggin anions: A DFT Study of alpha/beta-[XW₁₂O₄₀]ⁿ⁻ (X = Cr^{VI}, V^V, Ti^{IV}, Fe^{III}, Co^{III}, Ni^{III}, Co^{II}, Zn^{II}) Relative Stability.” In: *The Journal of Physical Chemistry. A* 111.1 (Jan. 2007), pp. 159–166. DOI: 10.1021/jp064732a.
- [80] Ira A. Weinstock et al. “Equilibria between α and β Isomers of Keggin Heteropolytungstates”. In: *Journal of the American Chemical Society* 121.19 (May 1999), pp. 4608–4617. ISSN: 0002-7863. DOI: 10.1021/ja982908j.
- [81] R. D. Shannon. “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides”. In: *Acta Crystallographica Section A* 32.5 (Sept. 1976), pp. 751–767. ISSN: 0567-7394. DOI: 10.1107/S0567739476001551.

- [82] Amy Kaufman Katz et al. "Calcium Ion Coordination: A Comparison with That of Beryllium, Magnesium, and Zinc". In: *Journal of the American Chemical Society* 118.24 (Jan. 1996), pp. 5752–5763. ISSN: 0002-7863. DOI: 10.1021/ja953943i.
- [83] Kris F. Tesh et al. "Structural relationships between mono- and dimeric bis(alkoxides) and bis(aryloxides) of calcium and barium." In: *Inorganic Chemistry* 31.26 (Dec. 1992), pp. 5572–5579. ISSN: 0020-1669. DOI: 10.1021/ic00052a037.
- [84] Danielle C Hutchison et al. "Butyltin Keggin Ion with a Rare Four-Coordinate Ca Center." In: *Inorganic Chemistry* 59.5 (Mar. 2020), pp. 2900–2909. DOI: 10.1021/acs.inorgchem.9b03261.
- [85] Axel D. Becke. "Density-functional thermochemistry. III. The role of exact exchange". In: *J. Chem. Phys.* 98.7 (1993), p. 5648. ISSN: 00219606. DOI: 10.1063/1.464913.
- [86] P. C. Hariharan and J. A. Pople. "The influence of polarization functions on molecular orbital hydrogenation energies". In: *Theoretica chimica acta* 28.3 (1973), pp. 213–222. ISSN: 0040-5744. DOI: 10.1007/{BF00533485}.
- [87] Willard R. Wadt and P. Jeffrey Hay. "Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi". In: *The Journal of Chemical Physics* 82.1 (Jan. 1985), pp. 284–298. ISSN: 0021-9606. DOI: 10.1063/1.448800.
- [88] Aleksandr V Marenich, Christopher J Cramer, and Donald G Truhlar. "Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions." In: *The Journal of Physical Chemistry. B* 113.18 (May 2009), pp. 6378–6396. DOI: 10.1021/jp810292n.
- [89] R. Krishnan et al. "Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions". In: *J. Chem. Phys.* 72.1 (1980), p. 650. ISSN: 00219606. DOI: 10.1063/1.438955.
- [90] Rebecca Stern et al. "Alkyltin Keggin clusters as EUVL photoresist technology". In: *International Conference on Extreme Ultraviolet Lithography 2019*. Ed. by Kurt G. Ronse et al. SPIE, Sept. 2019, p. 72. ISBN: 9781510629974. DOI: 10.1117/12.2538639.
- [91] Markus J Kalmutzki, Nikita Hanikel, and Omar M Yaghi. "Secondary building units as the turning point in the development of the reticular chemistry of MOFs." In: *Science Advances* 4.10 (Oct. 2018), eaat9180. DOI: 10.1126/sciadv.aat9180.
- [92] Dong Yang et al. "The surface chemistry of metal oxide clusters: from metal–organic frameworks to minerals". In: *ACS Central Science* (Aug. 2020). ISSN: 2374-7943. DOI: 10.1021/acscentsci.0c00803.
- [93] Shuai Yuan et al. "Stable Metal-Organic Frameworks with Group 4 Metals: Current Status and Trends." In: *ACS central science* 4.4 (Apr. 2018), pp. 440–450. DOI: 10.1021/acscentsci.8b00073.

- [94] Priscilla Rocío-Bautista et al. “Metal-Organic Frameworks in Green Analytical Chemistry”. In: *Separations* 6.3 (June 2019), p. 33. ISSN: 2297-8739. DOI: 10.3390/separations6030033.
- [95] Ignas Pakamorić et al. “An ambient-temperature aqueous synthesis of zirconium-based metal-organic frameworks”. In: *Green Chemistry* 20.23 (2018), pp. 5292–5298. ISSN: 1463-9262. DOI: 10.1039/C8GC02312C.
- [96] Stuart L James et al. “Mechanochemistry: opportunities for new and cleaner synthesis.” In: *Chemical Society Reviews* 41.1 (Jan. 2012), pp. 413–447. DOI: 10.1039/c1cs15171a.
- [97] Krunoslav Užarević et al. “Mechanochemical and solvent-free assembly of zirconium-based metal-organic frameworks.” In: *Chemical Communications* 52.10 (Feb. 2016), pp. 2133–2136. DOI: 10.1039/c5cc08972g.
- [98] Jasmina Hafizovic Cavka et al. “A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability.” In: *Journal of the American Chemical Society* 130.42 (Oct. 2008), pp. 13850–13851. DOI: 10.1021/ja8057953.
- [99] Christoph Hennig et al. “Solution species and crystal structure of Zr(IV) acetate.” In: *Inorg Chem* 56.5 (Mar. 2017), pp. 2473–2480. DOI: 10.1021/acs.inorgchem.6b01624.
- [100] A. Clearfield and P. A. Vaughan. “The crystal structure of zirconyl chloride octahydrate and zirconyl bromide octahydrate”. In: *Acta crystallographica* 9.7 (July 1956), pp. 555–558. ISSN: 0365-110X. DOI: 10.1107/S0365110X56001558.
- [101] George M. Muha and Philip A. Vaughan. “Structure of the complex ion in aqueous solutions of zirconyl and hafnium oxyhalides”. In: *The Journal of Chemical Physics* 33.1 (July 1960), pp. 194–199. ISSN: 0021-9606. DOI: 10.1063/1.1731077.
- [102] Thomas C. W. Mak. “Refinement of the crystal structure of zirconyl chloride octahydrate”. In: *Canadian journal of chemistry* 46.22 (Nov. 1968), pp. 3491–3497. ISSN: 0008-4042. DOI: 10.1139/v68-579.
- [103] Daiqin Chen et al. “In Vivo Targeting and Positron Emission Tomography Imaging of Tumor with Intrinsically Radioactive Metal-Organic Frameworks Nanomaterials.” In: *ACS Nano* 11.4 (Apr. 2017), pp. 4315–4327. DOI: 10.1021/acsnano.7b01530.
- [104] Martino Rimoldi et al. “Catalytic Zirconium/Hafnium-Based Metal-Organic Frameworks”. In: *ACS catalysis* 7.2 (Feb. 2017), pp. 997–1014. ISSN: 2155-5435. DOI: 10.1021/acscatal.6b02923.
- [105] Marialore Sulpizi and Johannes Lützenkirchen. “Atypical titration curves for GaAl₁₂ Keggin-ions explained by a joint experimental and simulation approach.” In: *The Journal of Chemical Physics* 148.22 (June 2018), p. 222836. DOI: 10.1063/1.5024201.

- [106] Niny Rao et al. “Computational study of the Zr^{4+} tetranuclear polymer, $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$.” In: *J Phys Chem A* 111.45 (Nov. 2007), pp. 11395–11399. DOI: 10.1021/jp0734880.
- [107] Niny Rao, Marian N Holerca, and Vojislava Pophristic. “Computational study of the small $\text{Zr}(\text{IV})$ polynuclear species.” In: *Journal of Chemical Theory and Computation* 4.1 (Jan. 2008), pp. 145–155. DOI: 10.1021/ct7001094.
- [108] Takayuki Sasaki et al. “Hydrolysis constant and coordination geometry of zirconium(IV)”. In: *Journal of nuclear science and technology* 45.8 (Aug. 2008), pp. 735–739. ISSN: 0022-3131. DOI: 10.1080/18811248.2008.9711474.
- [109] D B Jansen van Vuuren, H M Krieg, and C G C E van Sittert. “Computational chemistry study of zirconium monomers in low acid concentration aqueous solutions”. In: *IOP Conference Series: Materials Science and Engineering* 430.1 (Oct. 2018), p. 012017. ISSN: 1757-899X. DOI: 10.1088/1757-899X/430/1/012017.
- [110] Anjali M Patel et al. “Efficient Pourbaix diagrams of many-element compounds.” In: *Physical Chemistry Chemical Physics* 21.45 (Dec. 2019), pp. 25323–25327. DOI: 10.1039/c9cp04799a.
- [111] Arunima K Singh et al. “Robust and synthesizable photocatalysts for CO_2 reduction: a data-driven materials discovery.” In: *Nature Communications* 10.1 (Jan. 2019), p. 443. DOI: 10.1038/s41467-019-08356-1.
- [112] Paul F. Newhouse et al. “Discovery and Characterization of a Pourbaix-Stable, 1.8 eV Direct Gap Bismuth Manganate Photoanode”. In: *Chemistry of Materials* 29.23 (Dec. 2017), pp. 10027–10036. ISSN: 0897-4756. DOI: 10.1021/acs.chemmater.7b03591.
- [113] Aniketa Shinde et al. “Discovery of Manganese-Based Solar Fuel Photoanodes via Integration of Electronic Structure Calculations, Pourbaix Stability Modeling, and High-Throughput Experiments”. In: *ACS Energy Letters* 2.10 (Oct. 2017), pp. 2307–2312. ISSN: 2380-8195. DOI: 10.1021/acsenenergylett.7b00607.
- [114] Kristin A. Persson et al. “Prediction of solid-aqueous equilibria: Scheme to combine first-principles calculations of solids with experimental aqueous states”. In: *Physical Review B* 85.23 (June 2012), p. 235438. ISSN: 1098-0121. DOI: 10.1103/PhysRevB.85.235438.
- [115] Arunima K. Singh et al. “Electrochemical stability of metastable materials”. In: *Chemistry of Materials* 29.23 (Dec. 2017), pp. 10159–10167. ISSN: 0897-4756. DOI: 10.1021/acs.chemmater.7b03980.
- [116] Anubhav Jain et al. “Commentary: The Materials Project: A materials genome approach to accelerating materials innovation”. In: *APL materials* 1.1 (2013), p. 011002. ISSN: 2166532X. DOI: 10.1063/1.4812323.
- [117] M. J. Frisch et al. *Gaussian 16 Revision A.03*. Gaussian Inc. Wallingford CT. 2016.

- [118] Johannes Kreutzer, Peter Blaha, and Ulrich Schubert. “Assessment of different basis sets and DFT functionals for the calculation of structural parameters, vibrational modes and ligand binding energies of Zr_4O_{12} (carboxylate) clusters”. In: *Computational and Theoretical Chemistry* 1084 (May 2016), pp. 162–168. ISSN: 2210271X. DOI: 10.1016/j.comptc.2016.03.030.
- [119] Yue Yang, Michael N Weaver, and Kenneth M Merz. “Assessment of the ”6-31+G** + LANL2DZ” mixed basis set coupled with density functional theory methods and the effective core potential: prediction of heats of formation and ionization potentials for first-row-transition-metal complexes.” In: *The Journal of Physical Chemistry. A* 113.36 (Sept. 2009), pp. 9843–9851. DOI: 10.1021/jp807643p.
- [120] A Klamt and G Schüürmann. “COSMO: A New Approach to Dielectric Screening in Solvents with Explicit Expressions for the Screening Energy and its Gradient”. In: *J. Chem. Soc., Perkin Trans. 2* 5 (1993), pp. 799–805.
- [121] Edina Balogh et al. “Rates of oxygen-isotope exchange between sites in the $[\text{HxTa}_6\text{O}_{19}]^{(8-x)-}$ (aq) Lindqvist ion and aqueous solutions: comparisons to $[\text{HxNb}_6\text{O}_{19}]^{(8-x)-}$ (aq).” In: *Inorganic Chemistry* 46.17 (Aug. 2007), pp. 7032–7039. DOI: 10.1021/ic700845e.
- [122] NM O’Boyle, AL Tenderholt, and KM Langner. “cclib: A library for package-independent computational chemistry algorithms”. In: *J Comput Chem* 29 (2008), pp. 839–845. DOI: 10.1002/jcc.20823.
- [123] Shyue Ping Ong et al. “Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis”. In: *Computational Materials Science* 68 (Feb. 2013), pp. 314–319. ISSN: 09270256. DOI: 10.1016/j.commatsci.2012.10.028.
- [124] Camelia Hagfeldt, Vadim Kessler, and Ingmar Persson. “Structure of the hydrated, hydrolysed and solvated zirconium(IV) and hafnium(IV) ions in water and aprotic oxygen donor solvents. A crystallographic, EXAFS spectroscopic and large angle X-ray scattering study.” In: *Dalton Transactions* 14 (July 2004), pp. 2142–2151. DOI: 10.1039/b402804j.
- [125] A. Singhal et al. “Zirconium(iv) tetramer/octamer hydrolysis equilibrium in aqueous hydrochloric acid solution”. In: *Journal of the American Chemical Society* 118.46 (Jan. 1996), pp. 11529–11534. ISSN: 0002-7863. DOI: 10.1021/ja9602399.
- [126] Paul L Brown et al. *Chemical Thermodynamics of Zirconium, Volume 8*. 1st ed. Elsevier, Dec. 2005, pp. i–544. ISBN: 9780080457536.
- [127] Wei Wang et al. “Synthesis of the hydroxide cluster $[\text{Al}_{13}(\mu_3\text{-OH})_6(\mu\text{-OH})_{18}(\text{H}_2\text{O})_{24}]^{15+}$ from an aqueous solution.” In: *Inorganic Chemistry* 50.11 (June 2011), pp. 4683–4685. DOI: 10.1021/ic200483q.
- [128] Rolf Koole et al. *Nanoparticles: Workhorses of Nanoscience*. 1st ed. Springer-Verlag Berlin Heidelberg, 2014, pp. 13–51. ISBN: 978-3-662-44823-6.

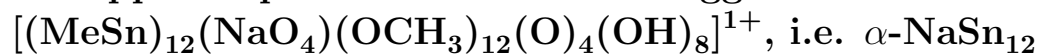
- [129] Long Pan et al. “Synthesis and structural determination of a hexanuclear zirconium glycine compound formed in aqueous solution.” In: *Inorganic Chemistry* 47.13 (July 2008), pp. 5537–5539. DOI: 10.1021/ic800292e.
- [130] Luke Huelsenbeck et al. “Generalized approach for rapid aqueous MOF synthesis by controlling solution ph”. In: *Crystal growth & design* 20.10 (Oct. 2020), pp. 6787–6795. ISSN: 1528-7483. DOI: 10.1021/acs.cgd.0c00895.
- [131] Hui Xu et al. “The Chemistry of Nucleation: In Situ Pair Distribution Function Analysis of Secondary Building Units During UiO-66 MOF Formation.” In: *Chemistry - A European Journal* 25.8 (Feb. 2019), pp. 2051–2058. DOI: 10.1002/chem.201805024.
- [132] Marcel Pourbaix. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. 2nd ed. National Association of Corrosion Engineers, 1974, pp. i–644. ISBN: 978-0915567980.

