Thorium coordination: A comprehensive review based on coordination number

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Graphical Abstract

Chemical compounds discussed in this article

1,2-dimethoxyethane (PubChem CID: 8071); Bis(2-diphenylphosphinophenyl) ether (PubChem CID: 4285986); 2-pyridinol-1-oxide (PubChem CID: 69975); Nitrilotriacetic acid (PubChem CID: 8758); N-(2-hydroxyethyl)iminodiacetic acid (PubChem CID: 7152); Nitrilitripropionic acid (PubChem CID: 98537); Citric Acid (PubChem CID: 311); 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid (PubChem CID: 18465)

Abstract

Although thorium comprises roughly 8.1 ppm of the Earth, its chemical characteristics and properties have been relatively underexplored. In large part due to its radioactivity and propensity to form oxides at pH above 5, thorium has been much less extensively investigated than first row transition metals. Today, there are close to 700,000 registered structures with an R-factor of 0.075 or better on the Cambridge Crystallographic Database, about 50% of which are complexes containing transition metals. The actinides make up roughly 8% of total number of database structures, with close to 85% of those being uranium containing complexes and 11% of the actinide structures containing thorium. Herein, we explore the various unique coordination environments of thorium with coordination numbers ranging from 5 to 12.

Keywords*

Thorium, actinide, f-element

1.1 Introduction

Although it is the most abundant radioactive element found in nature, thorium has a unique chemistry that has remained relatively unexplored. [1] The Th(IV) ion has been demonstrated to possess the ability to reach multiple coordination numbers from 4 to 15, thus allowing it to coordinate a wide-range of ligands with potential in numerous applications. [2]

The potential for covalency offered by thorium and the involvement of the d-orbital in bonding, as well as the high Lewis acidity, the propensity to remain in the +4 oxidation state, and large ionic radii it possesses, results in very unusual reactivity. [3,4,5,6] In the nine-coordinate environment, it was found that Th(IV) has an ionic radius of 1.09 Å, making it the largest stable

* [XA₂] = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene; BDPP = 2,6-bis(2,6-diisopropylanilidomethyl)pyridine dianion; DPEPhos = (diphenylphosphinophenyl)ether; dme = 1,2-dimethoxyethane; Th(sal)₄ = tetrakis(salicylaldehydato)thorium(IV); Th(TTA)₄ = tetrakis(thenoyltrifluoroacetato)thorium(IV); ETAM = N,N'-diethyl-2,3-dihydroxyterephthalamide; Me₃BnN = trimethylbenzylammonium; DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid; DTPA = diethylenetriaminepentaacetic acid; TAM = 6,19-bis(2-((2,3-Dihydroxy-4-((2-methoxyethyl)carbamoyl)benzoyl)amino)ethyl)-12,13,25,26-tetrahydroxy-2,10,15,23-tetraoxo-3,9,16,22-tetraaza-6,19-diazoniatriacyclo[22.2.2.2^{11,14}]triaconta-1(26),11,13,24,27,29-hexaene dichloride tetrahydrate; BMMim = 1-butyl-2,3-dimethylimidazolium; Th(pyOS)4(dmf) = dimethylformamidetetrakis(1-oxo-2-thiopyridinato) Thorium(IV); HOPO = hydroxypyridinone; 1,2-HOPO = 1-hydroxy-2(1*H*)-pyridinone; 3,2-HOPO = 3-hydroxy-2(1*H*)-pyridinone; 3,4-HOPO = 3-hydroxy-4(1*H*)-pyridinone; H₂IDA = iminodiacetic acid; H₃NTA = nitrilotriacetic acid; H₄EDTA = ethylenediaminetetraacetic acid; DHPTA = 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid; HEDTA = (2-hydroxyethyl)ethylenediaminetriacetic acid; HEIDI = N-(2-hydroxyethyl)iminodiacetic acid; NTP = nitrilitripropionic acid; CIT = citric acid; 1,3,5-tCPBA = 1,3,5-tri(4'-carboxylphenyl) benzoic acid; H₃TPO = tris-(4-carboxylphenyl)phosphineoxide; DPO = cis-ethylenebis-diphenylphosphine oxide

tetravalent metal ion. [7] Because it is so prevalent naturally, thorium possesses desirable characteristics that make of interest to the civilian nuclear fuel industry. [3] Much of the research dedicated to developing a more complete understanding of thorium chemistry is the result of an interest in sequestering actinide ions as they relate to the nuclear fuel industry, whether as a fuel source in itself or as a surrogate to Pu(IV) in nuclear waste separation studies. [8]

