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Thorium(IV)−Selenate Clusters Containing an Octanuclear Th(IV) Hydroxide/Oxide Core

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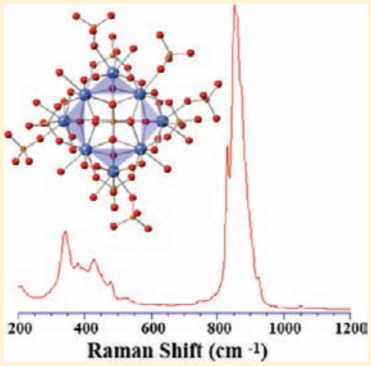
S *Supporting Information*



ABSTRACT: Four Th(IV) hydroxide/oxide clusters have been synthesized from aqueous solution. The structures of $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{15}(SeO_4)_8{\cdot}7.5H_2O]$ (**1**), $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{17}(SeO_4)_8{\cdot}nH_2O]$ (**2**), $[Th_9(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{21}(SeO_4)_{10}]$ (**3**), and $Th_9(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{21}(SeO_4)_{10}{\cdot}nH_2O$ (**4**) were determined using single crystal X-ray diffraction. Each structure consists of an octanuclear core, $[Th_8O_4(OH)_8]^{16+}$, that is built from eight Th(IV) atoms (four Th in a plane and two up and two down) linked by four "inner" μ_3-O and eight "outer" μ_2-OH groups. Compounds **3** and **4** additionally contain mononuclear $[Th(H_2O)_5(SeO_4)_4]^{4-}$ units that link the octamers into an extended structure. The octanuclear units are invariably complexed by two selenate anions that sit in two cavities formed by four planar Th(IV) and four extra-planar Th(IV) atoms, thus making $[Th_8O_4(OH)_8(SeO_4)_2]^{12+}$ a common building block in **1**−**4**. However, changes in hydration as well selenate coordination give rise to structural differences that are observed in the extended structures of **1**−**4**. The compounds were also characterized by Raman spectroscopy. Density functional theory calculations were performed to predict the geometries, vibrational frequencies, and relative energies of different structures. Details of the calculated structures are in good agreement with experimental results, and the calculated frequencies were used to assign the experimental Raman spectra. On the basis of an analysis of the DFT results, the compound $Th_8O_8(OH)_4(SeO_4)_6$ was predicted to be a strong gas phase acid but is reduced to a weak acid in aqueous solution. Of the species studied computationally, the dication $Th_8O_6(OH)_6(SeO_6)_6^{2+}$ is predicted to be the most stable in aqueous solution at 298 K followed by the monocation $Th_8O_7(OH)_5(SeO_6)_6^{+}$.

■ INTRODUCTION

Hydrolysis and condensation reactions are prevalent in the aqueous chemistry of most metal ions, particularly in those of high charge density, acidity, and electronegativity.[1−3] Tetravalent metal ions, for example, readily form a number of mononuclear and polynuclear complexes via hydrolysis and condensation, respectively. With respect to the latter, our lack of knowledge regarding the identity of the oligomeric species has manifested itself as "unanticipated" behaviors (e.g., transport and migration) of heavy elements in the environment.[4,5] Such species have also posed significant challenges in process chemistry[6,7] and, more fundamentally, have generated large discrepancies in thermodynamic data.[8−10] However, absent information regarding the formation, composition, stability, and reactivity of the condensation products in solution, it is little wonder that researchers have struggled to predict the aqueous behavior of these cations. That is not to say that such reactions have been ignored. In fact, the hydrolysis and condensation of M(IV) cations in aqueous solution has been probed using a variety of techniques for many decades.[1,11−15] Nevertheless, the solution and solid-state structures of surprisingly few oligomers have been reported.

Early investigations into the solid state structural chemistry of M(IV) polynuclear complexes suggested that the d- and f-block ions exhibited remarkably similar chemistry. For example, the hydroxysulfate $M(OH)_2SO_4$ has been reported for many of the tetravalent metal ions (M = Zr, Hf, Th, U, Np).[16−19] Yet, later studies have shown that differences in chemistry of these ions are quite profound. A tetrameric unit of composition $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ is prevalent in the aqueous and solid state chemistry of zirconium,[20−22] while dimeric $[Th_2(OH)_2]^{6+}$ and, more recently, hexameric $[Th_6(O)_4(OH)_4]^{12+}$ clusters are most commonly reported for thorium.[14,15,23−26] Plutonium exhibits strikingly different oligomers in terms of both size and composition. Whereas Th(IV) forms oxo/hydroxo complexes, the polynuclear complexes reported to date for Pu(IV) contain exclusively oxo bridges.[27,28] Interestingly, no purely oxo bridged complexes have been described for thorium. Moreover, the largest oxo/hydroxo bridged oligomer reported for thorium is a hexanuclear cluster,[14,25] in contrast to plutonium, for which a $[Pu_{38}O_{56}]^{40+}$ cluster has been described.[27,28]

Such differences may be attributed to the mechanism of condensation (olation versus oxolation), as it is related to the size, charge, and electronegativity of the metal ion.[3] In traversing the An(IV) series, there is a systematic decrease in ionic radius[29] concurrent with an increase in the equilibrium constant for the formation of the first hydrolysis product.[8,9,30]

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Table 1. Crystallographic Data and Structure Refinement for 1−4

	1	2	3	4
formula	$H_{52}O_{66.5}Se_8Th_8$	$H_{42}O_{61}Se_8Th_8$	$H_{50}O_{73}Se_{10}Th_9$	$H_{50}O_{73}Se_{10}Th_9$
MW^a	3604.42	3506.34	4096.36	4096.36
temp. (K)	100	100	295	100
λ (Mo Kα)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	tetragonal	tetragonal
space group	$P\bar{1}$	$P\bar{1}$	$P4/n$	$P4/n$
a	9.223(1)	12.808(1)	18.907(2)	18.650(2)
b	13.186(1)	13.184(1)	18.907(2)	18.650(2)
c	25.144(2)	25.061(2)	9.489(1)	12.788(1)
α	97.320(1)	83.364(1)	90	90
β	94.989(1)	89.530(1)	90	90
γ	109.788(3)	71.266(1)	90	90
V	2825.9(3)	3979.0(6)	3391.9(7)	4447.8(6)
Z	2	2	2	2
D_{calc} (g cm^{-3})	4.236	2.927	4.011	3.059
μ (mm^{-1})	26.262	18.642	25.148	19.178
$R_1{}^b$ [$I > 2\sigma(I)$]	0.0420	0.0372	0.0636	0.0529
$wR_2{}^b$	0.0866	0.0866	0.1884	0.1570

[a]The molecular weights and densities given for compounds **2** and **4** do not reflect the solvent water that exists between the clusters. [b]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

The increased propensity of Pu(IV) to undergo hydrolysis as compared to Th(IV) can be viewed, albeit somewhat simplistically, in terms of the Brønsted acidity of the metal's aquo ion for which an apparent increase in acidity is accompanied by a decrease in size or an increase in the charge density of the metal ion. Such differences seem to have a significant effect on the condensation behavior of the M(IV) ions that is perhaps best reflected in the structural chemistry of the polynuclear complexes formed by these ions.