Chapter 5

Appendix

5.1 Ground state geometries for Sn-Keggin clusters from Chapter 3.

Uncapped Alpha Na-centered Sn-Keggin ion:



```

C -1.27815 -2.41781 -4.94536
C 0.34119 4.81636 -2.99498
C 4.27881 2.53849 -2.88122
C 5.62559 -0.07890 1.34643
C 4.22678 -2.62284 -2.86087
C -1.22052 2.50488 -4.91981
C -2.85038 4.88017 1.11208
C -4.18143 2.37673 -3.12938
C 0.43064 5.67347 0.29609
C 1.65331 -3.24809 4.29373
C 1.78416 3.13793 4.32497
C 0.27942 -5.67623 0.31880
C -3.80555 0.06233 4.17943
C -5.11453 2.42583 0.20920
C 2.83350 0.00655 4.90942
C -1.63128 2.54393 4.81419
C -1.60868 -2.63265 4.74487
C 0.16808 -4.81789 -3.06893
C -4.25478 -2.13056 -3.11098
C -2.98507 -4.82192 1.05167
C -5.18490 -2.30592 0.11586

```

C 4.75943 3.12753 0.48593
C 2.95462 -0.03138 -4.82161
C 4.65685 -3.28688 0.38424
H -2.85726 -4.48131 2.08599
H -5.41064 -2.43603 1.17890
H -4.58730 -1.08575 -3.07465
H -0.37165 -4.96100 -4.00997
H 5.75813 2.86202 0.12764
H 3.54908 3.35489 -2.94329
H -2.38124 5.86223 0.99839
H -5.04421 2.86541 -2.66570
H 6.15505 -1.03509 1.30510
H -0.25844 2.37278 -5.42441
H 3.53541 -3.47389 -2.90180
H 1.13135 5.30557 -2.41454
H 5.65143 -3.01235 0.02109
H -0.27862 -2.61885 -5.34263
H 3.68708 0.17801 4.24102
H -0.89424 3.13417 5.36993
H -0.96217 -3.05116 5.52357
H -5.27821 2.45307 1.29071
H 2.72235 -3.40165 4.11641
H 4.04172 -0.03267 -4.94169
H 2.86024 3.15970 4.12526
H -3.58153 -0.02649 5.24681
H 1.50909 5.78095 0.14217
H 1.33348 -5.83331 0.07000
H 4.46115 4.07749 0.03216
H 4.71901 -3.50036 1.45587
H 0.14743 -5.83588 1.39306
H 1.37255 4.13246 4.12665
H 5.21766 0.06122 2.35420
H -2.70812 4.53168 2.14207
H -4.42507 1.32418 -3.31863
H 5.18106 -2.95723 -2.44257
H -1.53125 3.54874 -5.02261
H 4.49307 2.17664 -3.89100
H -0.34206 5.58843 -3.36980
H -5.77959 -1.47017 -0.26606
H -4.05464 -4.91350 0.83728
H -4.00634 -2.38202 -4.14752
H 1.18636 -4.47508 -3.29312

H -0.09198 6.36530 -0.37089
H -5.41853 3.38620 -0.21753
H -2.54403 -2.30868 5.21402
H 2.81426 0.79733 5.66676
H -2.15027 3.20637 4.10952
H -1.72453 -1.59973 -5.51898
H 2.54666 0.86028 -5.30647
H 1.50436 -3.01539 5.35260
H -4.29658 1.02478 4.00510
H -1.89352 -3.31320 -5.07388
H 0.20259 5.94163 1.33236
H 4.33445 -4.19648 -0.13238
H 1.63104 2.90190 5.38231
H 1.12697 -4.18039 4.06576
H 2.97675 -0.95199 5.42028
H -5.73980 1.63721 -0.21999
H -1.83642 -3.41990 4.01534
H -2.36005 2.14924 5.52973
H 0.22645 -5.78403 -2.55691
H -2.52466 -5.80846 0.93995
H -5.47659 -3.21556 -0.41748
H -5.07884 -2.77638 -2.79026
H 4.79433 3.25257 1.57245
H 2.54332 -0.91733 -5.31385
H -4.49854 -0.73730 3.89976
H -0.32574 -6.40832 -0.22361
H -1.96056 1.86646 -5.41200
H 6.33804 0.72274 1.13055
H 0.81031 4.31789 -3.85061
H 5.20740 2.91707 -2.44332
H 4.40305 -2.26519 -3.87999
H -3.97816 2.87186 -4.08417
H -3.92233 4.98488 0.91692
H 2.12472 -3.76847 -1.00949
H -2.65456 0.05170 -1.69220
H 2.25260 3.71919 -0.96014
H 1.34199 2.15530 -2.13038
H 1.26553 -2.17411 -2.14902
H -1.15145 -2.35048 1.76629
H 2.52178 0.21932 1.88640
H -1.55576 2.11618 1.79082
Na -0.03234 -0.00235 -0.00715

O 1.67048 -2.99743 -0.62007
O -2.27846 3.96720 0.16737
O 2.25740 -0.01761 -0.70332
O 0.94468 -1.51058 -2.80736
O -1.10200 -1.90890 -0.80786
O -1.05904 1.93793 -0.78469
O -0.07170 -0.00838 2.29751
O 1.80195 2.93926 -0.58360
O -3.19706 0.06461 -0.82418
O -0.35946 3.87237 -2.18488
O -3.04070 2.50451 -2.27423
O -0.11379 2.83695 1.74969
O -2.40086 1.55671 1.70072
O 1.00810 1.50428 -2.79447
O -1.62250 0.04921 -2.87538
O 2.46771 1.23508 1.80900
O -2.48517 -1.48449 1.68748
O 4.58549 -0.07167 0.35836
O -2.39222 -3.90629 0.12299
O 2.43790 -1.36843 1.80721
O -0.24026 -2.80781 1.70863
O 3.69612 -1.55986 -2.06283
O -0.53068 -3.87586 -2.25185
O 3.77901 1.45619 -2.08428
O -3.11560 -2.34829 -2.27534
O -0.96580 -1.51548 4.12947
O 1.59873 -0.00802 4.19265
O -0.97986 1.46528 4.14281
Sn 0.83768 1.69674 3.06848
Sn 0.91935 -1.67344 3.05486
Sn -2.03331 -0.06091 2.99525
Sn -1.05496 1.94894 -2.86915
Sn -0.17655 3.65653 -0.04481
Sn -3.06714 2.02954 -0.20301
Sn 3.35922 1.60623 -0.00599
Sn -3.10842 -1.89926 -0.14225
Sn 2.41672 -0.03572 -2.76739
Sn -1.13923 -1.87072 -2.89003
Sn 3.25874 -1.71097 0.05585
Sn -0.31189 -3.69049 -0.16216

Uncapped Beta Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{1+}$, i.e. $\beta\text{-NaSn}_{12}$

C 1.43198 2.33547 -4.92536
 C -0.12861 -4.88372 -2.91146
 C -4.20216 -2.57993 -2.98812
 C -5.77410 0.00411 1.06370
 C -4.20219 2.50676 -3.00185
 C 1.41119 -2.50112 -4.85233
 C 2.92552 -4.91861 1.15557
 C 4.30256 -2.36767 -2.97465
 C -0.34869 -5.67454 0.32200
 C -3.70749 0.05260 4.21328
 C 1.81097 -3.13734 4.30305
 C -0.33672 5.70305 0.17071
 C 1.81090 3.26466 4.21666
 C 5.14365 -2.43024 0.35431
 C -1.58346 -2.48456 4.81951
 C 2.96719 -0.02079 4.81395
 C -1.46320 2.72393 4.70996
 C -0.11346 4.78857 -3.10693
 C 4.31155 2.22677 -2.98935
 C 2.90588 4.96963 1.00102
 C 5.13701 2.42389 0.25864
 C -4.76454 -3.18414 0.31218
 C -2.78564 -0.05456 -4.90264
 C -4.73297 3.19706 0.21242
 H 2.18088 5.45909 1.65865
 H 5.36845 2.42359 1.32838
 H 4.57609 1.16788 -3.10156
 H 0.01535 5.80286 -2.71516
 H -5.75649 -2.88851 -0.04137
 H -5.15330 -2.93693 -2.58196
 H 3.39122 -5.64008 0.47446
 H 5.16449 -2.81709 -2.47174
 H -5.85323 0.91257 1.66752
 H 0.44902 -2.43656 -5.37017
 H -3.52166 3.36608 -3.05104
 H -1.21407 -4.71808 -2.93533
 H -5.70658 2.89212 -0.18203
 H 0.45956 2.28842 -5.42553

H -2.11266 -3.13031 4.10746
H 2.98314 -0.82551 5.55650
H -2.38507 2.42271 5.21958
H 5.31222 -2.40829 1.43515
H -4.22145 -0.89986 4.05266
H -3.86683 -0.02901 -5.06587
H 1.39788 -4.12901 4.09481
H 1.73995 3.01604 5.28028
H -1.26326 -5.90036 -0.23480
H -1.26988 5.91816 -0.35865
H -4.47043 -4.11033 -0.19151
H -4.84031 3.42371 1.27775
H -0.50249 5.85537 1.24156
H 2.88933 -3.16136 4.11850
H -5.83451 -0.86296 1.72784
H 2.18291 -5.43804 1.76876
H 4.52526 -1.31604 -3.19307
H -5.16645 2.83661 -2.60381
H 1.80388 -3.51580 -4.96401
H -3.48966 -3.41301 -3.02338
H 0.06474 -5.88378 -2.50934
H 5.76844 1.67658 -0.23148
H 3.72681 4.58730 1.61479
H 4.13518 2.65372 -3.98257
H 0.30437 4.75420 -4.11733
H 0.43851 -6.36153 -0.00343
H 5.41844 -3.41969 -0.02354
H -0.79319 3.17025 5.45234
H -0.85592 -3.09245 5.36855
H 3.78051 -0.18562 4.09610
H 2.09793 1.60413 -5.39383
H -2.38289 -0.96613 -5.35387
H -3.46575 0.14264 5.27681
H 2.86185 3.44519 3.97094
H 1.85397 3.33422 -5.06977
H -0.54154 -5.84262 1.38626
H -4.41453 4.10849 -0.30351
H 1.64498 -2.90686 5.35996
H -4.38506 0.86681 3.93929
H -2.30579 -2.08611 5.53945
H 5.79167 -1.68275 -0.11301
H -1.71024 3.48123 3.95576

H 3.14642 0.92673 5.33422
H -1.18630 4.56323 -3.16425
H 3.30486 5.70791 0.29595
H 5.37856 3.40896 -0.15178
H 5.15483 2.75586 -2.53447
H -4.81268 -3.37484 1.38845
H -2.33319 0.81081 -5.39580
H 1.24694 4.18529 4.03826
H 0.43244 6.40253 -0.17016
H 2.10789 -1.80348 -5.32751
H -6.60798 -0.02811 0.35386
H 0.24926 -4.84876 -3.93810
H -4.37352 -2.21744 -4.00586
H -4.35977 2.12607 -4.01582
H 4.13774 -2.89963 -3.91724
H 3.69349 -4.50685 1.81737
H -2.16025 3.74419 -1.13815
H 2.76461 -0.02984 -1.61641
H -2.17489 -3.76503 -1.04024
H -1.24802 -2.19384 -2.13408
H -1.22687 2.14127 -2.19597
H -1.03478 2.41043 1.64419
H -1.53227 -2.07262 1.71009
H 2.59088 -0.25355 1.74629
Na 0.02150 0.00071 -0.00909
O -1.70493 2.98238 -0.73298
O 2.29654 -3.86896 0.41255
O -2.23861 -0.02507 -0.75681
O -0.87420 1.47108 -2.83450
O 1.10269 1.91303 -0.77153
O 1.11962 -1.92603 -0.71632
O -0.00589 0.03646 2.29297
O -1.74501 -2.98047 -0.65105
O 3.27979 -0.02630 -0.73676
O 0.53430 -3.90173 -2.11592
O 3.14257 -2.49567 -2.14605
O -0.14785 -2.77837 1.74403
O 2.49824 -1.27551 1.76008
O -0.89521 -1.54581 -2.79542
O 1.72029 -0.05393 -2.80976
O -2.37478 -1.48243 1.71366
O 2.51908 1.30636 1.74050

O -4.52607 -0.00152 0.35938
 O 2.28570 3.89160 0.29207
 O -2.35706 1.55670 1.68365
 O -0.10600 2.83820 1.65538
 O -3.66894 1.46728 -2.17534
 O 0.57216 3.85426 -2.27050
 O -3.70613 -1.50688 -2.17803
 O 3.14522 2.39355 -2.17992
 O -0.84144 1.57994 4.12237
 O -0.91396 -1.40938 4.16013
 O 1.69378 0.01577 4.16887
 Sn 0.88614 -1.67474 3.05395
 Sn -1.94114 0.12760 3.01820
 Sn 1.03264 1.68168 3.01467
 Sn 1.17653 -1.95963 -2.80338
 Sn 0.23599 -3.64719 0.01007
 Sn 3.10613 -1.99145 -0.07506
 Sn -3.33744 -1.65730 -0.08428
 Sn 3.08024 1.94554 -0.04516
 Sn -2.32683 -0.02407 -2.82955
 Sn 1.20905 1.85656 -2.85901
 Sn -3.28167 1.65539 -0.04611
 Sn 0.26516 3.69187 -0.18161

Uncapped Gamma Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{1+}$, i.e. $\gamma\text{-NaSn}_{12}$

C 1.69676 5.34443 0.71560
 C 4.21057 1.97067 3.30996
 C 2.08534 3.26009 -4.14813
 C -2.94935 3.55143 -3.31109
 C -1.18363 -0.45970 5.48654
 C -3.67231 3.01415 3.03658
 C -5.74878 -0.17824 -0.53295
 C -1.04753 5.70317 -1.37585
 C 4.83755 2.01210 -2.37785
 C -4.60213 3.48094 -0.19746
 C 1.15448 0.45975 -5.61435
 C 5.64588 -0.99125 -0.98843
 C 1.24969 -2.87247 -4.90394

C 4.04093 -2.98137 -3.06196
C 2.79869 -4.28193 2.47385
C -2.00294 -4.03149 -3.76037
C -4.62486 -1.96154 -3.14393
C -2.12030 -4.47809 2.58445
C 0.59973 -3.17589 4.81805
C 4.79678 -1.51015 2.92193
C 1.56564 1.61181 5.23203
C -1.62954 -5.47133 -0.71129
C -4.83990 -2.42271 1.90082
C -0.81303 4.76122 2.87091
H -1.21362 -4.78826 -3.75781
H 6.19701 -0.22540 -0.43323
H -5.93960 0.54729 -1.32940
H 2.85125 2.96301 -4.87061
H 1.24571 -3.91071 -4.55965
H -2.95188 -5.12155 2.28250
H -2.34597 -4.04824 3.56457
H 2.13672 -2.71449 -5.52523
H 5.81744 -1.95730 -0.50340
H -6.11534 0.23976 0.40969
H 2.30180 5.22747 1.62057
H 4.53329 1.49460 4.24090
H 1.03465 6.20439 0.85018
H 2.41475 4.17592 -3.64730
H -1.21582 -5.08742 2.66668
H -2.97192 -4.53127 -3.66647
H -3.47780 2.76470 -3.85877
H 3.83099 2.97024 3.54425
H -6.30856 -1.09265 -0.75115
H 0.35875 -2.70292 -5.51464
H 2.37015 5.55492 -0.12192
H 1.15968 3.48048 -4.69000
H -1.97442 -3.49210 -4.71086
H 5.08002 2.07546 2.65337
H 6.04696 -1.03813 -2.00556
H -3.67726 4.29917 -2.98281
H 3.18831 -4.31258 3.49575
H 3.62346 -4.46604 1.77864
H -2.23331 4.03037 -3.98580
H 2.05793 -5.07844 2.35525
H -0.46581 -0.70791 6.27404