The focus herein is coordination chemistry with oxo- or aza- donors and thorium coordination environments, hence a few noteworthy areas will not be discussed, including, research pertaining to zeolites [9] and organometallic compounds featuring cyclopentadienyl ligands [10, 11]. Herein, we explore the multiple thorium (IV) coordination environments and unique flexible coordination geometry using a chronological and numerical approach to compare complexes described in the literature, ranging from 1971-2016.

Table 1. The Th(IV) complexes in this review.

Entry Number	Complex	Coord. #	idealized geometry	ref
3	BDPPTTh(CH ₃ SiMe ₃) ₂	5	square pyramidal	12
4	XA ₂ Th(CH ₃ SiMe ₃) ₂	5	square pyramidal	12
5	Th(BDPP) ₂	6	distorted tetrahedron	12
6	BDPPTThCl(dme)	7	pentagonal bipyramidal	12
7	XA ₂ ThCl(dme)	7	pentagonal bipyramidal	12
8	[N(o-NH) ₂ P/Pr ₂ C ₆ H ₄] ₃ Th[Co(CO) ₃]	7	trigonal bipyramidal	16
9	Th(GH ₅ O ₂) ₄	8	dodecahedron	21
10	Na ₄ Th(GH ₅ O ₂) ₄ ·2H ₂ O	8	trigonal-faced dodehedra	23
11	Th(GHF ₃ O ₂ S) ₄	8	dodecahedron	24
12	Th[(CH ₃) ₂ CHN(O)O(O)C(CH ₃) ₃] ₄	8	cubic	26
13	Th[(CH ₃) ₂ CHN(O)O(O)C(CH ₃) ₃] ₄	8	dodecahedron	26
14	[Th(GH ₅ O ₂) ₄] ₂ ·C ₆ H ₅ NH ₂	8	square antiprism	31
15	[Me ₃ BrN] ₄ Th(ETAM)]	8	between the bicapped trigonal prismatic and trigonal dodecahedron	33
17	ThTAM ₄ (DMF) ₂ (MeOH) ₂ ·THF	8	novel	37
18	Th ₂ [κ ² (O, O')-μ-O(CH ₂) ₂ OCH ₃] ₃ (DME)	8	bicapped trigonal pyramidal	39
19	Th ₂ (μ ₂ -O)(μ-Cl) ₄ [κ ² (O, O')-μ-O(CH ₂) ₂ OCH ₃] ₆	8	distorted tetrahedron	39
20	[BMMim] ₂ [Th ₂ (PO ₃) ₄ (H ₂ P ₂ O ₇) ₃]	8	square antiprism	42
21	Th(pyOS)4(dmf)	9	monocapped square antiprism	43
22	(C ₃ H ₅ NO ₂) ₄ (H ₂ O)Th	9	amonocapped Archimedean antiprism and the ₃₆ tricapped trigonal prism	44
26	Th(3,2-HOPO) ₂ ·H ₂ O	9	distorted monocapped square-antiprismatic	47
27	(NMe ₄) ₄ Th(ETAM)MeOH] ₂	9	dimer	33
28	[Th(NTA)(hNTA)(H ₂ O)·H ₂ O]	9	capped square antiprismatic	49
29	[Th(EDTA)(hEDTA)(H ₂ O)·H ₂ O]	9	capped square antiprismatic	49
30	Na ₄ [Th ₂ O ₂ (hecta) ₆] ₂ ·8H ₂ O	9	distorted monocapped square-antiprismatic	52
31	[Th(GO ₄ NH ₂) ₂ ·(H ₂ O)(NO ₃)]·2.5H ₂ O	9	distorted monocapped square antiprismatic geometry.	52
32	[ThA ₆ (OH) ₄ (H ₂ O) ₁₂ (C ₆ O ₅ NH ₆) ₄ (NO ₃) ₆ ·57H ₂ O]	9	distorted monocapped antiprismatic	52
33	(C ₆ N ₂ H ₁₂)[ThFe ₂ (OH) ₄ (H ₂ O) ₂ (C ₆ O ₅ H ₆) ₂ (C ₆ O ₄ H ₄) ₂ ·5H ₂ O]	9	distorted monocapped antiprismatic	52
35	[C ₆ H ₁₁ N ₃] ₃ Th(1,3,5-tCPBA)Cl ₃ ·Cl	9	muffi n-type	53
36	[C ₆ H ₁₁ N ₃][Th(TPO)Cl] ₃ ·18H ₂ O	9	irregular muffi n-type	59
37	[NH ₄] ₂ Th(NO ₃) ₆	12	irregular icosahedron	60
38	[Th(HDA)(C ₆ O ₄)]·H ₂ O	10	bicapped square antiprismatic	49
39	Th(NO ₃) ₂ ·DPO·(NO ₃) ₂	10	distorted bicapped square antiprism	61
40	[Th(TPO)(OH)(h ₂ O)] ₂ ·8H ₂ O	10	spherical sphenocorona	59