In an effort to explore how the systematic decrease in ionic radius and increase in acidity across the series affects the mechanisms of cluster formation and the nature of the resulting species, we are investigating the hydrolysis and condensation behavior of An(IV) ions. As part of this effort, we reported three hexanuclear clusters decorated by 12 carboxylate functionalized ligands wherein the hexanuclear core $[Th_6(O)_4(OH)_4]^{12+}$ was identified as a stable structural unit.[25] Interestingly, similar inorganic units have also been identified for other metal ions such as Bi(III),[31] Ln(III),[32] and M(IV) (M = Zr, Ce, U),[14,33−41] suggesting that the hexanuclear unit is a common, fundamental building block that exists in many inorganic systems. To further explore this chemistry and also the effects of the complexing anions on the resulting structures, we have been investigating the condensation of thorium in the presence of inorganic oxygen donor ligands such as sulfate and selenate. Here, we report the synthesis and characterization of four new octanuclear Th−hydroxide/oxide clusters. The compounds all consist of a $[Th_8O_4(OH)_8]^{16+}$ core that, to the best of our knowledge, represents the largest Th(IV) oligomer yet described.

■ EXPERIMENTAL SECTION

***Caution!** ^{232}Th is an α-emitting radioisotope, and standard precautions for handling radioactive materials should be followed when working with the quantities used in the syntheses that follow.*

Synthesis. An amorphous Th precipitate was obtained from a 1 mL solution of 0.4 M $Th(NO_3)_4$ in H_2O by the addition of concentrated NH_4OH. The resulting white precipitate was washed several times with distilled water until the pH of the supernatant was near neutral, as determined by pH strips. A 1 mL aliquot of 0.38 M H_2SeO_4 and 3 mL of H_2O were then added to the precipitate. For compounds **1** and **2**, the resulting slurry was then transferred to a beaker, placed on a hot plate, and brought to a boil for approximately 10 min, after which the reaction was removed from heat and allowed to cool. The slurry (approximately 3 mL) was transferred to a 15 mL conical tube, and colorless crystals of compounds **1** $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{15}(SeO_4)_8{\cdot}7.5H_2O]$ and **2** $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{17}(SeO_4)_8{\cdot}nH_2O]$ were obtained in varying yields after several hours to several days. Note that compound **1** can be obtained in relatively pure yield via evaporation of the mother liquor. Compounds **3** and **4** were prepared from reactions analogous to those described above but at room temperature without heating. Upon sitting, colorless crystals of **3** $[Th_9(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{21}(SeO_4)_{10}]$ and **4** $Th_9(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{21}(SeO_4)_{10}{\cdot}nH_2O$ are obtained from the reaction in varying yields after several hours to several days. Compound **3** can be obtained as a pure phase by removing the crystals from the mother liquor and allowing the solution to completely evaporate.

X-Ray Structure Determination. Reflections were collected at 100 K (**1**, **2**, **4**) or 295 K (**3**) on a Bruker AXS SMART diffractometer equipped with an APEXII CCD detector using Mo Kα radiation. The data were integrated and corrected for absorption using the APEX2 suite of crystallographic software.[42] The structures were solved by direct methods using SHELXS-97[43] (**1**, **3**, **4**) or SIR-92[44] (**2**), and all structures were refined using SHELXL-97.[43] Satisfactory refinements as well as tests for missing symmetry using PLATON[45] suggest no obvious space group changes. Crystallographic data for **1**−**4** are provided in Table 1, and CIF data are available as Supporting Information. Crystallographic data have also been deposited with the Inorganic Crystal Structure Database (ICSD) and may be obtained at http://icsd.fiz-karlsruhe.de by referencing nos. 423803 (**1**), 423804 (**2**), 423805 (**3**), and 423806 (**4**).

All non-hydrogen atoms were located using difference Fourier maps and were ultimately refined anisotropically. Hydrogen atoms of the bound water molecules (O13−O27) in **1** were not found during refinement; however, Th−O bond lengths of 2.475(6)−2.622(6) Å are consistent with metal-bound water molecules. Hydrogen atoms of the μ_2-OH sites in **1** were also not located during refinement, but charge balance requirements as well as bond valence summation[46,47] values of 1.1−1.2 for O5−O12 suggest protonation of these sites. Bond valence summation values of ~2.0 suggest that the μ_3-oxygen sites, O1−O4, are not protonated. Average Th−μ_2-OH and Th−μ_3-O bond distances are 2.38(2) Å and 2.30(1) Å, respectively. Hydrogen atoms of the solvent water molecules were not found during the refinement of **1**.

Twenty-one fully occupied solvent water molecules were located during the refinement of **2**. An additional seven water molecules were disordered over 11 sites resulting in 28 water molecules per formula unit. Refinement of the model including the water molecules did not yield a satisfactory refinement. They were thus removed from the structure, and the data of **2** were corrected for disordered solvent residing in the voids of the structure using SQUEEZE[48] within PLATON.[45] The total solvent accessible void volume and electron count per cell were found to be 1529.9 Å^3 and 559 e$^-$, respectively. We note that the latter is consistent with 28 solvent water molecules per formula unit. Hydrogen atoms of the bound water molecules (O13–O29) were not located during the refinement of **2**, but Th–O bond distances for Th–O13 through Th–O29 ranging from 2.515(6) to 2.615(6) Å are consistent with thorium bound water molecules. Hydrogen atoms of the μ_2-OH sites in **2** were not located during refinemen,t but charge balance requirements as well as bond valence summation values[46,47] (~1.2) suggest protonation of the eight μ_2-oxygen sites, O5–O12. The four μ_3-oxygen sites, O1–O4, are not protonated, as evidenced by bond valence summation values (~2.0) as well as an average Th–μ_3-O bond distance of 2.303(10) Å, consistent with a μ_3-oxo site. Selenate oxygen atom O61 was disordered over two sites (O61A and O61B), and a problematic thermal parameter for O61B required constraint of the thermal parameter (EADP) to that of a better behaved oxygen atom, O61A.

Hydrogen atoms of the bound water molecules (O4–O9) in **3** were not found during refinement, but lengthened Th–O bond distances of 2.484(24)–2.670(14) Å as compared to the average Th–O bond distance of 2.47(12) Å are consistent with assignment of these atoms as bound water molecules. Hydrogen atoms of the μ_2-OH sites in **3** were also not located during refinement, but charge balance requirements as well as bond valence summation values (~1.2) suggest protonation of the μ_2-oxygen sites, O2 and O3. A bond valence summation value of 2.1 suggests that the μ_3-oxygen site, O1, is not protonated. Average Th–μ_2-OH and Th–μ_3-O bond distances are 2.36(2) Å and 2.30(1) Å, respectively.