H -1.95612 -1.23485 5.46345
H -1.66126 0.49233 5.73946
H -3.22498 3.06492 4.03479
H -0.40172 -3.16235 5.25751
H -4.54890 2.35995 3.09003
H -4.00754 4.01797 2.75713
H 0.81593 -4.19475 4.48256
H 1.32955 -2.89483 5.58702
H -1.68963 6.00717 -0.54001
H -1.59289 5.85210 -2.31352
H -0.15856 6.34193 -1.39117
H 4.88434 2.54793 -1.42261
H 4.72576 2.74132 -3.18689
H 5.77698 1.47106 -2.52925
H -5.01075 3.07260 -1.12837
H -4.76081 4.56623 -0.19096
H 1.34586 -0.42552 -6.22786
H 0.08146 0.68749 -5.64785
H 1.71031 1.29896 -6.04027
H 4.75053 -3.25288 -2.27593
H 4.59772 -2.65525 -3.94783
H 3.45392 -3.86964 -3.31746
H -5.22337 -1.04679 -3.18286
H -4.15810 -2.10941 -4.12276
H -5.28301 -2.81055 -2.92863
H 5.36106 -0.70238 3.39904
H 5.21026 -1.68533 1.92194
H 4.91910 -2.41864 3.52126
H 1.26542 2.59992 4.86073
H 2.57329 1.68446 5.65417
H 0.87997 1.31969 6.03447
H -1.86362 -5.99137 0.22185
H -2.19755 -5.93783 -1.52151
H -0.55740 -5.57392 -0.91702
H -4.66470 -1.70120 2.70758
H -5.82745 -2.24049 1.46632
H -4.82752 -3.43438 2.31846
H -0.35398 4.15524 3.66239
H -1.78079 5.13049 3.22686
H -0.17121 5.62632 2.67739
H -5.15376 3.04206 0.63967
H -3.15130 0.60813 -2.63457

H -0.66594 1.86205 -3.74595
H -0.98329 -0.17929 -2.90215
H 0.69204 -3.84622 -2.00713
H 0.45859 -3.02235 -0.02966
H 2.75847 -2.91304 -0.37871
H 0.45889 2.05051 2.35769
H -2.26526 -0.55348 2.00226
Na 0.00124 -0.02886 -0.00297
O -0.90666 2.10188 0.00147
O 1.12277 -0.50935 1.97292
O 1.61631 -0.15520 -1.76192
O -1.79609 -1.57246 -0.42441
O 1.32030 2.35435 1.89515
O 3.74118 1.09167 -2.40886
O 3.18302 -1.93791 -2.59038
O -0.64792 4.33480 -1.25992
O -3.84190 -2.31513 0.87771
O -3.21052 3.18324 -0.07478
O -0.87697 1.42620 2.86494
O 1.59573 0.22632 -4.27209
O -0.99667 4.00919 1.67138
O 3.42923 0.69502 0.53407
O -3.06111 0.47200 1.18112
O 0.38893 -2.93278 -1.84632
O -1.68293 -1.29212 2.42258
O -2.00583 -4.09271 -0.59400
O 1.75375 2.71602 -1.02208
O -3.61803 -1.83374 -2.13349
O 1.54474 0.63059 4.19470
O -0.80301 -1.10760 -3.16982
O -0.42293 1.74031 -2.80889
O 0.65262 -2.27463 3.71029
O 3.41364 -1.15017 2.86566
O 2.80940 -2.11164 0.17157
O -2.90284 0.84033 -1.72265
O 0.25042 -3.05502 0.93619
Sn 3.56189 -0.50092 -0.98949
Sn 1.26899 -1.53935 -3.24204
Sn -1.73504 -2.68363 -2.14110
Sn 1.73434 1.73666 -2.68806
Sn 2.69041 0.82682 2.33507
Sn 0.61122 3.54413 0.31793

Sn -1.82767 -2.91746 1.17414
 Sn -3.65993 -0.57647 -0.37063
 Sn -2.23972 2.23736 1.64427
 Sn -0.24091 -0.31427 3.57320
 Sn -1.92883 2.71187 -1.64026
 Sn 1.91818 -2.38780 2.05974

Uncapped Delta Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{1+}$, i.e. $\delta\text{-NaSn}_{12}$

C 2.15574 -4.97411 1.48911
 C -2.52385 -4.60764 2.16292
 C -2.04745 -1.96035 -5.02302
 C 1.25214 -3.35895 -4.63366
 C 1.97054 -1.25960 5.07332
 C 5.72346 -0.58412 -1.44693
 C 5.15316 2.95000 -0.38292
 C 1.24437 -5.35450 -1.82250
 C -4.52420 -2.47223 -2.77986
 C 3.76094 -1.23745 -4.18586
 C -1.88994 1.31686 -5.20193
 C -5.80461 -0.85196 -0.23228
 C -2.98972 3.83116 -3.25308
 C -5.18577 2.39721 -1.17354
 C -3.54402 1.47118 4.15961
 C -0.18861 5.64317 -1.74140
 C 2.91559 4.45188 -2.36856
 C 0.78229 3.51942 4.21080
 C -0.80193 0.57034 5.64920
 C -4.28407 -1.88123 3.44323
 C -0.01655 -3.91138 4.28935
 C -0.53744 5.49323 1.65399
 C 3.91781 3.17094 2.78405
 C 4.94130 -2.94558 0.84966
 H -1.18951 5.98377 -1.45958
 H -5.88243 -1.88854 0.11037
 H 5.44897 2.87383 -1.43384
 H -3.03165 -1.68429 -5.41505
 H -3.38989 4.56915 -2.55071
 H 1.24358 4.51106 4.24219

H 1.32652 2.85695 4.88955
H -3.79363 3.52666 -3.93091
H -6.26370 -0.20708 0.52389
H 5.84282 2.34942 0.21771
H 2.46553 -4.72832 2.50840
H -2.74332 -4.78200 3.22027
H 2.93610 -5.58040 1.01949
H -1.99872 -3.04995 -4.93841
H -0.25386 3.60276 4.55034
H 0.54254 6.37889 -1.39202
H 1.26870 -2.63599 -5.45479
H -1.82484 -5.37471 1.81621
H 5.23603 3.99607 -0.07191
H -2.20008 4.30870 -3.84051
H 1.23198 -5.55857 1.52782
H -1.28481 -1.63414 -5.73652
H -0.13676 5.58955 -2.83265
H -3.45258 -4.69339 1.59085
H -6.36919 -0.75146 -1.16469
H 2.15481 -3.97487 -4.69329
H -3.63412 0.91566 5.09745
H -4.54014 1.57640 3.71835
H 0.37682 -4.00350 -4.75423
H -3.15486 2.47037 4.38034
H 1.39229 -1.63148 5.92393
H 2.44898 -0.31715 5.35643
H 2.75077 -1.98697 4.83054
H 6.26384 -0.42457 -0.50895
H 0.20206 0.61445 6.08088
H 5.91720 0.26680 -2.10680
H 6.10651 -1.49237 -1.92237
H -1.26999 1.55135 5.76319
H -1.39175 -0.17353 6.19783
H 1.77817 -6.06748 -1.18714
H 1.43962 -5.60691 -2.86869
H 0.16857 -5.43512 -1.62889
H -4.96911 -2.98340 -1.92024
H -3.99337 -3.21540 -3.38302
H -5.32503 -2.03258 -3.38563
H 3.14370 -0.47585 -4.67861
H 3.86054 -2.10107 -4.85087
H -2.17617 2.36447 -5.32834

H -0.81396 1.22300 -5.39402
H -2.43573 0.71837 -5.93797
H -6.07411 1.82684 -0.88736
H -5.44235 3.03405 -2.02553
H -4.88289 3.02918 -0.33064
H 3.14142 3.68941 -3.12441
H 2.24611 5.19465 -2.81046
H 3.84478 4.95222 -2.07715
H -4.35200 -2.94482 3.69238
H -4.95178 -1.67006 2.60000
H -4.61243 -1.29960 4.31038
H -0.14567 -4.86701 3.77417
H -0.74061 -3.84325 5.10914
H 0.99519 -3.87126 4.70166
H -0.30035 5.69586 2.70272
H -0.38505 6.41167 1.07924
H -1.58808 5.19076 1.57689
H 4.18042 2.16158 3.12191
H 4.80712 3.65059 2.36470
H 3.57969 3.75835 3.64286
H 4.98439 -2.27139 1.71308
H 5.87499 -2.86713 0.28529
H 4.83703 -3.97436 1.20702
H 4.75658 -0.82091 -4.00814
H 3.41073 1.38433 -2.66683
H 0.61747 -0.15138 -4.22788
H 0.39258 1.68248 -2.66401
H -1.43889 2.33005 1.10635
H -0.55638 -2.85870 -0.52392
H 2.24313 0.63321 1.94408
H 2.63281 -1.11650 1.59827
H -2.87739 -2.76735 -0.42930
Na 0.05249 0.02442 -0.10583
O 1.72365 -1.56625 -0.90561
O -0.80377 -0.81183 1.97184
O -1.93933 0.19965 -1.46727
O 1.10073 2.22007 0.23663
O -0.25083 -3.14102 0.40479
O -3.61688 -1.46143 -2.33208
O -4.13923 1.49172 -1.54647
O 1.72159 -4.02752 -1.55822
O 2.88234 3.13317 1.79415

O 3.18040 -1.64360 -2.94191
 O 2.00349 -1.79896 1.92952
 O -2.22123 0.88254 -3.88045
 O 3.83545 -2.62313 -0.00419
 O -2.88461 -2.09484 0.27452
 O 3.31750 0.36901 0.58641
 O -1.61617 2.98213 -0.46191
 O 1.54688 0.81557 2.63446
 O 0.33458 4.47042 1.15368
 O -0.71510 -2.45789 -2.11560
 O 2.29516 3.86606 -1.22004
 O -0.20129 -2.83445 3.36233
 O -0.13330 2.49971 -2.56138
 O 0.36098 -0.46422 -3.34204
 O -0.72079 0.23167 4.26111
 O -2.92594 -1.54529 3.13654
 O -3.33575 0.63061 1.14580
 O 2.94230 1.06924 -1.87336
 O -1.11323 2.08146 2.03078
 Sn -3.74796 -0.31629 -0.49595
 Sn -2.23110 2.14507 -2.17012
 Sn 0.19747 3.73685 -0.85703
 Sn -1.72878 -1.04642 -3.11338
 Sn -1.67696 -2.67805 1.87237
 Sn 1.83023 -3.19495 0.37751
 Sn 0.83832 2.73949 2.23746
 Sn 3.14851 2.25948 -0.12588
 Sn 3.63280 -0.77270 -1.05374
 Sn 0.72957 -0.95393 3.37336
 Sn 1.18084 -2.34567 -2.75671
 Sn -2.26688 0.47501 2.76811

Uncapped Epsilon Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{1+}$, i.e. $\epsilon\text{-NaSn}_{12}$

C 0.29516 -5.69324 1.53962
 C -1.34947 -1.45112 -5.25800
 C 5.96723 0.05696 -1.41262
 C 5.40244 -2.27341 1.30506
 C -2.45667 -5.36317 -0.54732

C 1.08235 -0.90212 5.48399
C -1.24614 1.61512 5.34182
C 3.44743 -4.82691 0.61716
C 3.99028 -0.74423 -4.13526
C 3.99139 -0.57128 3.99552
C 5.10912 3.22884 -0.65430
C 1.27816 0.57590 -5.39480
C 2.47884 5.18714 -1.44016
C 1.08067 3.65009 -4.13424
C -5.94932 -0.27569 -1.29371
C -0.12605 5.83122 0.92371
C 0.19620 4.21310 3.90372
C -5.34030 2.63888 0.73819
C -5.13800 -3.43212 -0.42547
C -4.06974 0.01938 -4.11771
C -1.18873 -4.28076 -3.56010
C -3.10086 5.03273 -0.16304
C -4.23876 1.51784 3.73857
C -0.18583 -3.79671 4.31322
H -0.30322 6.26015 -0.06680
H 1.39259 -0.44388 -5.77153
H -0.25017 1.73129 5.77675
H 6.38213 0.56678 -2.28762
H 1.59429 5.76986 -1.71143
H -5.48119 3.52277 1.36799
H -5.97367 1.83251 1.11719
H 3.21732 5.27650 -2.24309
H 0.37010 1.00612 -5.82585
H -1.71926 0.73421 5.78482
H -0.72392 -5.88292 1.88536
H -2.21538 -2.08101 -5.48463
H 0.99825 -6.09112 2.27769
H 6.15906 -1.01529 -1.50554
H -5.64975 2.88234 -0.28173
H -0.83229 6.28204 1.62818
H 6.03325 -1.38657 1.40327
H -0.44791 -1.96234 -5.60717
H -1.84315 2.49772 5.59102
H 2.90492 5.61067 -0.52578
H 0.44819 -6.21360 0.59081
H 6.47353 0.42896 -0.51760
H 0.89017 6.08857 1.23645

H -1.45020 -0.51137 -5.80735
H 2.13712 1.16736 -5.72704
H 5.55492 -2.91502 2.17849
H -6.38379 -1.00802 -1.98087
H -6.13769 0.72860 -1.68211
H 5.70337 -2.82424 0.40971
H -6.43534 -0.37471 -0.31944
H -3.23443 -5.60720 -1.27719
H -2.83201 -5.58531 0.45509
H -1.58024 -5.98466 -0.74352
H 0.10647 -0.98416 5.96941
H -4.93741 -4.25620 0.26360
H 1.54587 0.04162 5.78410
H 1.71520 -1.72657 5.82691
H -5.94228 -2.81883 -0.01103
H -5.45036 -3.83481 -1.39455
H 4.32977 -4.96861 1.24672
H 3.75820 -4.64679 -0.41690
H 2.83899 -5.73303 0.65395
H 3.48760 -1.71757 -4.09921
H 5.03886 -0.87721 -3.85220
H 3.95487 -0.36068 -5.15897
H 3.81380 0.50928 4.00861
H 4.99660 -0.76100 3.60936
H 4.93223 4.30088 -0.76681
H 5.27431 3.00191 0.40486
H 6.00180 2.95987 -1.22634
H 1.27797 3.33192 -5.16237
H 1.53122 4.63688 -3.98941
H -0.00305 3.73235 -3.98958
H 1.17386 3.73786 4.04134
H 0.34497 5.23646 3.54788
H -0.32267 4.25385 4.86569
H -3.89557 -0.43115 -5.09804
H -3.70689 1.05343 -4.12659
H -5.14614 0.02070 -3.92416
H -0.09579 -4.29797 -3.48215
H -1.47178 -4.16010 -4.60922
H -1.58527 -5.23574 -3.20280
H -4.13986 4.79434 -0.40495
H -3.08260 5.92447 0.47098
H -2.56113 5.23743 -1.09347