2.1 5-7 Coordinate

2.1.1

Interest in thorium coordination chemistry is not solely limited to actinide sequestration or waste remediation. Emslie [12] and co-workers were investigated non-carbocyclic organoactinide complexes for their potential in organometallic catalysis. This group was interested in sufficiently thermal stable Th(IV) dialkyl complexes that could accommodate thorium's size and

DPEPPhos = (diphenylphosphinophenyl)ether

1

[illegible]

Although proposed for potential catalytic properties, the results garnered very interesting unusual coordination environments for thorium(IV) based on the bulkiness of the ligands. Through the reaction of $\text{Li}_2[\text{BDPP}]$ and $\text{Na}_2[\text{XA}_2]$ with $[\text{ThCl}_4(\text{dme})_2]$ in benzene at 0 °C or in toluene at room temperature, respectively, resulted in the unusual 7-coordinate Th(IV) dichloride complexes **6** and **7**. The ^1H NMR spectra supports the presence of symmetric pentagonal bipyramidal products through shifts representative of one molecule of symmetrically coordinated dme, a 1,2-dimethoxyethane, and a lone CHMe_2 signal. The pentagonal bipyramidal geometry was confirmed through single crystals of complex **6**·2toluene and shows the two chloride anions

in the apical positions with an angle of $156.38(10)^\circ$ for [Cl(1)-Th-Cl(2)] and Th-Cl bond lengths of 2.698(3) and 2.686(3) Å. The Th-O₁ and Th-O₂ bond lengths were found to be 2.674(8) and 2.724(8) Å, respectively. The bite angle of the O₁-Th-O₂ was found to be $59.9(2)^\circ$. Structure 6 also contained two bite angles, N₁-Th-N₂ and N₂-Th-N₃, with values of $65.2(3)^\circ$ and $64.3(3)^\circ$, respectively. *The bite angles are of interest because the bite angles of a bidentate or tridentate ligand may play a role in the final coordination geometry of the metal center due to sterics.* The crystals show that the BDPP, 2,6-bis(2,6-diisopropylanilidomethyl)pyridine dianion, ligand is planar and binds to the Th⁴⁺ center through short Th-N_{anilido} bonds with lengths of 2.305(9) and 2.321(8) Å.