The data of **4** were corrected for disordered interstitial water molecules using SQUEEZE[48] within PLATON.[45] The total solvent accessible void volume and electron count per cell were found to be 1512.5 Å^3 and 553 e$^-$, respectively. Hydrogen atoms of the bound water molecules (O4–O9) were not located during the refinement of **4**, but an average Th–O bond distance of 2.53(7) Å is consistent with metal bound water molecules. Hydrogen atoms of the μ_2-OH sites in **4** were not located during refinement, but charge balance requirements as well as bond valence summation values (~1.2) suggest protonation of the μ_2-oxygen sites O2 and O3. The μ_3-oxygen site, O1, is not protonated, as evidenced by a bond valence summation value of ~2.1 as well as an average Th–μ_3-O bond distance of 2.298(2) Å. Positional disorder of oxygen atoms O30 and O31 of one of the selenate ligands (Se(30)O$_4^{2-}$) required using a PART command wherein component A accounted for 51% of oxygen atoms, O30 and O31, while B accounted for 49%. The total occupancy for the two components, A and B, was fixed to 100%. Finally, the coordinates of oxygen atom O9 were constrained; the x and y coordinates were set to 3/4 so that O9 lies on the 4-fold axis.

Raman Spectroscopy. Raman spectra were collected for crushed single crystals **1** and **3**, which were verified by single crystal XRD, on a Renishaw inVia Raman Microscope with an excitation line of 532 nm.

Computational Approach. The geometries of the Th$_8$O$_{12}^{8+}$ core and the Th$_8$O$_{12}$H$_n^{m+}$ core with n = 4, 6, and 8 and m = 12, 14, and 16, respectively, decorated with six SeO$_4^{2-}$ groups (Th$_8$O$_8$(OH)$_4$(SeO$_4$)$_6$, Th$_8$O$_6$(OH)$_6$(SeO$_6$)$_6^{2+}$, Th$_8$O$_4$(OH)$_8$(SeO$_6$)$_6^{4+}$) were optimized using density functional theory (DFT).[49] The calculations were done with the hybrid B3LYP exchange correlation functional.[50,51] The DZVP basis set[52] for H, Se, and O (polarized double-ζ on the Se and O and double-ζ on the H) and the Stuttgart large core effective core potential and basis set for Th were used with only two tighter f's.[53] The calculated structures were all shown to be minima by analysis of the calculated second derivatives. These calculations were done with the Gaussian09 program system.[54]

■ RESULTS

Synthetic Approach. It is well-known that metal hydroxides can be precipitated from aqueous solutions by pH adjustment.[1,6] As the pH is increased, prior to precipitation, the metal ions undergo hydrolysis, resulting in a number of hydrolysis products that may then condense to form larger, polynuclear species. Previously, we explored the formation of such polynuclear complexes by precipitating an amorphous product of thorium hydrolysis that was subsequently dissolved in organic acids. We were able to isolate hexanuclear Th(IV) molecular clusters from these solutions.[25] On the basis of those results, we investigated the formation of oligomeric complexes in the presence of an inorganic complexing anion, selenic acid, which offers a range of coordination modes. This approach resulted in the isolation of four compounds [Th$_8$(μ_3-O)$_4$(μ_2-OH)$_8$(H$_2$O)$_{15}$(SeO$_4$)$_8$·7.5H$_2$O] (**1**), [Th$_8$(μ_3-O)$_4$(μ_2-OH)$_8$(H$_2$O)$_{17}$(SeO$_4$)$_8$·nH$_2$O] (**2**), [Th$_9$(μ_3-O)$_4$(μ_2-OH)$_8$(H$_2$O)$_{21}$(SeO$_4$)$_{10}$] (**3**), and Th$_9$(μ_3-O)$_4$(μ_2-OH)$_8$(H$_2$O)$_{21}$(SeO$_4$)$_{10}$·nH$_2$O (**4**), *all* built from an octameric Th–hydroxide–oxide core.

Structure Descriptions. All of the isolated compounds (**1**–**4**) have structures based on an octanuclear core, [Th$_8$O$_4$(OH)$_8$]$^{16+}$, built from eight Th(IV) atoms linked by four "inner" μ_3-O and eight "outer" μ_2-OH groups. As illustrated in Figure 1, four of the Th(IV) sites (Th1–Th4) are bridged by two inner μ_3-oxo groups to two adjacent Th(IV) centers to form a planar, square entity with average Th–Th distances of 4.181(10) Å. The μ_3-oxo groups further bridge each pair of adjacent "inner" Th(IV) atoms to an outer Th(IV) cation. Two μ_2-hydroxo sites otherwise link the inner Th(IV) atoms to two additional Th(IV) atoms (Th5–Th8 in Figure 1b), one lying above and the other below the plane, at Th$_{\text{inner}}$–Th$_{\text{outer}}$ distances of 3.876(11) Å to form octanuclear units that resemble a Th$_4$ square within a Th$_4$ square, as shown in Figure 1a. As illustrated in Figure 1b, the four outer Th(IV) sites are displaced alternately above and below the plane

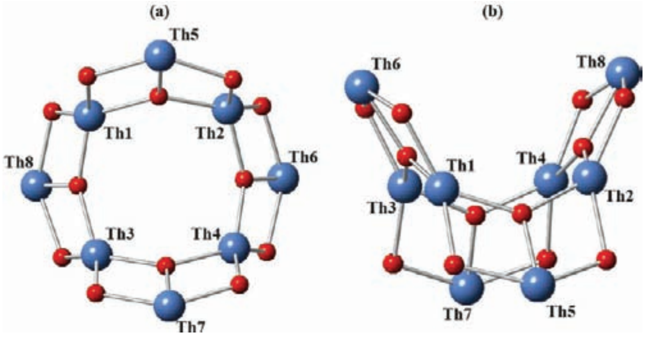

Figure 1. Representation of the [Th$_8$(O)$_4$(OH)$_8$]$^{16+}$ cores in **1**–**4** wherein each Th(IV) center is linked to two additional Th(IV) sites via a combination of μ_3-hydroxo and μ_2-oxo linkages. As shown in part a, Th1–Th4 are bound to two "inner" μ_3-oxo and two "outer" μ_2-hydroxo groups. Alternatively, Th5–Th8 are coordinated to only one μ_3-oxo and two μ_2-hydroxo groups. As illustrated in part b, Th1–Th4 form a nearly planar entity with Th5–Th8 lying alternatively above and below the plane. Note that the labeling scheme shown is consistent with compounds **1** and **2**; Th1–Th4 and Th5–Th8 are equivalent to Th1 and Th2, respectively, in compounds **3** and **4**. Blue and red spheres are thorium and oxygen, respectively.

defined by the four inner Th(IV) ions. Note that although the coordination environment about the Th(IV) sites in **1**−**4** vary between structures, the inner four Th(IV) atoms are always bound to two μ_3-O and two μ_2-OH groups while the outer four Th(IV) atoms are always bound to one μ_3-O and two μ_2-OH groups. Similarly, the octanuclear Th−hydroxide/oxide units are invariably complexed by two selenate anions (Figure 2a and b) that sit in the two cavities formed by the four planar Th(IV) sites and the four extra-planar Th(IV) atoms. The resulting $[Th_8O_4(OH)_8(SeO_4)_2]^{12+}$ unit is a common building block in **1**−**4**. All of the Th(IV) sites in **1**−**4** are nine-coordinate, but changes in the local coordination environment about the Th(IV) metal centers are observed. The selenate anions bind each individual Th(IV) center exclusively in a mondentate manner. However, overall, these units exhibit a range of coordination modes, binding through one oxygen atom to a single metal center or alternatively via two, three, or four oxygen atoms to multiple Th(IV) sites. In fact, the selenate anions exhibit three distinct structural roles: (i) limiting connectivity, (ii) linking multiple metal centers, and (iii) filling "voids" created by the oligomeric units. In addition to the diversity of selenate coordination modes, changes in the levels of hydration and hydrogen bonding interactions contribute to noticeable differences in the extended structures of **1**−**4**. Average bond distances for **1**−**4** are in Table 2 for comparison with the optimized DFT structures discussed below.