H -4.64370 0.53963 3.45811
H -3.89862 1.47969 4.77631
H -5.02606 2.27304 3.65667
H -1.24695 -3.55734 4.18457
H 0.13144 -3.50262 5.31676
H -0.04229 -4.87506 4.20469
H 3.92850 -0.96179 5.01498
H 1.34579 1.55438 2.20045
H 3.04575 0.94059 1.17508
H -0.63480 2.69001 -1.65792
H -2.24788 1.37553 -1.66040
H 0.54804 -2.71005 -1.28266
H -3.02301 -0.53370 1.42772
H -1.48055 -2.07119 1.71929
H 2.32674 -1.65752 -1.35131
Na -0.03532 0.01284 -0.09382
O 1.29306 -1.62408 1.38857
O -1.89938 -1.29980 -1.12487
O 1.90659 1.06218 -1.35519
O -1.28297 1.82404 1.16622
O 0.15921 -3.42435 -0.71622
O 3.35872 0.19061 -3.25238
O 1.66020 2.71381 -3.22187
O 2.67939 -3.71469 1.10671
O -3.14012 1.87749 2.88879
O 3.02533 -1.23375 3.16613
O -1.40300 -2.96056 1.29096
O 3.97705 2.50530 -1.15777
O 0.61979 -3.10782 3.34299
O 0.71256 -1.30844 -2.64670
O -1.00512 -0.56379 2.88876
O -0.17641 3.43073 -1.21062
O -3.68645 -0.04877 0.90384
O -2.49813 3.93002 0.52573
O 3.20370 -1.53920 -0.91805
O -0.60137 3.48731 2.95907
O -1.74614 -3.20801 -2.78982
O 1.45751 2.94679 0.78426
O 3.71363 0.32342 0.82571
O -3.95365 -2.63176 -0.56760
O -3.39847 -0.75550 -3.11395
O -0.78416 0.84021 -2.81581

O 1.00622 1.10456 3.01250
 O -3.11796 1.37052 -1.18373
 Sn 1.20582 0.60609 -3.24933
 Sn 1.94356 3.13620 -1.15641
 Sn -0.39524 3.71004 0.87922
 Sn 3.87845 0.43334 -1.27503
 Sn -1.26026 -1.12099 -3.13820
 Sn 0.61467 -3.60371 1.31497
 Sn -3.30039 2.04135 0.79973
 Sn -1.10367 1.42350 3.21812
 Sn 0.90327 -0.99995 3.35681
 Sn -1.96778 -3.30353 -0.71867
 Sn 3.35296 -1.72575 1.17512
 Sn -3.86048 -0.61295 -1.10153

Capped Alpha Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_8(\text{OH})_4(\text{Sn}(\text{H}_2\text{O})_2)]^{1+}$, i.e. $\alpha\text{-NaSn}_{13}$

C 0.16345 0.12768 5.62641
 C 5.00529 -2.96736 0.03420
 C 4.99568 2.99346 -0.07081
 C 1.29814 4.85493 -2.63503
 C 1.31190 4.94399 2.43337
 C 3.73810 -2.50702 3.17307
 C 1.29327 -4.94018 -2.44503
 C 1.34995 -4.85412 2.61421
 C 3.73297 -2.64110 -3.06564
 C -4.23865 3.15407 -2.64060
 C 0.11927 -0.13952 -5.62896
 C -4.23930 3.25420 2.52799
 C -4.27095 -3.25756 -2.48040
 C -0.84500 -5.63890 0.12265
 C -1.89413 2.49118 -4.77653
 C -1.88807 -2.66409 -4.70833
 C -5.59809 -0.07233 -2.19336
 C -1.87289 2.68755 4.68712
 C -1.85729 -2.48877 4.79491
 C -5.58109 0.05540 2.22761
 C -4.20906 -3.16607 2.66999
 C 3.73563 2.52905 -3.15911

C 3.75285 2.63394 3.05204
C -0.85862 5.63802 -0.10800
H -5.86202 0.20757 1.17813
H -5.00875 -3.37157 1.95116
H -1.37060 -3.34639 4.31266
H -2.84852 2.98325 5.08924
H 4.14994 3.49061 -2.84781
H 4.52594 3.97847 -0.10804
H 1.14274 -5.92833 -1.99931
H 1.17627 -5.85056 2.19648
H 1.13502 5.85389 -2.21892
H 4.45754 -1.69470 3.30556
H 0.46455 4.70887 3.08809
H 5.62162 -2.85461 0.92973
H -0.06578 6.39176 -0.11057
H 0.75686 1.03027 5.80621
H -1.43729 3.35822 -4.28242
H -1.66889 -2.29694 -5.71704
H -6.01837 0.88735 -2.51276
H -1.48364 -5.79818 -0.75141
H -3.67564 4.08228 -2.78415
H 4.16944 3.58944 2.72504
H 0.80968 0.68386 -5.83978
H -4.66808 -3.05451 -3.47944
H 4.54096 -1.90699 -3.10279
H -3.71694 4.21654 2.54726
H 4.53239 1.78182 -3.17316
H -1.47241 5.77072 -1.00389
H -5.09328 3.34055 1.84851
H 0.64605 -1.08065 -5.81886
H 0.45862 4.59796 -3.29183
H 2.20258 -4.97114 -3.05268
H 0.52374 -4.59821 3.28813
H 1.15803 5.93229 1.98931
H 4.25727 -3.39695 2.81063
H 5.61736 2.84998 -0.95702
H 5.62817 -2.83750 -0.85461
H -3.64044 -4.08941 2.82244
H -5.99917 -0.89850 2.56669
H -1.24817 -2.18622 5.65342
H -1.22064 2.43884 5.53086
H 4.13652 -3.60205 -2.73837

H -0.05071 -6.39109 0.11859
H -6.04119 -0.86319 -2.80910
H -1.25925 2.20388 -5.62168
H -1.07512 -3.33405 -4.39773
H 0.79740 -0.73958 5.83903
H 4.54922 1.88633 3.08437
H -4.68618 2.87031 -3.59809
H -3.76183 -4.22684 -2.49783
H -0.67574 0.12215 6.32937
H 3.32083 -2.75706 -4.07327
H -1.48713 5.79284 0.77413
H -0.72244 -0.07217 -6.32561
H -5.04228 3.34947 -1.92335
H -2.87037 2.79069 -5.17393
H -1.44789 -5.76985 1.02616
H -5.87488 -0.24472 -1.14594
H -2.81542 -3.24359 -4.75520
H -1.44006 3.54620 4.15779
H -6.02274 0.85782 2.82931
H -4.66209 -2.87814 3.62366
H -2.83511 -2.80864 5.17177
H 3.33145 2.62956 -4.17155
H 3.34624 2.75366 4.06143
H -5.11127 -3.32463 -1.78186
H -4.61507 3.04403 3.53398
H 3.29207 -2.73135 4.14721
H 2.21881 4.87437 -3.22601
H 4.55559 -3.96219 0.02397
H 5.61660 2.92258 0.82643
H 2.22671 4.97401 3.03282
H 2.28194 -4.87854 3.18664
H 0.44031 -4.70510 -3.09247
H -0.48664 2.41646 2.06722
H -0.48119 -2.32940 2.16704
H 5.60606 -0.06819 -2.31057
H 6.55916 -0.62244 -1.19188
H -0.50188 -2.42619 -2.07004
H -0.50834 2.33408 -2.16565
H 6.08852 0.80669 1.76248
H 5.86616 -0.72304 1.99167
Na -0.27622 0.00634 0.00476
O -1.16637 2.83405 1.43846

O 1.44709 -3.96396 -1.40519
O 1.20502 1.91585 -0.04727
O 0.62461 1.55727 2.80878
O -1.67908 0.03852 1.82963
O 1.20479 -1.90934 0.03531
O -1.69322 -0.04305 -1.81835
O 2.88471 -0.02267 -1.48012
O -1.15897 -2.77178 1.55410
O 3.93888 -1.99041 0.03846
O 1.46960 -3.90313 1.54657
O 0.60621 -1.54921 -2.81366
O -1.17501 -2.84649 -1.43757
O 2.88453 0.03213 1.45252
O 0.62556 -1.43642 2.87831
O 0.60226 1.44180 -2.89074
O -3.46320 -1.65335 0.04830
O 1.43715 3.90865 -1.56582
O -4.16414 0.04832 2.40004
O -1.18083 2.76789 -1.54327
O -3.47388 1.64379 -0.02295
O 1.45589 3.96818 1.39148
O -2.01582 1.55990 3.82685
O 3.94596 1.99955 -0.03277
O -2.01260 -1.39555 3.89304
O -4.18173 -0.06007 -2.37027
O -2.04465 1.39385 -3.87869
O -2.04262 -1.56469 -3.81395
O 5.85445 0.03452 -1.36937
O 5.91420 -0.03609 1.29401
Sn 4.20769 0.00670 -0.01475
Sn -0.52200 -0.07517 -3.58262
Sn -2.94156 1.61845 -1.89504
Sn -2.93472 -1.71620 -1.82497
Sn 2.19209 -1.89940 1.84867
Sn 2.17935 -1.97164 -1.77967
Sn -0.04122 -3.66922 0.07526
Sn 2.16982 1.90602 -1.86776
Sn -2.91972 -1.62757 1.91665
Sn 2.19365 1.98072 1.76468
Sn -0.49300 0.07713 3.58391
Sn -0.04942 3.67043 -0.07558
Sn -2.92589 1.70577 1.84425

Capped Beta Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_8(\text{OH})_4(\text{Sn}(\text{H}_2\text{O})_2)]^{1+}$, i.e. $\beta\text{-NaSn}_{13}$

C 3.59833 -2.58170 -3.24007
 C -2.06563 2.54811 -4.77449
 C 1.17543 4.88662 -2.52639
 C 4.95591 2.98675 -0.22478
 C 1.45869 4.99112 2.42184
 C -0.02715 -0.01890 -5.67767
 C -5.58489 -0.02387 -2.48848
 C -2.05655 -2.58502 -4.76349
 C -4.37580 3.16728 -2.28787
 C -1.36997 3.17412 4.63459
 C -5.69954 -0.02366 1.31064
 C 3.89103 -2.59689 2.92609
 C -1.35214 -3.15194 4.65688
 C -4.35646 -3.20669 -2.26917
 C -4.28986 2.55934 3.08987
 C -4.27688 -2.56206 3.11320
 C -0.57224 0.01716 5.71441
 C 5.00545 -2.93565 -0.22073
 C 1.22838 -4.88007 -2.51235
 C 1.45179 -4.95139 2.47536
 C -0.81163 -5.64944 0.01849
 C -0.85735 5.64191 0.00579
 C 3.59059 2.59536 -3.23401
 C 3.87087 2.61799 2.92231
 H 0.62365 -4.77537 3.17147
 H -1.40316 -5.85892 0.91555
 H 0.35895 -4.65060 -3.14027
 H 4.58266 -3.94229 -0.20252
 H -0.07514 6.35825 -0.26159
 H 1.30114 5.89373 -2.11547
 H 5.61381 2.87615 0.63978
 H -5.65999 -0.02836 -3.58259
 H -2.98644 -3.16370 -4.76035
 H 2.40562 4.98694 2.97026
 H 0.56984 0.86851 -5.91172
 H -1.23588 3.21751 -4.51495
 H 4.27815 3.56319 2.55644
 H 6.45949 -0.58354 -1.47576

H 4.08682 -3.50587 -2.92217
H -4.25762 3.22306 2.21611
H -5.29332 -2.17116 3.23757
H -0.87441 0.90258 6.28594
H -5.12305 -3.19381 -1.48844
H -1.65186 4.14015 4.20340
H 4.00313 3.56774 -2.95446
H -6.02900 0.84467 0.73204
H -2.11813 -2.85429 5.38007
H -3.89244 4.14914 -2.27765
H 4.67692 -1.83840 2.91904
H 5.71384 -0.01422 2.07349
H -1.66432 5.71631 -0.73053
H 3.53945 2.75698 3.95667
H 6.60388 -0.58893 0.91961
H 3.56266 -2.74625 3.95997
H -6.01998 -0.93253 0.79236
H 0.63892 4.84180 3.13423
H -6.09290 0.86482 -2.10208
H -1.22509 -3.25287 -4.50498
H -0.91274 -0.02091 -6.32036
H 4.50366 3.98068 -0.21197
H 0.17965 4.80616 -2.97769
H -2.99640 3.12538 -4.77426
H -1.45250 -5.78300 -0.85859
H 1.32955 -5.93846 2.01800
H 2.12396 -4.89662 -3.14115
H 5.58460 -2.79940 -1.13793
H -4.85574 3.02150 -3.26016
H -4.84155 -3.06372 -3.23933
H -0.86202 -0.87042 6.28904
H -5.30892 2.16917 3.19365
H -4.26142 -3.22231 2.23625
H 4.35636 -1.80443 -3.36852
H 3.13750 2.67757 -4.22711
H -2.13806 2.88276 5.35809
H -1.63651 -4.12053 4.23330
H 3.11342 -2.75527 -4.20608
H 5.40627 -0.01857 -2.48476
H -5.14579 3.15114 -1.51056
H 4.65715 1.85984 2.90890
H -6.18681 0.00784 2.29023

H -0.42323 3.30035 5.16975
H -4.05886 3.14645 3.98424
H -3.86813 -4.18599 -2.26061
H 0.52131 0.02463 5.61583
H -4.03045 -3.15319 4.00067
H 5.65894 -2.80086 0.64489
H 2.39090 -4.94644 3.03724
H 0.00671 -6.37383 -0.03230
H 1.09899 -5.87519 -2.07600
H -1.25995 5.91607 0.98606
H 4.40282 1.86609 -3.28215
H -0.40430 -3.27562 5.19057
H 4.29759 -3.53838 2.54993
H 0.57012 -0.90748 -5.90646
H 1.34199 5.96906 1.94373
H -1.90445 2.16254 -5.78649
H 1.92648 4.74012 -3.30873
H 5.53627 2.86037 -1.14143
H -1.89828 -2.20061 -5.77638
H -6.09024 -0.91075 -2.09465
H -0.53573 -2.42535 -2.13166
H -0.55392 2.41244 -2.14656
H -2.43660 2.09228 0.61092
H -2.41761 -2.10412 0.62378
Na -0.32033 -0.00247 0.00943
O 5.73833 0.07313 -1.56862
O 2.90793 0.01094 1.40901
O -4.21737 -0.01967 -2.07107
O 1.16363 1.89881 -0.00307
O 2.79676 0.00650 -1.54709
O 1.18358 -1.89345 0.00962
O -1.70458 -0.01070 -1.84942
O -1.55129 0.00028 1.95147
O -1.23615 2.82125 -1.51754
O -1.21542 -2.83749 -1.50100
O -2.16709 1.45540 -3.85849
O -2.15775 -1.49126 -3.84889
O -3.15786 1.51444 0.14757
O -3.14405 -1.53554 0.15702
O 0.52700 1.50338 -2.89160
O 0.53749 -1.51361 -2.87638
O -1.31549 2.79105 1.38607

O -1.29025 -2.78889 1.40284
 O 1.48159 3.96711 1.42117
 O 1.50211 -3.95159 1.45096
 O 0.81500 1.52444 3.02362
 O 0.83080 -1.50294 3.04395
 O 3.89317 2.00946 -0.16647
 O 3.91814 -1.98622 -0.16980
 O 1.35334 3.91528 -1.48941
 O 1.39081 -3.91556 -1.46630
 O -1.22120 0.01041 4.44708
 O -3.36387 1.48053 2.96994
 O -3.35214 -1.48401 2.98070
 O 5.90356 0.06799 1.11631
 Sn 4.15457 0.01403 -0.11232
 Sn -3.57651 -0.00840 1.51221
 Sn -1.15669 1.70118 3.08852
 Sn -1.14239 -1.68911 3.10070
 Sn -0.56149 -0.01239 -3.60776
 Sn -2.93282 1.65153 -1.89388
 Sn -2.92113 -1.68174 -1.88352
 Sn -0.11272 3.64212 0.06991
 Sn -0.08596 -3.64249 0.08883
 Sn 2.10397 1.95386 -1.85111
 Sn 2.12275 -1.94909 -1.84065
 Sn 2.19277 1.97720 1.78042
 Sn 2.20510 -1.95453 1.79660

Capped Gamma Na-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_6(\text{OH})_6(\text{Sn}(\text{Me})(\text{OCH}_3))]^{1+}$, i.e.