Reacting complexes **6** and **7** with 2 equivalents of LiCH₂SiMe₃ afforded the base- and salt-free 5-coordinate dialkyl thorium(IV) complexes, **3** and **4**, respectively. Variable temperature ¹H and ¹³C NMR spectra confirmed the identity of these complexes. At 60 °C, ThCH₂ and CHMe₂ shifts were observed, with the ThCH₂ at -0.32 ppm for **5** or -0.17 ppm for **4** on the ¹H NMR spectra and 89 ppm for **3** or 97 ppm for **4**. Cooling the complexes to -80 °C produced two distinct CH₂SiMe₃ groups, two CHMe₂ signals, and ligand backbone resonances that support the loss of top-bottom symmetry. The authors, Emslie et al., were thus able to produce the first structurally characterized thorium dialkyl complex supported by a multidentate non-carbocyclic ancillary through the growth of single crystals of **6**-toluene that shows a square pyramidal geometry distorted in the square plane due to the rigidity of the ligand.¹² NMR analysis showed that the alkyl groups were not identical, and this was confirmed from the crystal structure featuring one alkyl group is located in the NON plane and the other is directly above the plane. Two interesting observations found in the crystal structure of **4** are 1) the Th-O bond length [2.534(3) Å] is similar to previous reports of coordinated dme and this is surprising since a diaryl ether is thought to be a far less effective donor than dme [14] and 2) the Th-C-Si bond angles of $127.6(3)^\circ$ and $126.8(3)^\circ$ are significantly larger than other observed sp³-hybridized carbon atoms; this has been attributed to α-agostic C-H-Th interactions. [15] The bite angle between the two carbon atoms and the thorium metal center was found to be 112.0° and an average bond distance of 2.4755 Å. The average bond angle of the O-Th-N atoms in complex **4** was calculated to be 62.93° and Th-N bond lengths were an average of 2.3015 Å. Other values associated with **4**-toluene can be viewed in Table 1. Both [BDPP] 5- and 7- coordinate complexes were used to synthesize 6-coordinate Th(IV) complex **5**; with the [XA₂] complexes resulting in no reaction. Solution NMR in d₅-bromobenzene between 20 and -35 °C supports the formation of a symmetrical product with only one CHMe₂ environment. Structural characterization using small molecule X-ray diffraction crystallography reveals that **5** forms a distorted tetrahedron geometry with four amido donors and the two N_{pyridine} directed toward the edges of the tetrahedron to form the 6-coordinate complex. Complex **5** has an average bite angle between the thorium center and the nitrogen atoms was calculated to be 63.80° and the bond lengths ranged from 2.368 to 2.615 Å.

2.1.2

The need for a greater understanding of the electronic structure and ability to form chemical bonds of actinides led Arnold and co-workers to probe the formation of bonds between actinides and transition metals. [16] With the idea that more in depth knowledge of the fundamental properties of metal-metal bonds involving 5f elements would aide in the separation of actinides from other present fission products in the nuclear fuel cycle. [17] The dearth of f-block element metal-metal bonds compared to non f-block elements is due, in large part, to the limited

synthetic routes available to form such bonds. [18] Arnold et al. took advantage of the hard/soft donor system facilitated by the $\text{N}[\text{o-NHCH}_2\text{P}^i\text{Pr}_2\text{C}_6\text{H}_4]_3$ ligand to bind the hard actinides to the soft transition metals. [19] This was achieved via UV irradiation of the 8-coordinate heterobimetallic complex $\{\text{N}[\text{o-NHCH}_2\text{P}^i\text{Pr}_2\text{C}_6\text{H}_4]_3\}\text{Th}[\text{Co}(\text{CO})_4]$, Scheme 3A, to produce a unique 7 coordinate complex $\{\text{N}[\text{o-NHCH}_2\text{P}^i\text{Pr}_2\text{C}_6\text{H}_4]_3\}\text{Th}[\text{Co}(\text{CO})_3]$, **8**, possessing a Co-Th bond - the first of its kind. The Th(IV) center is trigonal bipyramidal, Scheme 3B, and the Co-Th bond length is 3.0771(5) Å. The average Th-N bond length was calculated to be 2.405 Å, resulting in an average bite angle of 65.68°. The Th-P bonds averaged a length of 3.194 Å and had a bite angle of 96.62°.