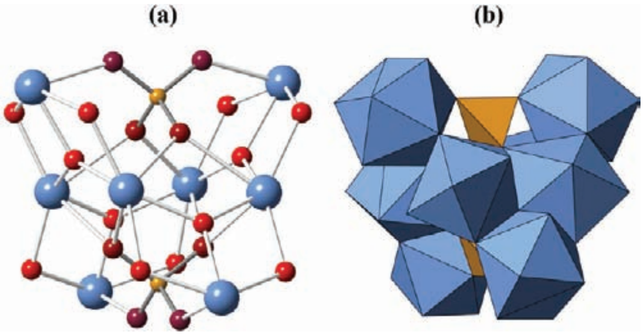

Figure 2. (a) The $[Th_8(O)_4(OH)_8]^{16+}$ cores shown in Figure 1b are capped by two selenate units to result in $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(SeO_4)_2]$ building units which are present in compounds **1**−**4**. (b) Polyhedral representation of the $[(ThO_9)_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(SeO_4)_2]^{12+}$ units in **1**−**4** that result from coordination of the Th(IV) centers to nine oxygen atoms from a combination of water molecules and selenate anions.

Compounds **1** and **2** both crystallize in the triclinic space group $P\bar{1}$. The structures are each built from eight crystallographically unique Th(IV) metal centers, eight unique selenate anions, four μ_3-oxo units, and eight μ_2-hydroxo groups. Compound **1** additionally contains 15 crystallographically unique bound water molecules and eight unique solvent water molecules, one of which is 50% occupied. The local structure of **1** is highlighted in Figure 3a and d. The voids created by the $[Th_8(O)_4(OH)_8]^{16+}$ cores in **1** (Figure 1b) are filled by two coordinatively saturated selenate units, Se(30) and Se(40), to result in the $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(SeO_4)_2]^{12+}$ units shown in Figure 2a,b. As illustrated in Figure 3, the coordination sphere of the Th(IV) ions in **1** is completed by coordination of the metal centers to the oxygen atoms from a combination of selenate anions and water molecules. The coordination environment about each of the eight, nine-coordinate Th(IV) sites is summarized in Table 3. Further, the octameric units in **1** are linked along [010] via coordinately saturated $Se(50)O_4^{2-}$ and $Se(80)O_4^{2-}$ groups and down [001] via $Se(60)O_4^{2-}$ groups to form thick two-dimensional sheets (Figure 4). However, two of the selenate anions, $Se(10)O_4^{2-}$ and $Se(70)O_4^{2-}$ are terminal, binding through a single oxygen atom to one metal center while the other three oxygen atoms of the selenate group are unbound and thus limit connectivity along [001]. $Se(90)O_4^{2-}$ caps three Th(IV) sites via three oxygen atoms and is likewise terminal in that the fourth oxygen atom remains unbound. Solvent water molecules fill the spaces between the clusters.

The structure of compound **2** is remarkably similar to that described for **1**. However, subtle changes in the local coordination environment about the Th(IV) centers (Table 3) as well as the connectivity of the selenate ligands give rise to a few differences that are perhaps most noticeable in the extended structure of **2** as compared to **1**. The structure of **2**, like **1**, is built from $Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(SeO_4)_2]^{12+}$ units wherein two selenate anions, $Se(5)O_4^{2-}$ and $Se(6)O_4^{2-}$, sit in the voids created by four in-plane and two out-of-plane Th(IV) sites (Figure 3b,e). However, in total, 17 water molecules complete the coordination spheres of the Th(IV) metal centers in **2**. Overall, the compound adopts a one-dimensional structure wherein octameric units are linked via selenate group $Se(3)O_4^{2-}$ into chains that extend infinitely along [010], as highlighted in Figure 5. The five remaining selenate groups are terminal. Selenate ligands $Se(1)O_4^{2-}$, $Se(2)O_4^{2-}$, and $Se(4)O_4^{2-}$ essentially "cap" three Th(IV) sites via coordination of three oxygen atoms to three metal centers, while the fourth oxygen atom remains unbound. Selenate anions, $Se(7)O_4^{2-}$ and

Table 2. Comparison of Calculated Bond Distances (Å) for $Th_8O_4(OH)_8(SeO_4)_6^{+4}$ with Average Experimental Values

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

[a] The labeling scheme for the Th(IV) sites is consistent with that in compounds **1** and **2** (Figure 1); Th1−Th4 and Th5−Th8 are equivalent to Th1 and Th2, respectively, in compounds **3** and **4**.

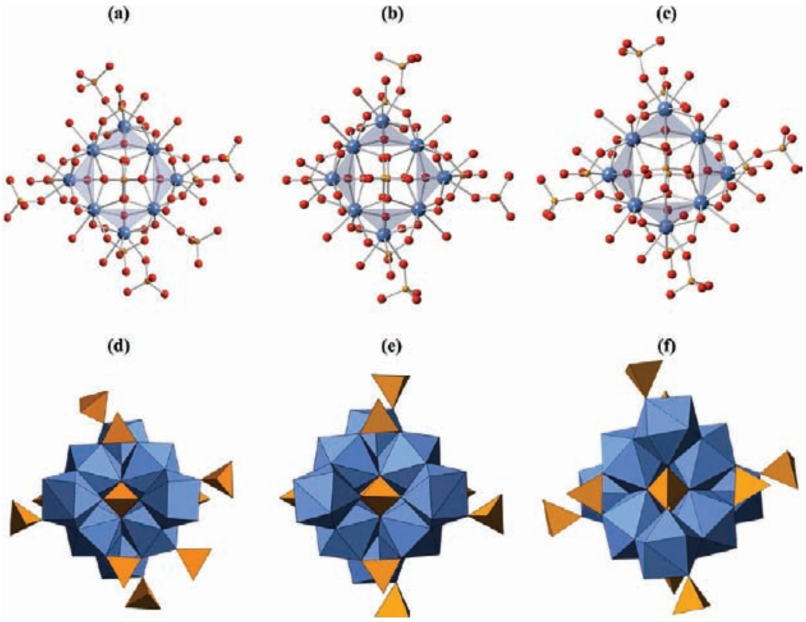

Figure 3. Ball and stick (a−c) and polyhedral (d−f) representations of the local structure in **1** (a,c), **2** (b, d), and **3**−**4** (c,f). Each Th(IV) site is nine-coordinate, bound to a combination of μ_3-oxo and μ_2-hydroxo groups, water molecules, and selenate anions. Each compound is constructed from an octanuclear core, highlighted in blue in a−c, yet differences in the number of bound selenate anions and water molecules are observed. Blue, red, and orange spheres in a−c are thorium(IV), oxygen, and selenium atoms, respectively. Blue and orange polyhedra in d−f represent ThO_9 and SeO_4^{2-} units, respectively.