$\gamma\text{-NaSn}_{13}$

C -4.65709 2.94107 2.09063
 C -1.37918 1.32618 5.41061
 C -1.39203 5.51112 -0.85562
 C -3.66974 2.03691 -4.11289
 C -1.96747 -4.56651 2.91624
 C -5.12663 -2.91261 -0.32266
 C -2.10761 -3.03471 -4.44529
 C -4.63042 3.64206 -1.22396
 C 0.43295 5.18760 2.08812

C -5.05009 -0.95869 -3.21138
C 1.40378 5.15454 -2.57915
C 2.92448 3.19983 3.28525
C 3.87943 2.93559 -3.02527
C 6.44652 0.96081 0.05321
C 4.28304 3.94149 0.22054
C 3.68824 -1.85658 3.58174
C 3.58218 -0.52136 -4.42249
C 0.55893 -1.46868 -5.60520
C 2.18139 -4.99754 -0.12939
C 1.40493 -4.30319 3.53293
C 1.81347 0.29840 5.36524
C -2.67808 -1.83732 4.91026
C 3.73516 -3.44304 -2.74817
C 5.23857 -2.04832 0.02528
C -0.46823 -5.15194 -2.24219
C -5.67981 -0.29253 1.73900
H 4.56049 -0.39606 -3.94939
H 2.25882 3.25671 4.15157
H -2.54305 -2.26763 -5.09274
H -0.67994 6.33496 -0.74923
H 4.77323 2.31730 -2.90041
H 2.43456 -5.57054 -1.02624
H 1.45783 -5.57177 0.45696
H 4.14727 3.97944 -2.84037
H 3.78099 2.56788 3.53669
H -2.92089 -3.63228 -4.02241
H -4.83899 2.52106 3.08515
H -1.03961 0.73684 6.26772
H -5.61649 3.03942 1.57343
H -2.21482 5.67071 -0.15192
H 3.08913 -4.86376 0.46690
H 3.61800 -1.39447 -5.08059
H -3.52605 1.31819 -4.92531
H -2.46579 1.44132 5.47143
H -1.47488 -3.68594 -5.05644
H 3.52939 2.84314 -4.05768
H -4.22764 3.94052 2.21721
H -1.79531 5.53012 -1.87293
H 3.37293 0.36523 -5.02801
H -0.92444 2.32024 5.46859
H 3.28519 4.20697 3.05766

H -4.73514 2.27538 -4.03719
H 3.46187 -2.23440 4.58403
H 4.37200 -1.00755 3.67696
H -3.12017 2.95191 -4.35535
H 4.19062 -2.64779 3.01706
H -1.62002 -4.86668 3.90944
H -1.71119 -5.35498 2.20215
H -3.05580 -4.45802 2.93971
H -5.16563 -3.36023 0.67535
H 0.82572 -5.15635 3.16687
H -4.89774 -3.70223 -1.04511
H -6.11201 -2.49927 -0.55761
H 2.44172 -4.42416 3.20523
H 1.37451 -4.29898 4.62881
H -5.70280 3.50122 -1.40652
H -4.18100 4.10011 -2.11193
H -4.50530 4.33054 -0.38280
H -0.29932 4.75911 2.78313
H -0.01501 6.05656 1.59515
H 1.30500 5.52693 2.65627
H -4.47325 -0.94621 -4.14231
H -5.97093 -0.38181 -3.35363
H 1.98646 4.95020 -3.48215
H 0.48346 5.66580 -2.87330
H 1.98499 5.81062 -1.92023
H 7.05802 0.04909 0.13357
H 4.77902 3.83168 1.18835
H 3.86816 4.95326 0.14116
H 7.04040 1.78909 0.46378
H 6.29375 1.16599 -1.01854
H 5.02635 3.79639 -0.56783
H -0.42504 -1.08270 -5.89395
H 1.31984 -0.77051 -5.96522
H 0.71564 -2.44069 -6.08566
H 1.68016 -0.41036 6.19151
H 1.43375 1.27620 5.67639
H 2.88225 0.39627 5.15235
H -3.59287 -1.50930 4.40196
H -2.57959 -1.28736 5.85197
H -2.76255 -2.90388 5.14171
H 3.21232 -4.01273 -3.52529
H 5.91188 -2.03601 0.88852

H 4.55138 -2.87826 -3.20626
H 4.73296 -3.01280 -0.02242
H 4.16185 -4.13835 -2.02096
H 5.83876 -1.90856 -0.87909
H -1.23137 -5.22065 -1.45782
H -0.93501 -5.36224 -3.20998
H 0.29885 -5.91074 -2.06020
H -6.39867 -1.01062 1.32948
H -6.23234 0.59966 2.05168
H -5.20268 -0.73791 2.62141
H -5.31767 -1.99457 -2.98270
H -1.11583 2.96083 -2.88524
H -1.39499 0.15023 -4.07511
H 0.25029 1.16965 -2.83219
H -2.73177 -0.85520 1.95358
H -1.16861 -2.91238 -0.23390
H -0.66520 2.30042 1.91523
Na -0.25906 0.01065 -0.01400
O -2.53054 0.38570 -0.47425
O -0.07568 -0.91812 2.13577
O 0.92285 2.04310 -0.21130
O 0.59624 -1.43202 -1.66283
O -2.52763 0.56963 2.49479
O 0.84431 4.23480 1.10259
O 3.24651 2.96133 0.09786
O -4.00736 2.39131 -0.92894
O 0.13522 -3.85392 -2.27322
O -4.28801 -0.40735 -2.13364
O -2.72970 -1.77885 1.49626
O 1.07810 3.92412 -1.92341
O -4.72160 0.06033 0.74159
O 0.07237 1.90815 2.52252
O -2.13008 -2.36035 -1.28515
O 3.03083 0.32003 -1.39620
O -0.42397 -3.18641 0.42388
O 2.83931 -2.54247 -2.08467
O -1.65683 2.81024 0.88087
O 0.64123 -1.59714 -4.18160
O -1.51941 -1.60949 4.10144
O 1.21202 1.14720 -3.02337
O -1.29782 2.49195 -2.05090
O 0.86601 -3.08636 3.01127

O 1.11532 -0.14885 4.20176
 O 2.63221 0.45516 1.64648
 O -1.55638 -0.11045 -3.15032
 O 2.28901 -1.86313 0.67293
 O 5.22828 0.86933 0.77230
 Sn 3.82376 -0.45704 0.23711
 Sn 1.87578 2.39135 1.61870
 Sn 2.36171 2.29690 -1.67500
 Sn 2.08933 -0.76936 -2.92355
 Sn -0.46659 3.62684 -0.45685
 Sn -0.86784 0.37628 3.57035
 Sn -3.29882 1.68159 1.01526
 Sn 1.36038 -3.10131 -0.64784
 Sn -0.97578 -2.13828 -2.87329
 Sn -3.61454 -1.40521 -0.37022
 Sn -1.08362 -2.72230 2.33013
 Sn -2.96582 1.21432 -2.27894
 Sn 1.87741 -1.26642 2.60711

Double-Capped Gamma Na-centered Sn-Keggin ion:
 $[(\text{MeSn})_{12}(\text{NaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{1+}$, i.e. $\gamma\text{-NaSn}_{14}$

B 3.54870 -3.12852 -2.50325
 B -2.68376 -3.94366 2.43527
 C 3.74633 -0.05176 -4.07858
 C 2.21941 4.70700 -2.86845
 C -2.47693 4.13450 -3.46378
 C -2.55430 -0.83115 -4.82283
 C 0.91380 -5.19066 -2.00234
 C 5.60548 0.80272 0.71955
 C 1.46366 4.56683 3.50630
 C -3.33216 3.98765 2.90411
 C -5.64489 -0.54857 -0.69605
 C 0.38372 -5.29305 1.89446
 C -4.08782 -3.76644 -1.61606
 C -3.61285 -1.04421 4.07680
 C 2.68092 -0.27936 4.83314
 C -5.36709 1.51060 1.95511
 C -2.96171 5.31416 -0.31427
 C -4.79160 1.57611 -3.11320

C -1.33608 -3.80553 -4.05230
C 0.68551 0.14839 -5.51466
C -0.67737 -0.14036 5.52769
C 4.89377 2.78858 -1.88498
C 1.58800 5.86723 0.32375
C 4.22627 2.65164 3.14633
C 2.23219 -3.43555 3.99587
C 4.88263 -2.70047 1.55155
H -2.08883 -1.39516 -5.63651
H -2.78949 0.17392 -5.18602
H 1.13915 -5.37499 -3.05687
H 0.03839 -5.78240 -1.71836
H 3.68286 0.93898 -4.53790
H 4.68772 -0.12686 -3.52653
H 3.74358 -0.80839 -4.86915
H 5.81005 0.30298 1.67079
H 6.13044 1.76374 0.71453
H 0.65378 5.29919 3.42895
H 2.41990 5.09447 3.43669
H -4.36550 4.23709 2.64475
H -2.75780 4.91489 2.99361
H -3.32715 3.48387 3.87605
H 5.85667 -2.49359 1.09858
H -5.71012 -1.09663 -1.64029
H -6.37681 0.26560 -0.71593
H -0.34257 -5.80350 1.25455
H 0.18307 -5.56046 2.93614
H -4.08812 -3.31608 -2.61020
H -5.09946 -3.73638 -1.20039
H -3.45019 -1.83531 4.81538
H -4.51867 -1.27667 3.50912
H 2.38848 -0.98586 5.61569
H 2.62987 0.73341 5.24500
H -5.09624 1.70627 2.99739
H -5.82020 0.51627 1.89806
H -6.10795 2.25388 1.63637
H -3.52447 5.67484 0.55372
H -3.45919 5.67830 -1.21945
H -1.94869 5.73432 -0.27514
H -4.99396 0.53167 -3.36960
H -4.35585 2.06857 -3.98789
H -5.73753 2.07183 -2.86565

H 3.14029 5.24500 -2.62376
H 1.39739 5.42616 -2.93320
H -2.33595 -3.55608 -4.41602
H -1.36932 -4.80320 -3.60493
H -0.63965 -3.81560 -4.89920
H 1.59605 -0.13812 -6.05222
H 0.69649 1.23379 -5.35353
H -0.17513 -0.10238 -6.14284
H 0.16376 -0.32367 6.20427
H -1.58228 -0.54739 5.99119
H -0.79921 0.94337 5.40535
H 4.59928 3.05932 -2.90338
H 5.51396 1.88863 -1.93274
H 5.48608 3.60623 -1.45766
H 2.15482 6.37237 -0.46622
H 1.85664 6.32302 1.28243
H 0.51695 6.02777 0.14571
H 3.66496 2.94999 4.03684
H 4.98633 3.41474 2.93838
H 4.72938 1.70288 3.35992
H 1.59907 -3.54738 4.88411
H 2.42102 -4.42354 3.56622
H 3.18954 -2.99939 4.29263
H -1.83802 5.01430 -3.34004
H -3.52321 4.45337 -3.43009
H -3.75815 -0.09533 4.60097
H 4.94508 -4.19147 -3.33806
H -2.59820 -4.61131 4.25868
H 4.77387 -3.78468 1.65897
H 0.39591 1.51703 -2.72691
H 4.82810 -2.22828 2.53383
H -0.41692 3.61823 -0.20648
H -3.77261 -4.81255 -1.68495
H 2.34074 4.22698 -3.84430
H -0.75109 1.31141 2.76150
H 1.40149 4.08986 4.49019
H 3.71822 -0.48631 4.55089
H 6.00457 0.18662 -0.09213
H -2.27671 3.69703 -4.44711
H 1.76670 -5.51675 -1.39898
H 1.38690 -5.63766 1.62591
H -5.90461 -1.22775 0.12168

H -3.48952 -1.32873 -4.54765
Na -0.04424 0.34435 0.00856
O 0.60241 -0.56617 -4.27942
O 0.37852 -1.05946 -1.82743
O -1.07436 1.26803 -2.87918
O 2.30092 -2.51351 -2.73693
O -0.27043 3.54443 -1.22462
O 3.15823 -0.38278 -0.95119
O 1.41906 1.57298 -2.55767
O -0.93121 -2.84580 -3.07078
O -2.94010 3.88565 -0.31585
O 3.73263 2.54191 -1.08873
O -2.56538 -1.04795 -1.57077
O 1.91578 4.47747 0.34592
O 0.74144 1.42779 2.90324
O 1.62782 -2.90079 0.12754
O 3.33748 2.51617 2.03732
O 1.65817 1.96914 0.23036
O -2.08699 1.51630 -0.22184
O -4.20710 1.56994 1.12470
O -3.88625 1.65693 -2.00962
O 4.15144 -3.05508 -1.29972
O -1.75686 1.12619 2.58225
O -0.87631 -3.20170 -0.18304
O -0.59965 3.49117 1.31301
O 2.74281 -0.43067 1.57122
O -1.61873 -3.05113 2.68690
O -0.43761 -0.78662 4.27559
O -2.97799 -1.16263 0.94907
O -0.10633 -1.15659 1.81325
O -3.27619 -4.00502 1.22698
O 4.09012 -3.80134 -3.58185
O 1.60293 -2.59405 3.02461
O -3.12274 -4.76400 3.45687
Sn 2.10300 -0.37068 -2.76295
Sn 1.77746 3.25194 -1.37884
Sn -2.05473 2.71484 -1.92768
Sn -1.25684 -0.70352 -3.12839
Sn 0.56262 -3.11830 -1.65974
Sn 3.50507 1.14248 0.47684
Sn 1.25486 3.10940 1.95231
Sn -2.43464 2.73861 1.42371

Sn 3.35467 -1.98984 0.26669
 Sn -3.68414 0.26933 -0.43167
 Sn 0.21362 -3.18959 1.60364
 Sn -2.77321 -2.74067 -0.30936
 Sn -1.94691 -0.91989 2.75531
 Sn 1.39588 -0.43672 3.12942

Uncapped Alpha Ca-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$, i.e. $\alpha\text{-CaSn}_{12}$

C -1.75427 -2.24806 -4.90628
 C -0.31778 5.12737 -2.84037
 C 4.74114 1.93976 -3.09019
 C 5.68920 -0.22437 0.92527
 C 4.37463 -2.30317 -3.20497
 C -1.60608 2.64693 -4.77924
 C -2.70566 4.92031 1.41791
 C -4.38910 2.50242 -2.76525
 C 0.55539 5.68148 0.40543
 C 2.02438 -3.36936 4.06361
 C 2.13074 3.07048 4.24709
 C 0.20064 -5.73112 0.10130
 C -3.48863 -0.05249 4.45553
 C -5.06513 2.52693 0.66530
 C 3.21356 -0.10963 4.71843
 C -1.20556 2.43055 5.03555
 C -1.21110 -2.71504 4.87987
 C -0.89829 -4.97619 -3.10323
 C -4.54568 -2.07701 -2.77036
 C -2.97403 -4.78683 1.20449
 C -5.20083 -2.23548 0.53731
 C 4.87280 3.05386 0.16561
 C 2.65169 0.05059 -5.04790
 C 4.65728 -3.33962 0.01315
 Ca -0.06701 0.01994 0.02376
 H -2.89101 -4.39858 2.22616
 H -5.32048 -2.34638 1.61893
 H -4.95934 -1.06701 -2.66119
 H -1.95567 -5.26546 -3.09633
 H 5.85567 2.76071 -0.21270