Scheme 3.

3.1 8 coordinate

3.1.1

Complexes that possess an eight-coordinate Th(IV) center are not in short supply and are comprised primarily of bi- and tetra-dentate ligands. In the early stages of structural characterization using single crystal X-ray crystallography, most reported thorium complexes featured 9-coordinate thorium with 8 coordinating oxygens and a solvent molecule occupying the 9th coordination site. [20] In fact, prior to 1976, only the β -diketone and dithiocarbamate complexes showed 8-coordinate complexes until Rickard and Hill [21] synthesized and determined the structure of tetrakis(salicylaldehydato)thorium(IV), $\text{Th}(\text{sal})_4$, **9**. The authors sought to take advantage of the idea that an asymmetric chelating ligand could help stabilize the dodecahedron (D_{2d}) solid-state geometry as preferred relative to a potential square antiprism (D_{4d}) geometry through the ordering of different donor atoms into non-equivalent sets of sites. It was determined that the eight O-atoms lie along the m edges in a dodecahedron geometry with an approximate D_{2d} symmetry. The phenolate oxygens occupy the B sites and the aldehyde oxygens occupy the A sites, with M-A/B distances of 2.520 and 2.315 Å, respectively. [21] Recall that a perfect dodecahedron contains A and B sites with θ_A and θ_B angles, both at 45°. Variation from this idealized dodecahedron results in distorted dodecahedrons, such as the square antiprismatic. [22]

3.1.2

The coordination of tetravalent actinides is of keen interest in part due to the concept of using thorium as Th(IV) as a structural model for Pu(IV), based on its lower radioactivity, similar ionic radius, and relative ease of characterization. Highly selective ligands that could be of use in the case of an accidental exposure or plutonium poisoning arose from studies that demonstrated that plutonium is moved and stored by the iron transport and storage compounds, transferrin and ferritin, in mammals. Model systems based on siderophores-naturally occurring iron sequestration compounds produced in marine bacteria - have been the basis for designing actinide sequestering agents. [23] An ongoing project in the Raymond laboratories was inspired by the design and characterization of such agents. [24] Mimicking iron (Fe^{3+}) sequestering agents in bacteria, in which three bidentate catechol ligands coordinate iron, the group employed four catechol ligands to coordinate the tetravalent thorium metal center. The tetrakis(catecholato) thorate (**10**), $\text{Na}_4[\text{Th}(\text{C}_6\text{H}_4\text{O}_2)_4 \cdot 21\text{H}_2\text{O}]$, synthesized in 1978 was the first report of the structural analysis of these types of chelators with Th using single-crystal X-ray diffraction, and was found to be in a trigonal-faced dodecahedron (D_{2d}) geometry with a bond length ratio of 1.00, $\theta_A = 37.9^\circ$ and $\theta_B = 75.4^\circ$. The Th-O bond lengths are nearly identical, with Th-O₁ found to be 2.418(3) Å and Th-O₂ found to be 2.412(3) Å, with a bite angle of 66.798°. [24]

Figure 1.

3.1.3

Interest in the properties of Th(IV) chelated with β -diketones lead Lenner [25] and Lindqvist to synthesize tetrakis(thenoyltrifluoroacetato)thorium(IV), **11**, $\text{Th}(\text{TTA})_4$, to determine the effect of an asymmetric ligand on the coordination of thorium (IV). Crystals were grown from an aqueous solution of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ with a benzene solution of HTTA. The complex was found to be an 8-coordinate distorted dodecahedron, with four of the bidentate ligands coordinated to the Th center with a Th-O bond with an average length of 2.397 Å and an average bite angle of 69.575°. Each of the four ligands serve as the leg of the two perpendicular trapezoids of the dodecahedron, with the angle between the trapezoids measuring at 94.5°, versus the ideal 90°, Figure 2. The TTA ligand is relatively planar aside from the fluorine atoms and the thienyl rings; the plane of the ligand is folded over the line of the oxygen atoms, with the thorium atom over

this line resulting in an average of 13.68° for the fold of $\text{Th}(\text{TTA})_4$. The molecule is shown to be propeller like, with all the CF_3 groups on the same side of the plane and the thienyl groups on the other side of the plane, Figure 3. [25]

Figure 2.