Table 3. Summary of the Coordination Environment about the Th(IV) Sites in 1−4

	1							
	Th1	Th2	Th3	Th4	Th5	Th6	Th7	Th8
N (μ_3-O)	2	2	2	2	1	1	1	1
N (μ_2-OH)	2	2	2	2	2	2	2	2
N (H_2O)	1	0	1	1	3	3	3	3
N (SeO_4^{2-})	4	5	4	4	3	3	3	3
	2							
	Th1	Th2	Th3	Th4	Th5	Th6	Th7	Th8
N (μ_3-O)	2	2	2	2	1	1	1	1
N (μ_2-OH)	2	2	2	2	2	2	2	2
N (H_2O)	1	1	1	1	3	4	3	3
N (SeO_4^{2-})	4	4	4	4	3	2	3	3
	3			4				
	Th1	Th2	Th3	Th1	Th2	Th3		
N (μ_3-O)	2	1	0	2	1	0		
N (μ_2-OH)	2	2	0	2	2	0		
N (H_2O)	1	3	5	1	3	5		
N (SeO_4^{2-})	4	3	4	4	3	4		

$Se(8)O_4^{2-}$, are monodentate and terminal, binding to a single metal center through one oxygen atom, leaving the other three selenate oxygen atoms unbound.

Compounds **3** and **4** crystallize in the higher symmetry, tetragonal space group *P*4/*n*. The structures both consist of three crystallographically unique Th(IV) metal centers, three unique selenate anions, one μ_3-oxo unit, two μ_2-hydroxo groups, and six unique water molecules. The local structure for compound **3** is shown in Figure 3c,f, and inspection of Table 3 suggests that the coordination environment about the three unique Th(IV) sites in **3** is identical to that in **4**. In fact, both compounds form two-dimensional sheets wherein octanuclear $[Th_8(O)_4(OH)_8(H_2O)_{16}(SeO_4)_2]^{12+}$ units are linked along [100] and [010] via mononuclear $[Th(H_2O)_5(SeO_4)_4]^{4-}$ units into an extended structure (Figures 6 and 7). Differences in the two structures are thus attributed to hydrogen bonding interactions and solvent water that are absent in **3** (Figure 6) but reside in the interlayer in **4** (Figure 7). It is worth noting that in the structures of **1**−**4** hydrogen bonding schemes exist between SeO_4^{2-} groups and bound and/or solvent water molecules.

Raman Spectroscopy. The Raman spectra for **1** and **3** are provided as Supporting Information. Peaks in the Raman spectrum for **1** are observed at 130, 162.5, 210, 343, 380, 427.5, 480, 528, 748, 833, 853, 925, 3317, 3501, and 3642 cm^{-1}. Assignments and a comparison of the experimental values with the average calculated vibrational spectra are given in Table 4. Peaks in the Raman spectrum for **3** are observed at 127, 153, 183, 343, 377, 433, 478, 534, 832, 846, 870, and 1047 cm^{-1}.

Computational Results. We have previously shown that DFT is of significant benefit in assigning the proton positions in $[Th_6(O)_4(OH)_4]^{12+}$ clusters[25] and have used the same approach here to help determine the likely positions of the protons in the core. The lowest energy calculated structures for the $Th_8O_{12}^{8+}$ core, $Th_8O_8(OH)_4(SeO_4)_6$, $Th_8O_6(OH)_6(SeO_6)_6^{2+}$, and $Th_8O_4(OH)_8(SeO_6)_6^{4+}$, are shown in the Supporting Information together with additional higher energy structures and a table of the relative energies for the eight isomers of $Th_8O_8(OH)_4(SeO_4)_6$ and five isomers of $Th_8O_6(OH)_6(SeO_6)_6^{2+}$. For $Th_8O_8(OH)_4(SeO_4)_6$, the lowest energy structure has two OH groups bridging an in-plane Th(IV) species with two out-of-plane Th(IV) atoms, one above-the-plane and one below-the-plane. The two OH groups are located on two in-plane Th(IV) sites that are separated as much as possible. The second lowest energy isomer is only 1 kcal/mol higher in energy and involves three in-plane Th(IV) groups: one Th(IV) with two OH groups, as in the most stable structure, and the

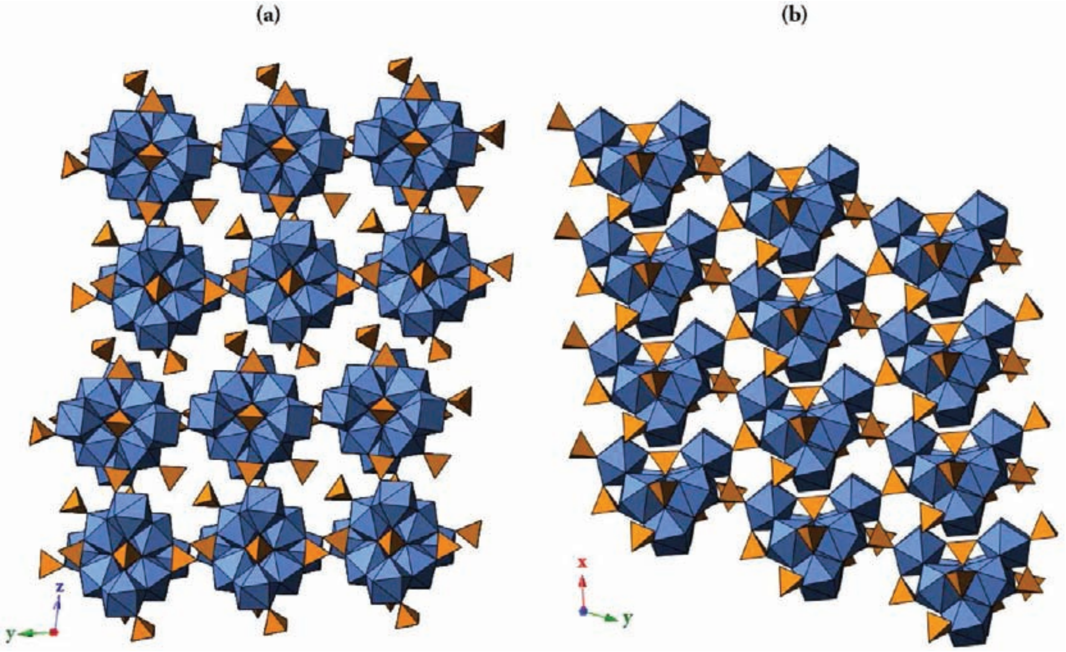

Figure 4. Polyhedral representation of **1** viewed down the [100] and [001] directions. (a) The octameric units highlighted in Figure 3d are connected by selenate anions along [010] and [001] to form double layers that extend infinitely along [010]. The double layers are connected via hydrogen bonding along the [001] direction. Shown in part b, the selenate groups link the octameric units shown in Figure 2b along [100] and [010] to form 2-dimensional sheets.