H 5.53700 1.18673 -3.07428
H -2.14494 5.85715 1.35809
H -5.24309 2.80614 -2.15331
H 6.34661 -1.04534 0.62816
H -0.66669 2.64587 -5.33903
H 3.96546 -2.41349 -4.21372
H 0.44211 5.79343 -2.41828
H 5.59040 -3.14814 -0.52340
H -0.79813 -2.38489 -5.41948
H 4.04385 0.21765 4.07950
H -0.42187 2.83719 5.68273
H -0.45561 -3.11627 5.56227
H -5.12116 2.60948 1.75447
H 3.06411 -3.51213 3.75547
H 3.71939 -0.07237 -5.24728
H 3.17776 3.14257 3.93897
H -3.20943 -0.11052 5.51128
H 1.54447 5.85327 -0.03018
H 1.12772 -5.97461 -0.42633
H 4.61054 4.01430 -0.28863
H 4.88791 -3.43400 1.07859
H 0.37719 -5.87888 1.17051
H 1.66748 4.05310 4.11981
H 5.34110 -0.38904 1.95114
H -2.63522 4.52587 2.43851
H -4.56647 1.48828 -3.14340
H 4.55691 -3.30404 -2.80283
H -2.04536 3.64615 -4.84163
H 5.12664 2.87028 -2.66375
H -1.28117 5.65090 -2.83704
H -5.82098 -1.39583 0.21004
H -4.02725 -4.96322 0.96907
H -4.37463 -2.27242 -3.83319
H -0.57811 -4.80619 -4.13560
H -0.12831 6.43281 0.00117
H -5.42831 3.46275 0.23096
H -2.04901 -2.34861 5.48133
H 3.14685 0.55817 5.58326
H -1.64179 3.25037 4.44961
H -2.27907 -1.41577 -5.38411
H 2.32753 1.00533 -5.47131
H 2.00496 -3.18126 5.14079

H -4.04042 0.87793 4.29474
H -2.35015 -3.15509 -5.03713
H 0.64175 5.83615 1.48501
H 4.26465 -4.30506 -0.32143
H 2.10271 2.80967 5.30865
H 1.47983 -4.29724 3.86688
H 3.43326 -1.11685 5.08636
H -5.73091 1.71886 0.34918
H -1.57018 -3.52361 4.23039
H -1.98313 2.00311 5.67493
H -0.30540 -5.80227 -2.69757
H -2.44560 -5.74227 1.14348
H -5.57116 -3.14406 0.05434
H -5.27539 -2.80510 -2.40410
H 4.95148 3.20904 1.24558
H 2.10908 -0.75016 -5.55809
H -4.15521 -0.88930 4.22775
H -0.56762 -6.43790 -0.22389
H -2.28835 1.93844 -5.25788
H 6.26471 0.70394 0.88811
H -0.03336 4.90910 -3.87480
H 4.44656 2.13855 -4.12409
H 5.32847 -1.76658 -3.25992
H -4.31296 3.19309 -3.61016
H -3.75271 5.13441 1.18581
H 1.97174 -3.76316 -1.36331
H -2.77208 0.13426 -1.46551
H 2.22942 3.68636 -1.16357
H 1.21479 2.22682 -2.29959
H 1.07358 -2.15767 -2.40895
H -1.00442 -2.38147 1.77104
H 2.64818 0.15091 1.66193
H -1.36961 2.06872 1.92187
O 1.58926 -3.04213 -0.83367
O -2.18261 3.98559 0.46630
O 2.17195 -0.01222 -0.89815
O 0.68392 -1.39925 -2.89470
O -1.16384 -1.89589 -0.78574
O -1.09093 2.00827 -0.69053
O 0.12349 -0.06529 2.33991
O 1.82596 2.94755 -0.67537
O -3.19364 0.13235 -0.53206

O -0.38555 3.91551 -2.08680
 O -3.18898 2.56074 -1.98652
 O 0.11628 2.64427 1.67600
 O -2.20549 1.49703 1.85354
 O 0.78734 1.51605 -2.82469
 O -1.74699 0.13850 -2.63637
 O 2.59389 1.16918 1.59870
 O -2.24137 -1.41570 1.74392
 O 4.58266 -0.14534 0.01131
 O -2.42127 -3.86408 0.25717
 O 2.41805 -1.39416 1.47744
 O -0.09659 -2.82433 1.60296
 O 3.44009 -1.60403 -2.37395
 O -0.68134 -3.79258 -2.32905
 O 3.59929 1.49917 -2.34092
 O -3.31767 -2.21445 -2.05028
 O -0.65853 -1.64320 4.11723
 O 1.97994 -0.11005 4.00303
 O -0.66234 1.41791 4.19064
 Sn 1.11313 1.62735 3.06735
 Sn 1.15132 -1.76759 2.97451
 Sn -1.79174 -0.11666 3.17937
 Sn -1.27380 2.05797 -2.76763
 Sn -0.13228 3.70100 0.03853
 Sn -3.07084 2.10788 0.07465
 Sn 3.40092 1.57099 -0.23049
 Sn -3.16130 -1.87177 0.06433
 Sn 2.21591 0.00950 -2.97460
 Sn -1.41292 -1.79873 -2.85919
 Sn 3.24258 -1.76878 -0.24335
 Sn -0.39308 -3.71704 -0.23724

Uncapped Beta Ca-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$, i.e. $\beta\text{-CaSn}_{12}$

C -1.94146 -1.69046 -5.02394
 C 1.08852 4.99483 -2.65868
 C 4.76153 1.64691 -2.96330
 C 5.72192 -1.33473 0.82421
 C 3.94722 -3.02759 -3.14180

C -0.85115 2.99702 -4.72079
C -1.79871 5.45248 1.35452
C -3.69457 3.45973 -2.77931
C 1.58697 5.46457 0.62932
C 3.66162 -1.17931 4.09184
C -0.95339 3.29524 4.46325
C -0.96540 -5.68804 -0.14597
C -2.52882 -2.95856 4.10371
C -4.51044 3.49091 0.55904
C 2.15817 1.77495 4.93732
C -2.86796 0.44951 4.84208
C 0.81800 -3.21953 4.59917
C -1.74601 -4.59836 -3.31729
C -4.73936 -1.08941 -2.97941
C -3.97060 -4.27111 0.78024
C -5.56164 -1.25555 0.27412
C 5.40699 2.01590 0.40152
C 2.76144 -0.31002 -4.95057
C 3.95760 -4.16249 0.02319
Ca -0.04845 0.01399 -0.00840
H -3.38962 -5.00346 1.34892
H -5.76004 -1.23493 1.34979
H -4.89753 -0.00637 -2.90731
H -1.36110 -5.54507 -2.92568
H 6.31185 1.53959 0.01388
H 5.63230 1.96576 -2.38475
H -1.98489 6.25655 0.63455
H -4.39432 4.09614 -2.23073
H 5.69996 -2.32745 1.28079
H 0.11600 2.86371 -5.21322
H 3.53706 -3.02811 -4.15637
H 2.16384 4.77317 -2.72358
H 4.94395 -4.10188 -0.44427
H -1.00615 -1.97918 -5.51225
H 2.79666 2.40164 4.30253
H -2.72997 1.31282 5.50002
H 1.79540 -3.14406 5.08621
H -4.68316 3.43424 1.63757
H 4.40839 -0.39523 3.93824
H 3.77168 -0.68156 -5.14306
H -0.24079 4.11408 4.32813
H -2.34524 -2.84877 5.17642

H 2.51815 5.55817 0.06238
H -0.12754 -6.09910 -0.71695
H 5.35848 3.03125 -0.00328
H 4.09081 -4.38478 1.08629
H -0.80066 -5.93316 0.90720
H -1.95682 3.66763 4.23848
H 6.00099 -0.60965 1.59391
H -1.02091 5.77065 2.05523
H -4.20335 2.52989 -3.06172
H 3.90804 -4.05238 -2.76121
H -1.14038 4.04844 -4.80013
H 4.21034 2.53410 -3.30097
H 0.95928 5.97819 -2.19588
H -6.02252 -0.36928 -0.17082
H -4.64707 -3.76100 1.47211
H -4.59806 -1.35494 -4.03148
H -2.83893 -4.66163 -3.37729
H 0.96876 6.33735 0.40042
H -4.58505 4.53718 0.24963
H 0.07360 -3.44393 5.36916
H 1.57125 2.42106 5.59802
H -3.69017 0.65941 4.14682
H -2.28119 -0.75157 -5.47046
H 2.68838 0.71023 -5.33718
H 3.46314 -1.25441 5.16489
H -3.59373 -2.78915 3.92035
H -2.68863 -2.46177 -5.22817
H 1.84221 5.49233 1.69282
H 3.42214 -5.00929 -0.41670
H -0.92927 2.99196 5.51391
H 4.08234 -2.13142 3.75567
H 2.79073 1.13986 5.56470
H -5.30118 2.92393 0.05989
H 0.84718 -4.04356 3.87585
H -3.13881 -0.40861 5.46581
H -1.33828 -4.45798 -4.32300
H -4.56375 -4.79430 0.02275
H -6.03988 -2.14326 -0.14964
H -5.63123 -1.60689 -2.61480
H 5.50186 2.10176 1.48804
H 2.05292 -0.93507 -5.50123
H -2.28535 -3.98613 3.81938

H -1.87960 -6.18741 -0.47858
H -1.59151 2.39655 -5.25755
H 6.47420 -1.32634 0.02886
H 0.69560 5.04598 -3.67785
H 5.11907 1.10110 -3.84071
H 4.99357 -2.70517 -3.17756
H -3.39260 3.99123 -3.68642
H -2.71396 5.26498 1.92320
H 1.26543 -4.05468 -1.43101
H -2.67876 0.71481 -1.53859
H 2.99895 3.29715 -0.83417
H 1.71714 2.00192 -2.08604
H 0.73560 -2.25213 -2.37160
H 0.46220 -2.72453 1.51536
H 1.99430 1.59136 1.77914
H -2.44111 0.74253 1.79792
O 1.00649 -3.28319 -0.89834
O -1.39166 4.25711 0.67918
O 2.19405 -0.40795 -0.80936
O 0.51538 -1.42316 -2.85498
O -1.49021 -1.62748 -0.85877
O -0.67160 2.20011 -0.61846
O 0.02260 -0.16156 2.31071
O 2.40770 2.58857 -0.52733
O -3.14657 0.76987 -0.63614
O 0.39396 3.99640 -1.91597
O -2.54331 3.19733 -1.97045
O 0.73608 2.47365 1.76478
O -2.08501 1.70285 1.81991
O 1.18845 1.42674 -2.68770
O -1.56161 0.53899 -2.63792
O 2.65303 0.80351 1.70128
O -2.59587 -0.79847 1.62292
O 4.42723 -1.01690 0.29245
O -3.09755 -3.31846 0.16245
O 1.88357 -2.02133 1.46397
O -0.54214 -2.88157 1.48502
O 3.17412 -2.16147 -2.30211
O -1.33838 -3.51782 -2.47309
O 3.93207 0.79656 -2.16393
O -3.59746 -1.49877 -2.22058
O 0.49906 -1.98170 3.96249

O 1.28374 0.96308 4.15354
 O -1.65343 0.17508 4.14326
 Sn -0.45669 1.67633 3.17818
 Sn 1.89565 -0.72815 2.99766
 Sn -1.36565 -1.57789 2.98170
 Sn -0.74482 2.34236 -2.70389
 Sn 0.55622 3.65193 0.20137
 Sn -2.61897 2.65624 0.07934
 Sn 3.66306 0.88616 -0.05414
 Sn -3.46676 -1.23950 -0.08249
 Sn 2.29228 -0.33706 -2.88422
 Sn -1.61868 -1.41494 -2.94286
 Sn 2.86454 -2.34728 -0.17999
 Sn -1.10751 -3.57800 -0.36317

Uncapped Gamma Ca-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$, i.e. $\gamma\text{-CaSn}_{12}$

C -0.93766 -0.03591 5.51187
 C -3.40490 3.36631 3.05685
 C -2.30047 -4.17822 3.06066
 C 2.85372 -4.25806 2.55897
 C 1.99228 5.33167 0.15946
 C 4.54577 1.96665 2.81996
 C 5.50050 -1.30439 -1.18686
 C 1.60251 -2.40237 5.21635
 C -4.72791 -1.76623 2.48572
 C 5.01640 -1.45424 2.67237
 C -2.54047 -5.42021 -0.01734
 C -5.78708 0.11967 -0.16906
 C -2.53468 -4.29241 -3.25163
 C -5.10502 -2.23631 -2.37245
 C -2.93249 3.56560 -3.41280
 C 0.78975 -3.35055 -4.72612
 C 3.80357 -3.17543 -3.31603
 C 1.83475 2.90455 -4.39054
 C -0.18701 5.35191 -2.39801
 C -4.37855 3.95745 -0.24207
 C -0.43834 5.04478 2.62070
 C 1.48888 -0.17262 -5.74553

C 4.63668 1.52911 -2.89415
C 1.91488 1.90711 4.92177
Ca -0.26005 0.05163 0.26337
H -0.12249 -3.21214 -5.31383
H -6.03351 0.72568 0.70802
H 5.66659 -2.26370 -0.68739
H -3.20684 -4.74931 2.84230
H -2.72607 -3.83742 -4.22788
H 2.50385 2.59804 -5.19928
H 2.27095 3.77869 -3.89983
H -3.42417 -4.86079 -2.96603
H -6.02077 0.70875 -1.06076
H 6.05992 -0.54100 -0.63789
H -1.50991 0.89391 5.57742
H -3.60695 4.43006 2.90448
H -0.21633 -0.05564 6.33328
H -2.42514 -3.68979 4.03180
H 0.87846 3.19820 -4.83242
H 1.64130 -3.28000 -5.40807
H 3.17406 -4.76731 1.64474
H -2.95527 3.23683 4.04553
H 5.91338 -1.37010 -2.19739
H -1.70214 -4.99256 -3.36136
H -1.63172 -0.87151 5.64532
H -1.46534 -4.87906 3.15355
H 0.77065 -4.36206 -4.31073
H -4.35697 2.82778 3.04216
H -6.42960 -0.76482 -0.16361
H 3.72524 -4.18362 3.21591
H -3.07050 4.64565 -3.30992
H -3.91929 3.10369 -3.50740
H 2.11015 -4.88663 3.05814
H -2.37770 3.37702 -4.33625
H 1.38221 6.23207 0.04675
H 2.72714 5.30403 -0.65026
H 2.53664 5.39431 1.10610
H 4.26776 2.99238 3.07904
H 0.86668 5.64032 -2.45515
H 5.33468 2.01378 2.06340
H 4.94538 1.47842 3.71312
H -0.55433 5.20871 -3.41952
H -0.75064 6.16871 -1.93107