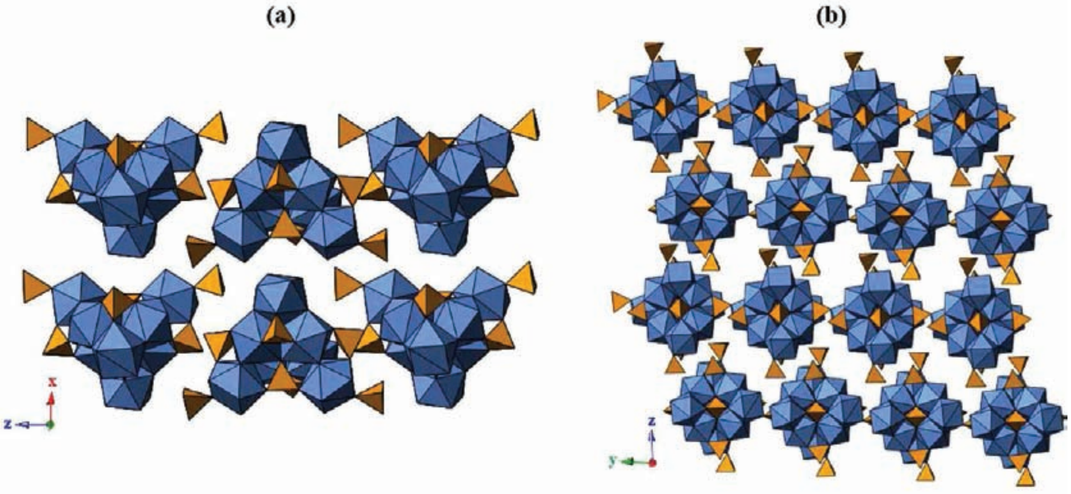

Figure 5. Polyhedral representation of **2** viewed down the [010] and [100] directions. Octameric units are linked via selenate ligands to form one-dimensional chains that extend infinitely along [010].

other two Th(IV) centers adjacent to it, each with one OH bridge to an out-of-plane Th(IV), one above and one below the plane. For $Th_8O_6(OH)_6(SeO_6)_6^{2+}$, the lowest energy structure can be described as a combination of structures A and E of $Th_8O_8(OH)_4(SeO_4)_6$. The two additional protons are added to two oxygen atoms that are at ~90° to the four OH groups with one oxygen bridging to an upper Th(IV) site and one to a lower Th(IV). Another structure that is within 1 kcal/mol adopts the same basic isomeric form but with the protons on the OH bridging groups to the Th(IV) with a single OH in different orientations.

The calculated geometry for $Th_8O_4(OH)_8(SeO_6)_6^{4+}$ is in good agreement with the experimental structure considering the absence of the two selenate anions as well as the water molecules of solvation. The geometry of the bare core $Th_8O_{12}^{8+}$ is also in reasonable agreement with the core that is fully protonated.

Comparison of the structure of $Th_8O_{12}^{8+}$ with the core of $Th_8(OH)_8O_4(SeO_4)_6^{4+}$ shows that the presence of the protons leads to some interesting changes in the structure. Absent the eight protons, which lead to the formation of the eight OH bridges, and the selenate anions, the core structure has shorter Th−O bonds in all cases except for the bond from the μ_3-oxygen to a Th(IV) that is not in the plane. Addition of the protons, even in the presence of the coordinating SeO_4^{2-} ions, leads to substantial elongation of most of the Th−O bonds except for the bond between the μ_3-oxygen and a Th(IV) not in the plane, which is substantially shortened by more than 0.20 Å. This short bond distance is comparable to the bridging O in C_{2h} Th_2O_4 but is much longer than the bond distance in the

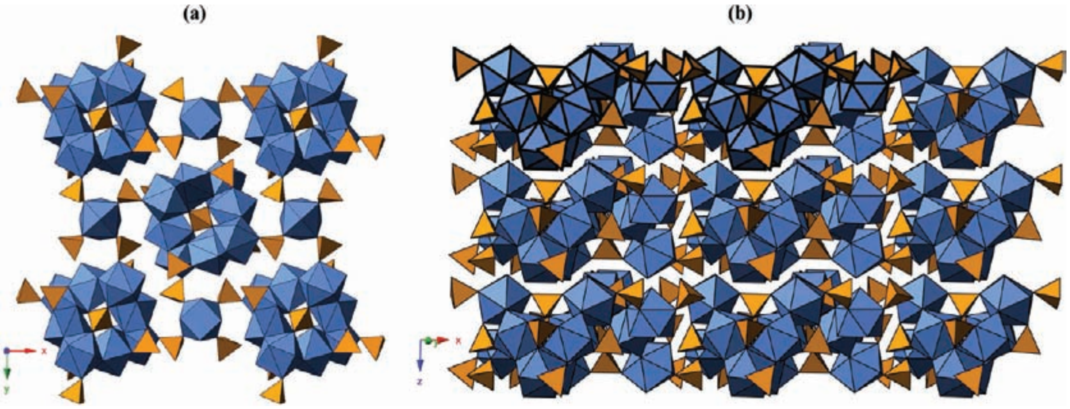

Figure 6. Polyhedral representation of **3** (a) highlighting the topology of the two-dimensional sheets. (b) Octameric $[Th_8(O)_4(OH)_8(H_2O)_{16}(SeO_4)_2]^{4+}$ units are linked along [100] and [010] via mononuclear $[Th(H_2O)_5(SeO_4)_4]^{4-}$ units into an extended structure.

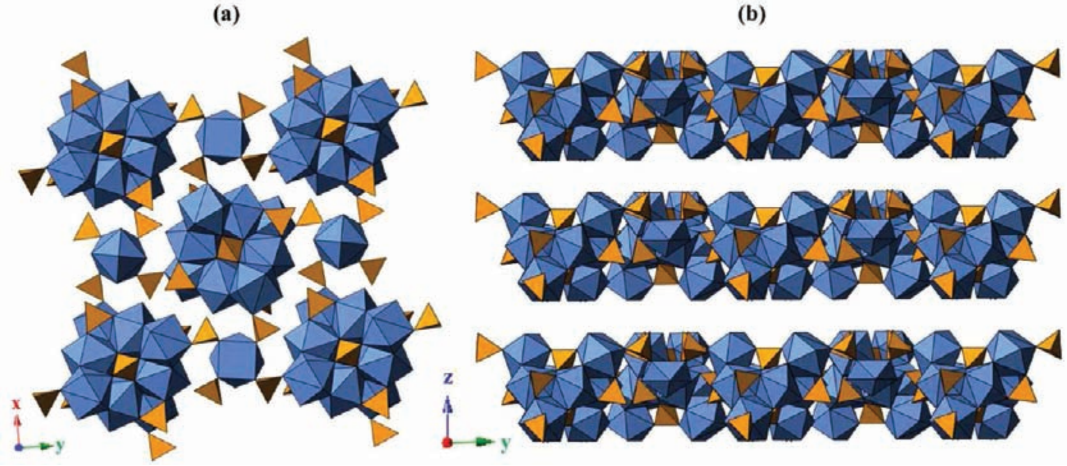

Figure 7. Illustration of **4** viewed down the (a) [001] and (b) [100] directions. Octameric $[Th_8(O)_4(OH)_8(H_2O)_{16}(SeO_4)_2]^{12+}$ units are linked along [100] and [010] via mononuclear $[Th(H_2O)_5(SeO_4)_4]^{4-}$ units into a layered structure. Solvent water that was not modeled during refinement resides in the interlayer.