H 2.40214 -1.71833 5.52341
H 2.00116 -3.42056 5.16398
H 0.80774 -2.39032 5.96814
H -4.34748 -0.97836 3.14537
H -4.79140 -2.70748 3.04015
H -5.73565 -1.50432 2.15155
H 5.25913 -2.29418 2.00976
H 5.23786 -1.74365 3.70672
H -2.21461 -5.92390 -0.93190
H -2.02796 -5.88887 0.82771
H -3.62057 -5.55580 0.10396
H -5.74765 -1.37754 -2.58401
H -5.63312 -2.92009 -1.69853
H -4.90563 -2.75073 -3.31725
H 4.61696 -3.48215 -2.65402
H 3.29073 -4.07574 -3.66446
H 4.22583 -2.64216 -4.17460
H -4.52597 4.74790 0.50038
H -5.09397 3.14827 -0.05103
H -4.58315 4.37908 -1.23114
H 0.11937 4.51784 3.40500
H -1.38036 5.41093 3.04050
H 0.14423 5.91193 2.29369
H 2.57273 -0.16006 -5.90397
H 1.06455 -1.04438 -6.25076
H 1.04586 0.72504 -6.18533
H 4.70346 2.21510 -2.04287
H 5.55389 0.93779 -2.95597
H 4.54042 2.10648 -3.81801
H 1.72903 2.88590 4.46283
H 2.92338 1.89885 5.34805
H 1.19988 1.76574 5.73869
H 5.66453 -0.61460 2.40336
H 2.73658 -3.11891 -0.34057
H 0.34064 -4.12825 1.15898
H 0.34364 -3.03865 -0.71845
H -1.56473 -1.32821 -4.00758
H -0.92814 0.56167 -2.88737
H -3.26228 0.59256 -2.55001
H 0.27720 2.04936 2.38102
H 2.47397 1.75637 -0.64361
O 1.30749 -0.47895 1.89608

O -0.81771 2.27920 -0.09309
O -1.91483 -1.54430 -0.24407
O 1.36628 -0.43283 -1.81038
O -0.60320 1.60467 2.66698
O -3.87427 -1.93688 1.34328
O -3.87394 -1.78551 -1.79004
O 1.05889 -2.02589 3.94655
O 3.50913 0.64701 -2.76123
O 3.65020 -1.07226 2.53560
O 1.52457 2.36829 1.55367
O -2.20555 -4.02888 -0.08122
O 1.78751 0.85543 3.96430
O -2.79258 0.83268 1.03996
O 3.24046 0.65200 0.11352
O -1.16911 -1.37103 -3.12060
O 1.84147 2.33833 -1.21100
O 1.18014 -0.22540 -4.34585
O -1.20399 -1.11983 2.38808
O 2.88590 -2.34132 -2.59071
O -0.70285 4.19164 1.50681
O 0.03388 -3.05405 -1.65338
O 0.24090 -3.16031 1.18778
O -0.31743 4.14235 -1.65096
O -3.03250 3.48531 -0.17763
O -2.97660 0.90292 -1.67550
O 2.69247 -2.26277 0.11440
O -0.53716 1.45335 -2.76214
Sn -3.71807 -0.38148 -0.11217
Sn -2.06478 -2.82975 -1.78362
Sn 0.93852 -1.92591 -3.15201
Sn -1.92376 -2.69313 1.58285
Sn -2.11848 2.57755 1.56286
Sn -0.01113 -0.18560 3.60551
Sn 1.53686 1.35659 -2.96971
Sn 3.43514 -0.77550 -1.18394
Sn 2.84638 0.94271 2.05165
Sn 0.81002 3.56656 0.13969
Sn 2.05828 -2.32594 2.13870
Sn -1.88082 2.76357 -1.74881

Uncapped Delta Ca-centered Sn-Keggin ion: $[(\text{MeSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$, i.e. $\delta\text{-CaSn}_{12}$

C 3.27529 -4.40572 1.47925
C -1.40003 -4.87485 2.57287
C -2.03127 -2.58863 -4.73810
C 1.41588 -3.36261 -4.55488
C 2.62320 -0.55390 4.88704
C 5.60811 0.42185 -1.97117
C 4.48210 3.81623 -0.96991
C 2.14726 -5.13373 -1.71578
C -4.38193 -3.24424 -2.41201
C 3.96715 -1.30149 -4.31033
C -3.09483 0.52010 -5.00058
C -5.52897 -1.99292 0.39749
C -4.00451 3.04204 -3.03811
C -5.63197 1.28480 -0.64844
C -3.40169 1.03105 4.38134
C -1.45049 5.44939 -1.91634
C 1.82488 5.35644 -2.27254
C 0.42911 3.83366 3.96774
C -0.42823 0.67524 5.65377
C -3.48913 -2.45448 3.91167
C 1.10729 -3.58137 4.43010
C -1.44684 5.36523 1.49492
C 3.45277 4.05477 2.25826
C 5.54543 -1.97659 0.39347
Ca 0.02564 0.08846 -0.23152
H -2.49676 5.54411 -1.61226
H -5.37591 -3.02878 0.71452
H 4.75421 3.70106 -2.02311
H -3.04962 -2.47703 -5.12163
H -4.40992 3.76259 -2.32169
H 0.73975 4.88233 3.95241
H 1.09255 3.29062 4.64572
H -4.84140 2.58584 -3.57501
H -5.98385 -1.44761 1.22970
H 5.28801 3.38915 -0.36629
H 3.64834 -4.05271 2.44424
H -1.41261 -5.05715 3.65107
H 4.09947 -4.89580 0.95304

H -1.83742 -3.65415 -4.58702
H -0.58816 3.78703 4.36609
H -0.91968 6.35271 -1.60290
H 1.17457 -2.72937 -5.41303
H -0.65600 -5.53577 2.11891
H 4.41876 4.88581 -0.75070
H -3.40116 3.59985 -3.76045
H 2.49644 -5.15230 1.65735
H -1.33970 -2.22560 -5.50315
H -1.42424 5.40327 -3.00923
H -2.38014 -5.14079 2.16727
H -6.23421 -1.99262 -0.43856
H 2.40864 -3.79172 -4.71814
H -3.32237 0.55342 5.36142
H -4.42614 0.91287 4.01724
H 0.69059 -4.17986 -4.52219
H -3.21229 2.10205 4.50229
H 2.23747 -0.98308 5.81578
H 2.92314 0.47975 5.08192
H 3.51775 -1.11019 4.59332
H 6.17027 0.78920 -1.10778
H 0.57329 0.92646 6.01393
H 5.57810 1.22343 -2.71480
H 6.15508 -0.42125 -2.40269
H -1.07079 1.54701 5.79734
H -0.81929 -0.15875 6.24771
H 2.84221 -5.67248 -1.06595
H 2.38734 -5.38498 -2.75213
H 1.12259 -5.45131 -1.49306
H -4.81439 -3.81143 -1.58334
H -3.87366 -3.94864 -3.07701
H -5.18810 -2.74936 -2.96515
H 4.64407 -2.15563 -4.19753
H 4.56158 -0.39428 -4.45259
H -2.43386 0.02242 -5.71626
H -4.11913 0.16144 -5.15267
H -3.06711 1.59465 -5.20537
H -6.42800 0.56695 -0.43221
H -5.99968 1.98281 -1.40542
H -5.37881 1.83180 0.26580
H 2.79114 5.19359 -2.75849
H 1.10352 5.63748 -3.04459

H 1.92046 6.17987 -1.55580
H -3.31022 -3.48181 4.24207
H -4.27132 -2.45451 3.14422
H -3.83476 -1.87430 4.77192
H 1.13830 -4.57991 3.98582
H 0.43625 -3.59433 5.29594
H 2.11513 -3.32238 4.76579
H -1.09019 5.76002 2.45052
H -1.60505 6.20853 0.81791
H -2.39662 4.84098 1.64913
H 4.01781 3.17632 2.59054
H 4.12539 4.74175 1.73805
H 3.04977 4.57152 3.13344
H 5.64993 -1.27898 1.23232
H 6.34074 -1.79138 -0.33280
H 5.65526 -2.99860 0.76604
H 3.35356 -1.44655 -5.20339
H 2.57480 1.76459 -3.09031
H 0.33240 0.24739 -3.61914
H -0.72590 2.60785 -3.55366
H -1.76994 2.07704 1.11943
H 0.01634 -3.00773 -0.34728
H 2.27967 1.17071 1.69257
H 2.93383 -0.50630 1.35282
H -2.08709 -3.12369 -0.24121
O 1.92103 -1.26840 -0.97522
O -0.42291 -0.84327 2.02051
O -2.07780 -0.26103 -1.29571
O 0.68915 2.40482 0.00042
O 0.44412 -3.09889 0.57100
O -3.44693 -2.28523 -1.90690
O -4.48779 0.58282 -1.15807
O 2.30317 -3.72045 -1.52013
O 2.38009 3.67779 1.38583
O 3.12648 -1.15493 -3.15958
O 2.46140 -1.26539 1.77074
O -2.65420 0.26449 -3.66529
O 4.26754 -1.83027 -0.24065
O -2.29785 -2.58113 0.54095
O 3.15689 0.99774 0.21423
O -2.06028 2.48688 -0.44089
O 1.55454 1.21802 2.37754

O -0.45781 4.48798 0.93657
 O -0.42525 -2.60841 -1.87405
 O 1.39908 4.15295 -1.62190
 O 0.66269 -2.63025 3.45445
 O -0.85153 2.31227 -2.63778
 O 0.13809 -0.57864 -3.15206
 O -0.37722 0.33410 4.26373
 O -2.27129 -1.88442 3.41604
 O -3.19347 0.01145 1.38237
 O 2.50998 1.47637 -2.16708
 O -1.24413 1.87448 1.97001
 Sn -3.67689 -1.07206 -0.11642
 Sn -2.85032 1.56653 -2.00935
 Sn -0.60001 3.70228 -1.03792
 Sn -1.78740 -1.52862 -2.90412
 Sn -0.95392 -2.84898 2.11476
 Sn 2.49036 -2.79348 0.34671
 Sn 0.49133 2.98551 2.02560
 Sn 2.64980 2.82288 -0.53090
 Sn 3.64413 -0.14868 -1.37179
 Sn 1.19863 -0.60806 3.31234
 Sn 1.36191 -2.26184 -2.73244
 Sn -2.08309 0.20021 2.93333

Uncapped Epsilon Ca-centered Sn-Keggin ion:

$[(\text{MeSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$, i.e. $\epsilon\text{-CaSn}_{12}$

C -0.87655 5.78215 1.14231
 C 1.02593 1.12250 -5.30061
 C -5.97709 -0.84417 -1.24516
 C -5.63191 1.89860 1.25255
 C 1.87961 5.56518 -0.99958
 C -1.00616 1.15099 5.34337
 C 1.51240 -0.98355 5.31565
 C -3.92523 4.62765 0.54854
 C -4.14354 -0.05202 -4.04402
 C -4.02120 1.03754 4.15362
 C -4.78544 -3.93935 -0.65940
 C -1.25282 -1.14446 -5.24582
 C -1.96234 -5.54440 -0.88183

C -0.92043 -4.11613 -3.77920
C 5.88170 0.84376 -1.46000
C 0.79939 -5.74636 1.32927
C 0.39039 -3.91122 4.14726
C 5.66779 -2.01390 0.79352
C 4.74286 3.90796 -0.71955
C 3.94438 0.11220 -4.17292
C 0.73801 4.10011 -3.87081
C 3.71070 -4.73098 0.22773
C 4.45075 -0.84358 3.71999
C -0.14912 4.07364 4.00294
Ca -0.00880 -0.08284 -0.08560
H 0.93717 -6.24676 0.36746
H -1.43916 -0.18135 -5.72356
H 0.57171 -1.19912 5.82584
H -6.36452 -1.52918 -2.00516
H -1.04218 -6.06112 -1.16533
H 5.92965 -2.81922 1.48645
H 6.21900 -1.11743 1.08771
H -2.73604 -5.79954 -1.61168
H -0.31791 -1.55114 -5.63775
H 1.86867 -0.00731 5.65384
H 0.11329 6.11566 1.46251
H 1.81868 1.81125 -5.60669
H -1.61359 6.16121 1.85673
H -6.27819 0.17153 -1.51517
H 5.99462 -2.30453 -0.20830
H 1.59106 -6.08427 2.00477
H -6.16086 0.99188 1.55752
H 0.07425 1.51287 -5.66824
H 2.24453 -1.73812 5.61831
H -2.27792 -5.92134 0.09518
H -1.08929 6.22884 0.16772
H -6.44817 -1.09468 -0.29061
H -0.16127 -6.06443 1.74353
H 1.20922 0.15901 -5.77951
H -2.06377 -1.82520 -5.52056
H -5.83762 2.68116 1.98873
H 6.22610 1.58072 -2.19159
H 6.18485 -0.14835 -1.80434
H -6.04313 2.21713 0.29083
H 6.38494 1.04276 -0.51024

H 2.64874 5.83907 -1.72788
H 2.19466 5.92842 -0.01814
H 0.95357 6.07405 -1.27654
H -0.03096 1.39737 5.76804
H 4.44182 4.75391 -0.09767
H -1.31824 0.18210 5.73947
H -1.72388 1.90401 5.68128
H 5.57946 3.40441 -0.22972
H 5.06001 4.27067 -1.70220
H -4.29671 5.05803 1.48304
H -4.76486 4.26620 -0.04878
H -3.40429 5.39675 -0.02541
H -3.94926 1.02277 -3.95864
H -5.20859 -0.23811 -3.87918
H -3.89288 -0.38775 -5.05264
H -3.68256 0.24816 4.82930
H -5.00006 0.75362 3.75717
H -4.51880 -4.75610 0.01507
H -5.68360 -3.45357 -0.26916
H -4.99947 -4.34330 -1.65424
H -1.08634 -3.81248 -4.81562
H -1.44067 -5.06464 -3.61789
H 0.15225 -4.26478 -3.61279
H -0.68867 -3.72308 4.13820
H 0.57371 -4.97666 3.98694
H 0.79928 -3.64028 5.12349
H 3.64978 0.44901 -5.16859
H 3.77237 -0.96582 -4.08448
H 5.01053 0.31818 -4.04649
H -0.31435 4.26855 -3.61826
H 0.81139 3.75989 -4.90523
H 1.28761 5.04162 -3.78316
H 4.67006 -4.39410 -0.17275
H 3.89538 -5.42939 1.04912
H 3.16207 -5.23656 -0.57190
H 5.00358 -0.02828 3.24254
H 4.05876 -0.48616 4.67428
H 5.12382 -1.68454 3.91102
H 0.93015 3.91357 3.91322
H -0.47231 3.83833 5.01889
H -0.37739 5.12390 3.80681
H -4.12286 1.97472 4.70921