ThO diatomic molecule of 1.845 Å. As such, the ThO moiety in the $Th_8(OH)_8O_4$ should not be described as a complexed ThO species.[55]

The calculated vibrational spectra can be used to aid in the assignment of the experimental Raman spectra. The calculated vibrational energies for SeO_4^{2-} are stretches at 789.4 (t) and 739.3 (a) cm^{-1} and bends at 391.0 (t) and 299.9 (e) cm^{-1}. The bridging OH stretching frequencies are calculated to be 2% too high, consistent with the fact that the calculated values are harmonic frequencies in contrast to the experimental values, which include anharmonic effects. Deletion of two protons raises the O−H stretch by about 40 cm $^{-1}$, but further removal does little. The experimental band at 925 cm $^{-1}$ can be assigned to a Se═O terminal stretch, and it is predicted to be about 7% too high. This band is predicted to decrease in frequency as protons are removed. The next bands at 830−850 cm^{-1} are predicted to be very intense and are assigned to a combination of Se−O stretches and OH bends. The calculated values are about 2% too low. The band at ~750 cm^{-1} can also be assigned to the combination of Se−O stretch and OH bend. The band at 528 cm^{-1} can be assigned to a Th−O stretch. The next few bands can be assigned to combinations of O−Se−O bends and Th−O stretches. The low frequency bands are assigned to various bend combinations.

The acidity was calculated of the neutral compound defined by the reaction $Th_8O_8(OH)_4(SeO_4)_6 \rightarrow Th_8O_9(OH)_3(SeO_4)_6^{-1} + H^+$. There are two low energy isomers, differing by 0.5 kcal/mol, that adopt very similar proton arrangements. The anion structures are given in the Supporting Information. The gas phase acidity (ΔH_{298K} = 297.2 and ΔG_{298K} = 289.6 kcal/mol) shows that the neutral compound is a strong gas phase acid. For comparison, the gas phase acidities (ΔG_{298}) of H_2SO_4, FSO_3H, and CF_3SO_3H are 301.6, 292.8, and 290.2 kcal/mol from high level calculations.[56] In addition, the gas phase acidities of WO_2OH_2, $WO(OH)_4$, $W(OH)_6$, $W_2O_5(OH)_2$, $W_3O_8(OH)_2$, and $W_4O_{11}(OH)_2$ are 309.6, 305.1, 303.1, 294.2, 273.8, and 267.8 kcal/mol.[57] The acidity in solution was also evaluated using the self-consistent reaction field approach[58] with the COSMO parametrization[59−61] using the ADF code.[62−64] The reaction energies were calculated directly using the previous value of −264.1 kcal/mol for the free energy of solvation of the proton.[65] The calculated pK_a = 14.6 (Table 5) shows that the complex is a weak acid and thus is unlikely to undergo much dissociation in aqueous solution. We also calculated the pK_a for $Th_8O_8(OH)_4(SeO_4)_6$ in water to be 9.5 relative to the known value of acetic acid in water (pK_a = 4.75).[66] The main result is that the very strong gas phase acid is a very weak acid in water. This large difference probably arises because of the shielding of the core protons by the SeO_4^{2-}

Table 4. Comparison of the Experimental and Average Calculated Vibrational Spectra

compound **1**		$Th_8O_4(OH)_8(SeO_4)_6^{+4}$				$Th_8O_6(OH)_6(SeO_4)_6^{+2}$				$Th_8O_8(OH)_4(SeO_4)_6$			
exp. freq. (cm^{-1})	assignment	calc. freq. (cm^{-1})[a]	no.	IR intensity (km/mol)[a]	Raman activity (Å^4/amu)[a]	calc. freq. (cm^{-1})	no.	IR intensity (km/mol)	Raman activity (Å^4/amu)	calc. freq. (cm^{-1})	No.	IR intensity (km/mol)	Raman activity (Å^4/amu)
3642, 3651	OH stretch	3720	8	256	124	3762	6	182	123	3764	4	137	84
925	Se═O stretch	988	4	141	40	969	4	171	35	944	4	199	31
853, 833	Se−O stretch + μ_3-OH bend	820	4	610	8	798	12	346	27	800	12	361	24
	μ_3-OH bend	794	8	80	22								
748	Se−O stretch + OH bend	736	16	243	10	726	14	196	4	713	12	176	10
528	Th−O stretch	511	12	154	1	535	12	127	3	550	12	120	5
480, 427.5, 380, 343, 210, 162.5, 130	Th−O stretch + Se−O bend + bends	457, 441, 420, 417, 402, 320, 308, 304, 220, 142			4−27	456, 439, 418, 409, 406, 402, 394, 380, 314, 282, 217, 209			4−10	469, 432, 407, 405, 400, 394, 314, 203, 136			4−10

[a] Average.

Table 5. Deprotonation Reaction Free Energies ΔG_{298}^{aq} in Aqueous Solution in kcal/mol

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

anions. The selenate groups distribute the excess negative charge over the whole cluster, rendering the anion very stable in the gas phase, thus leading to its high gas phase acidity. Yet the same charge delocalization combined with shielding by the exterior SeO_4^{2-} groups leads to the anion not being particularly well-solvated and a much less acidic species in solution.

The deprotonation reactions of the +4, +3, +2, and +1 Th−selenate clusters were calculated as shown in Table 5. The results show that it is exothermic to lose a proton from the +4 and +3 cations to form the +3 and +2 cations, respectively. However, the formations of the +1 and the neutral from the +2 and +1 cores are predicted to be endothermic. Thus, the most stable species in solution with no counterions present is predicted to be the cluster with a +2 charge. The free energy differences are small enough that it is likely that there is some $Th_8O_7(OH)_5(SeO_6)_6^{+}$ present ($K_{eq} \sim 0.02$) with much smaller amounts of $Th_8O_5(OH)_7(SeO_6)_6^{3+}$ ($K_{eq} \sim 0.002$) and $Th_8O_8(OH)_4(SeO_6)_6$ ($K_{eq} \sim 0.004$). The +4 cluster is not predicted to be present to any substantial amount, hence the need for the two additional coordinating SeO_4^{2-} groups found in the solid state. However, as noted before,[25] the additional anions lead to the precipitation process.

■ DISCUSSION

Four octanuclear Th(IV) hydroxide/oxide selenates, $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{15}(SeO_4)_8{\cdot}7.5H_2O]$ (**1**), $[Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{17}(SeO_4)_8{\cdot}nH_2O]$ (**2**), $[Th_9(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{21}(SeO_4)_{10}]$ (**3**), and $Th_9(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(H_2O)_{21}(SeO_4)_{10}{\cdot}nH_2O$ (**4**), resulting from the condensation of Th(IV) hydrolysis products have been crystallized and structurally characterized. All of the compounds consist of an octanuclear $[Th_8O_4(OH)_8]^{16+}$ core that represents the largest oligomeric Th(IV) species reported to date.

A number of mononuclear and polynuclear thorium hydroxide aqueous complexes have been proposed in the literature based on inferences from probes of solution speciation, but surprisingly few oligomeric Th(IV) complexes have been isolated. Dimeric, trimeric, tetrameric, and hexameric complexes, the stoichiometry of which is most commonly inferred from potentiometric titration data,[1,6,9,67,68] have been included in descriptions of Th(IV) hydrolysis and condensation. Of these complexes, the $Th_2(OH)_2^{6+}$ and $Th_6(OH)_{14}^{10+}$ or $Th_6(OH)_{15}^{9+}$ species are by far the most firmly established in the literature,[6] yet only recently have hexanuclear $[Th_6(OH)_4(O)_4]^{12+}$ clusters been crystallized and structurally characterized.[14,25] This is somewhat surprising, as their existence in aqueous solution has been hypothesized for over 50 years. Larger oligomers including the octameric units reported here are noticeably absent from nearly all discussions of thorium hydrolysis. The octamer structure is fundamentally different from the $[Th_6(O)_4(OH)_4]^{12+}$ hexamer as well as other polynuclear compounds reported for thorium, representing a different building unit that cannot be generated by simple transformation of the hexameric unit.

Unlike the hexameric $[Th_6(O)_4(OH)_4]^{12+}$ core, for which a number of other metal ions such as Bi(III),[31] Ln(III),[32] and M(IV) (M = Zr, Ce, U)[35,36,40] form a similar, fundamental structural unit, the octameric $[Th_8O_4(OH)_8]^{16+}$ core has not been reported, to the best of our knowledge, for other homometallic metal ion systems. Within the Zr(IV) literature, an octanuclear complex formed through the condensation of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ tetramers has been proposed on the basis of small-angle X-ray scattering measurements.[22] Neither of the two octamer configurations described by Singhal et al.[22] has been isolated in the solid state, but in any case, the solution state octameric moieties proposed are not structurally related to the $[Th_8O_4(OH)_8]^{16+}$ octamers observed in the solid state structures of the compounds reported here. The $[Th_8O_4(OH)_8]^{16+}$ cores are also different from the solid state structure of the octameric $[Al_8(OH)_{14}(H_2O)_{18}]^{10+}$ unit, resulting from the hydrolysis and condensation of Al(III) reported by Casey et al.[69] The eight Al(III) ions that constitute the core are bridged by solely hydroxo groups (μ_2-OH and μ_3-OH) into a nearly planar entity that is capped by water molecules. The homometallic octameric cores reported here are structurally related to the heterometallic octanuclear $[Cr(III)_4Dy(III)_4]$ molecular cluster recently reported by Rinck et al.[70] However, the chemistry of the 3d−4f clusters is notably different than that of the octameric Th(IV) cores, and these clusters are being explored for their interesting properties and potential application as single molecule magnets.

There are striking similarities between the octanuclear $[Th_8O_4(OH)_8]^{16+}$ core in **1−4** and a dodecanuclear U(IV)/U(V) unit described by Nocton et al.[39] The $Th_8(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_8(SeO_4)_2]^{12+}$ and the $[U_{12}(\mu_3\text{-}OH)_8(\mu_3\text{-}O)_{12}]^{16+}$ units are illustrated in Figure 8. Both cores contain a “butterfly” unit that consists of four in-plane and four out-of-plane metal centers. However, whereas the Th_8 unit is complexed by two selenate anions in **1−4**, the U_8 unit is further linked via oxo and hydroxo ligands to four additional U(IV)/U(V) sites to form a dodecamer. The octameric cluster may be related to or even be a precursor for the dodecanuclear unit, but the formation of a larger thorium cluster may be thwarted by thorium’s limited redox chemistry.

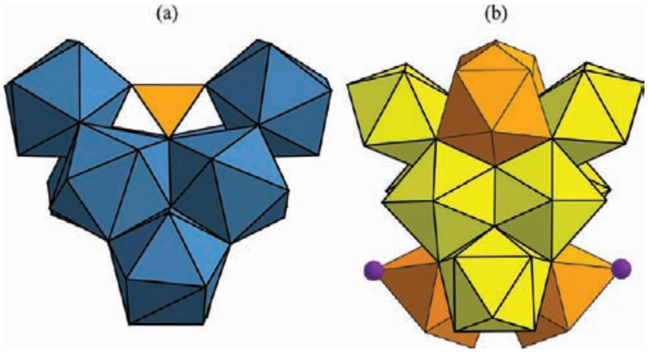

Figure 8. Polyhedral representation of (a) the octanuclear $[Th_8(O)_4(OH)_8(SeO_4)_2]^{12+}$ units in **1−4** and (b) the dodecanuclear $[U_{12}(OH)_8(O)_{12}]^{18+}$ clusters reported by Nocton et al.[39] Blue and orange polyhedra in part a are nine-coordinate Th(IV) and selenate ions, respectively. Yellow and orange polyhedra in part b are U(IV)/U(V) centers.

Alternatively, the anionic ligands may influence the nuclearity of the complexes. In their work, Nocton et al. found that the size of the clusters was dependent on the composition of the U(III) starting materials.[39] The $U_{12}O_{20}$ cluster was prepared from iodide salts, but in the absence of iodide, smaller U_6O_8 clusters were observed.[39] In fact, ligand influences on oligomer formation have been noted by a number of researchers. Clearfield, for example, has noted that the presence of complexing ligands including sulfate and carboxylates changes the polymerization pathway for Zr(IV).[21] The octanuclear units in **1−4** are invariably complexed by two SeO_4^{2-} units that sit in the two voids created by the four planar Th(IV) sites and a pair of Th(IV) atoms that are displaced above or below the plane. The results of the calculations are also consistent with these conclusions. The $Th_8O_6(OH)_6(SeO_6)_6^{2+}$ core is predicted to be the most stable in aqueous solution at 298 K for the clusters that were studied, showing that there is a complex relationship between protonation state and coordinating anions. The results suggest that there is a delicate balance between counterion stabilization in aqueous solution and precipitation of the neutral complex. The extent to which the selenate anions influence product formation or whether the octanuclear unit forms in the absence of SeO_4^{2-} groups is the subject of an ongoing investigation.

■ CONCLUSIONS

Four octanuclear Th(IV) selenates resulting from the hydrolysis and condensation of thorium in aqueous solution have been synthesized and structurally characterized. The structures consist of a polynuclear $[Th_8(O)_4(OH)_8]^{16+}$ core that represents the largest Th(IV) cluster isolated to date. The core is invariably complexed by two selenate anions. Further investigations into the effects of ligand identity on cluster nuclearity as well as differences in the condensation behavior of the M(IV) ions are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental Raman spectra for **1** and **3**; additional figures of different calculated isomers; selected bond lengths and angles for **1−4**; total energies in au and calculated entropies; relative energies for isomers of $Th_8O_9(OH)_3(SeO_4)_6^{-1}$; calculated frequencies (cm^{-1}), IR intensities (km/mol), and Raman activities ($Å^4$/amu) for the lowest energy isomers of $Th_8O_4(OH)_8(SeO_4)_6^{+4}$, $Th_8O_6(OH)_6(SeO_4)_6^{+2}$, and $Th_8O_8(OH)_4(SeO_4)_6$; and optimized Cartesian coordinates in Å for the lowest energy isomers. This information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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