H -1.18339 -1.64948 2.29601
H -3.68642 -1.17674 1.65138
H 0.89071 -2.82026 -1.57031
H 2.45262 -1.29937 -1.66416
H -0.88004 2.64574 -1.51822
H 3.05728 0.93751 1.39204
H 1.28556 2.39260 1.56973
H -2.59297 1.30069 -1.48144
O -1.45493 1.59426 1.20391
O 1.72428 1.40424 -1.17372
O -1.82197 -1.36644 -1.16191
O 1.53200 -1.59495 1.16583
O -0.51923 3.37350 -0.95070
O -3.36759 -0.78993 -3.09076
O -1.44854 -3.12148 -2.89517
O -3.02511 3.53698 0.81962
O 3.36627 -1.26734 2.88151
O -3.08500 1.18923 3.07513
O 1.09188 3.20563 1.03152
O -3.70727 -2.99334 -0.71409
O -0.86983 3.24494 3.07327
O -0.88823 0.97368 -2.48950
O 0.93201 0.83539 2.53816
O 0.52016 -3.51057 -0.98166
O 3.69186 0.48783 0.80567
O 2.95516 -3.60376 0.69380
O -3.39162 1.08606 -0.94172
O 1.05335 -3.15442 3.12384
O 1.32484 3.11846 -3.00333
O -1.01159 -2.94597 1.01489
O -3.59530 -0.54620 0.92169
O 3.64178 2.99194 -0.84906
O 3.19300 0.83446 -3.18490
O 0.76937 -0.95120 -2.51326
O -0.82466 -0.96690 2.93055
O 3.28071 -1.11084 -1.15216
Sn -1.21914 -1.01041 -3.11447
Sn -1.62721 -3.43952 -0.81918
Sn 0.86468 -3.62926 1.09472
Sn -3.85927 -0.97064 -1.10684
Sn 1.05432 0.99371 -3.16641
Sn -0.96613 3.66237 1.05022

Sn 3.57724 -1.64525 0.84685
 Sn 1.29173 -1.06397 3.19599
 Sn -0.96395 1.13461 3.21237
 Sn 1.60779 3.46052 -0.98911
 Sn -3.54495 1.53410 1.08429
 Sn 3.77406 0.93984 -1.21740

5.2 Ground state geometries for Zr clusters from Chapter 4.

Zr(IV) Monomer: $[\text{Zr}(\text{H}_2\text{O})_8]^{4+}$, i.e. $\{\text{Zr}^{4+}\}$

H -1.48883 2.25493 -1.05376
 H -0.97143 -1.96956 -1.85450
 H 0.52452 2.66074 0.99544
 H -2.10935 -0.71546 1.81832
 H 1.96956 -0.97143 -1.85450
 H 0.71546 -2.10935 1.81832
 H 0.97143 1.96956 -1.85450
 H 2.10935 0.71546 1.81832
 H -0.52452 -2.66074 0.99544
 H 2.66074 -0.52452 0.99544
 H 1.48883 -2.25493 -1.05376
 H 2.25493 1.48883 -1.05376
 H -2.25493 -1.48883 -1.05376
 H -1.96956 0.97143 -1.85450
 H -0.71546 2.10935 1.81832
 H -2.66074 0.52452 0.99544
 O -1.29973 -1.33025 -1.19173
 O -1.33025 1.29973 -1.19173
 O 0.00000 1.86081 1.20010
 O -1.86081 0.00000 1.20010
 O 1.33025 -1.29973 -1.19173
 O -0.00000 -1.86081 1.20010
 O 1.29973 1.33025 -1.19173
 O 1.86081 -0.00000 1.20010
 Zr 0.00000 0.00000 0.00276

Zr(IV) Dimer: $[\text{Zr}_2(\text{OH})_2(\text{H}_2\text{O})_{12}]^{6+}$, i.e. $\{\text{Zr}_2^{6+}\}$

H 1.25183 -1.62215 -2.29259
H 2.48485 2.50655 -1.14644
H -2.48504 -2.50661 1.14619
H -1.25175 1.62190 2.29271
H -0.00601 2.13106 -0.05978
H 0.00600 -2.13108 0.05987
H -4.58285 -0.64000 0.42134
H -1.75326 -0.13759 -2.88369
H -3.36115 -1.83598 -1.62651
H -2.83054 2.49977 -1.15717
H 1.75326 0.13788 2.88367
H 4.58279 0.63997 -0.42164
H 2.83057 -2.49968 1.15743
H 3.36125 1.83607 1.62629
H -4.58688 0.81454 -0.19928
H -1.88902 -2.39212 -1.66508
H -2.81743 2.72103 0.39617
H -1.03092 1.21730 -2.52514
H 4.58683 -0.81464 0.19880
H 2.81737 -2.72114 -0.39590
H 1.03094 -1.21706 2.52525
H 1.88915 2.39229 1.66484
H 1.93694 1.63332 -2.33746
H 2.64273 -0.92952 -2.58095
H -1.93716 -1.63352 2.33732
H -2.64266 0.92930 2.58107
O -2.36990 -1.58923 1.46226
O 0.02701 1.16669 0.08929
O -1.82988 0.87585 2.03936
O -0.02701 -1.16671 -0.08920
O -4.01427 0.06671 0.05763
O -1.62308 0.52243 -2.17585
O -2.49719 -1.80879 -1.17008
O -2.41308 2.20156 -0.32546
O 2.36972 1.58913 -1.46243
O 1.82995 -0.87608 -2.03925
O 1.62311 -0.52223 2.17591
O 4.01426 -0.06664 -0.05767
O 2.41315 -2.20149 0.32569

O 2.49726 1.80885 1.16990
 Zr -1.79429 0.01803 -0.01605
 Zr 1.79428 -0.01803 0.01605

Zr(IV) Tetramer: $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$, i.e. $\{\text{Zr}_4^{8+}\}$

H 0.90221 0.90158 2.06556
 H 1.75430 1.75451 -2.02027
 H -1.75430 -1.75451 -2.02027
 H -0.90221 -0.90158 2.06556
 H -1.75451 1.75430 2.02027
 H -0.90158 0.90221 -2.06556
 H 1.75451 -1.75430 2.02027
 H 0.90158 -0.90221 -2.06556
 H -4.28328 -2.24546 -0.63964
 H -5.10346 1.37787 -0.38747
 H -4.29511 -0.35330 -2.32651
 H -4.29615 0.35357 2.32540
 H -1.37770 5.10369 -0.38635
 H 2.24591 4.28317 -0.63837
 H -0.35330 4.29511 2.32651
 H 0.35357 4.29615 -2.32540
 H 2.24546 -4.28328 0.63964
 H -2.24591 -4.28317 -0.63837
 H 0.35330 -4.29511 2.32651
 H 0.91521 -3.44035 -2.61177
 H 5.10369 1.37770 0.38635
 H 3.44020 -0.91628 -2.61194
 H 3.44035 0.91521 2.61177
 H 4.28317 -2.24591 0.63837
 H -5.10369 -1.37770 0.38635
 H -3.44020 0.91628 -2.61194
 H -3.44035 -0.91521 2.61177
 H -4.28317 2.24591 0.63837
 H 1.37787 5.10346 0.38747
 H 0.91628 3.44020 2.61194
 H -2.24546 4.28328 0.63964
 H -0.91521 3.44035 -2.61177
 H -1.37787 -5.10346 0.38747
 H 1.37770 -5.10369 -0.38635
 H -0.35357 -4.29615 -2.32540

H -0.91628 -3.44020 2.61194
 H 4.29511 0.35330 -2.32651
 H 5.10346 -1.37787 -0.38747
 H 4.28328 2.24546 -0.63964
 H 4.29615 -0.35357 2.32540
 O -1.66995 -1.66995 -1.05409
 O -1.66995 1.66995 1.05409
 O -1.17431 -1.17399 1.17138
 O -1.17399 1.17431 -1.17138
 O -4.21123 -1.53316 0.02355
 O -4.21105 1.53336 -0.02453
 O -3.42217 0.05061 -2.16028
 O -3.42284 -0.04976 2.15964
 O 1.66995 1.66995 -1.05409
 O 1.17431 1.17399 1.17138
 O -1.53316 4.21123 -0.02355
 O 1.53336 4.21105 0.02453
 O 0.05061 3.42217 2.16028
 O -0.04976 3.42284 -2.15964
 O 1.66995 -1.66995 1.05409
 O 1.17399 -1.17431 -1.17138
 O 1.53316 -4.21123 -0.02355
 O -1.53336 -4.21105 0.02453
 O -0.05061 -3.42217 2.16028
 O 0.04976 -3.42284 -2.15964
 O 4.21123 1.53316 0.02355
 O 3.42217 -0.05061 -2.16028
 O 3.42284 0.04976 2.15964
 O 4.21105 -1.53336 -0.02453
 Zr -2.54413 0.00015 -0.00019
 Zr 0.00015 2.54413 0.00019
 Zr -0.00015 -2.54413 0.00019
 Zr 2.54413 -0.00015 -0.00019

Zr(IV) Hexamer: $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_{24}]^{12+}$, i.e. $\{\text{Zr}_6^{12+}\}$

H -2.03569 4.56853 0.32867
 H 2.03569 -4.56853 0.32867
 H 4.53940 2.15862 -0.30567
 H -4.53940 -2.15862 -0.30567
 H -0.32867 2.03569 4.56853

H 0.32867 -2.03569 4.56853
H 2.15862 -0.30567 4.53940
H -2.15862 0.30567 4.53940
H -0.30567 4.53940 2.15862
H 1.25567 -3.34694 2.51686
H 4.56853 -0.32867 2.03569
H -4.56853 0.32867 2.03569
H 2.02156 4.31560 1.22141
H -2.02156 -4.31560 1.22141
H 4.53940 -2.15862 0.30567
H -3.34694 2.51686 1.25567
H 0.30567 4.53940 -2.15862
H -0.30567 -4.53940 -2.15862
H 4.56853 0.32867 -2.03569
H -4.56853 -0.32867 -2.03569
H 0.32867 2.03569 -4.56853
H -0.32867 -2.03569 -4.56853
H 2.51686 1.25567 -3.34694
H -2.51686 -1.25567 -3.34694
H 2.03569 4.56853 -0.32867
H -1.25567 3.34694 2.51686
H -2.02156 4.31560 -1.22141
H 1.25567 3.34694 -2.51686
H -1.25567 -3.34694 -2.51686
H 2.02156 -4.31560 -1.22141
H 0.30567 -4.53940 2.15862
H -2.03569 -4.56853 -0.32867
H 4.31560 -1.22141 -2.02156
H 3.34694 -2.51686 1.25567
H 4.31560 1.22141 2.02156
H 3.34694 2.51686 -1.25567
H -4.31560 -1.22141 2.02156
H -3.34694 -2.51686 -1.25567
H -4.31560 1.22141 -2.02156
H -4.53940 2.15862 0.30567
H -2.51686 1.25567 3.34694
H 1.22141 2.02156 4.31560
H 2.51686 -1.25567 3.34694
H -1.22141 -2.02156 4.31560
H 1.22141 -2.02156 -4.31560
H 2.15862 0.30567 -4.53940
H -2.15862 -0.30567 -4.53940

H -1.22141 2.02156 -4.31560
H -1.99206 -1.99206 1.99206
H 1.99206 -1.99206 -1.99206
H 1.99206 1.99206 1.99206
H -1.99206 1.99206 -1.99206
O -1.42895 -1.42895 1.42895
O 1.42895 1.42895 1.42895
O -1.08069 1.08069 1.08069
O 1.08069 -1.08069 1.08069
O -1.55418 4.11359 -0.38786
O 1.55418 -4.11359 -0.38786
O 3.59054 1.99329 -0.46881
O -3.59054 -1.99329 -0.46881
O 0.38786 1.55418 4.11359
O -0.38786 -1.55418 4.11359
O 1.99329 -0.46881 3.59054
O -1.99329 0.46881 3.59054
O -0.46881 3.59054 1.99329
O 0.46881 -3.59054 1.99329
O 4.11359 0.38786 1.55418
O -4.11359 -0.38786 1.55418
O 1.55418 4.11359 0.38786
O -1.55418 -4.11359 0.38786
O 3.59054 -1.99329 0.46881
O -3.59054 1.99329 0.46881
O 0.46881 3.59054 -1.99329
O 1.08069 1.08069 -1.08069
O -1.42895 1.42895 -1.42895
O 1.42895 -1.42895 -1.42895
O -1.08069 -1.08069 -1.08069
O -0.46881 -3.59054 -1.99329
O 4.11359 -0.38786 -1.55418
O -4.11359 0.38786 -1.55418
O -0.38786 1.55418 -4.11359
O 0.38786 -1.55418 -4.11359
O 1.99329 0.46881 -3.59054
O -1.99329 -0.46881 -3.59054
Zr -0.00000 2.55139 0.00000
Zr -0.00000 -2.55139 0.00000
Zr 2.55139 -0.00000 0.00000
Zr -2.55139 0.00000 -0.00000
Zr -0.00000 0.00000 2.55139

Zr -0.00000 -0.00000 -2.55139

Zr(IV) Hexamer Ring: $[\text{Zr}_6(\text{O}_2)_6(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$, i.e. $\{\text{Zr}_6^{6+}\}$

H -0.06225 1.46009 -1.73161
 H -1.25535 -0.80900 -1.77921
 H 1.30280 -0.67336 -1.74486
 H 0.06225 -1.46009 1.73161
 H -1.30280 0.67336 1.74486
 H 1.25535 0.80900 1.77921
 H 2.16120 -5.30093 1.46875
 H -3.27362 4.32765 -1.99556
 H 3.51002 4.53951 1.46269
 H -2.11232 -4.99502 -2.01317
 H -5.39198 -0.65609 1.98059
 H 5.67163 -0.78572 -1.43217
 H 3.90153 -4.18278 -1.47664
 H -3.90153 4.18278 1.47664
 H 2.89669 4.57784 -1.98717
 H -1.71315 -5.46842 1.46899
 H -5.61253 -1.26122 -1.41923
 H 5.61253 1.26122 1.41923
 H 2.55139 -4.78790 -2.00251
 H 3.27362 -4.32765 1.99556
 H -2.89669 -4.57784 1.98717
 H -3.51002 -4.53951 -1.46269
 H -5.67163 0.78572 1.43217
 H -5.43889 0.19435 -1.97653
 H -2.55139 4.78790 2.00251
 H -2.16120 5.30093 -1.46875
 H 1.71315 5.46842 -1.46899
 H 2.11232 4.99502 2.01317
 H 5.39198 0.65609 -1.98059
 H 5.43889 -0.19435 1.97653
 O 3.80116 -1.97486 0.39070
 O -3.80116 1.97486 -0.39070
 O -0.18993 4.28674 0.38434
 O 0.18993 -4.28674 -0.38434
 O -3.61713 -2.30766 0.38297
 O 3.61713 2.30766 -0.38297
 O 2.80477 -1.45907 1.35164

O -2.80477 1.45907 -1.35164
O -0.14026 3.17106 1.35139
O 0.14026 -3.17106 -1.35139
O -2.67029 -1.70470 1.34251
O 2.67029 1.70470 -1.34251
O 1.97546 -1.02571 -1.13853
O -1.97546 1.02571 1.13853
O -0.09600 2.22926 -1.13869
O 0.09600 -2.22926 1.13869
O -1.88568 -1.20588 -1.15501
O 1.88568 1.20588 1.15501
O 2.41612 -4.36071 1.52958
O -2.41612 4.36071 -1.52958
O 2.57124 4.28134 1.53021
O -2.57124 -4.28134 -1.53021
O -4.97867 0.10501 1.52948
O 4.97867 -0.10501 -1.52948
O 2.93883 -4.02990 -1.52453
O -2.93883 4.02990 1.52453
O 2.03706 4.54940 -1.52478
O -2.03706 -4.54940 1.52478
O -4.97408 -0.52860 -1.51323
O 4.97408 0.52860 1.51323
Zr 1.80105 -2.82539 -0.00010
Zr -1.80105 2.82539 0.00010
Zr 1.54694 2.97580 0.00753
Zr -1.54694 -2.97580 -0.00753
Zr -3.34440 -0.14991 -0.00566
Zr 3.34440 0.14991 0.00566