Figure 3.

3.1.4

Again inspired by the iron-transport biomimetic approach [26] to design tetravalent actinide ligands, Raymond and co-workers prepared hydroxamate complexes with thorium(IV). [27] A positive attribute of these ligands is that they can be used as an archetype or analog of a macrochelate without the steric or solubility issues associated with macrochelates. [28] Prior to this point in 1980, such complexes had not been structurally characterized, although quantitative analysis and solvent extraction studies of hydroxamic acids with actinides had been reported. [29] The colorless complexes, $\text{Th}[(\text{CH}_3)_2\text{CHN}(\text{O})\text{O}(\text{O})\text{R}]_4$, where $\text{R} = \text{C}(\text{CH}_3)_3$ or

$\text{CH}_2\text{C}(\text{CH}_3)_3$, as shown in Figure 4, were both soluble in hydrocarbons, but displayed very different coordination geometries. [27] The stereochemistry constraints placed on the complex, **12**, from the *tert*-butyl substituents force the ligand to form a geometry around the thorium(IV) center that is nearly cubic (S_4). The neopentyl substituted complex, **13**, was found to have a dodecahedron (D_{2d}) geometry. In both complexes, the Th- O_N bond is shorter than the Th- O_C , for complex **12**, the bonds were 2.357(3) Å and 2.492(3) Å, respectively; for complex **13**, the bonds averaged 2.36(1) Å and 2.46(2) Å, respectively. Complex **12** was found to have a bite angle of 62.329° and complex **13** had bite angles ranging from 62.867° to 63.673° with an average of 63.228°. The authors attribute this to the unsymmetrical nature of the hydroxamate ligand and the localization of the charge on the oxygen atom that is bound to nitrogen. The aforementioned dodecahedral (D_{2d}) geometry of complex **13** was thought to give the maximum stability required for selective tetravalent actinide sequestration. [30]

Figure 4.

3.1.5

With an interest in thorium tetrakisacetylacetonate ammonia and aniline compounds, $2\text{ThA}_4 \cdot \text{NH}_3$ and $2\text{ThA}_4 \cdot \text{C}_6\text{H}_5\text{NH}_2$, as synthesized by Blitz [31] lead Smith and co-workers [32] to synthesize the adduct of thorium(IV) tetrakisacetylacetonate with aniline, **14**. Smith *et al.* proposed to determine three things: 1) whether the nitrogen was within the thorium coordination sphere; 2) whether a hydrogen bonded structure was formed; or 3) whether they were clathrates like the benzene adduct previously reported by Lenner. [33] To do this, thorium tetrakisacetylacetonate (abbreviated ThA_4) and aniline were reacted in hot ether, and subsequently cooled to produce crystals. Analysis of the resulting solids revealed two independent ThA_4 molecules. As shown in figure 5, the complexes were found to have antiprism coordination and the aniline, while clathrate without hydrogen-bonding to the complex, still has an effect on some of the ligand planes. The planes of the two ligands open to include the aniline that lies between them. This observation is supported by the mean dihedral angle, D , of 42.05° versus the $D = 27.9^\circ$ for the ligands opposite the aniline. [32] The median bond lengths between the Th_1 and oxygen atoms was 2.41 Å and a median bite angle of 69.70°. The second thorium atom possessed bite angles ranging from 67.6° to 71.1° with an average of 69.98° and $\text{Th}_2\text{-O}$ bond lengths that averaged 2.385 Å.

Figure 5.

3.1.6

The need to reduce the volumes of radioactive fission materials and spent fuels requiring long-term storage in geological repositories has been a hot topic for nuclear energy industry. [34] Following the biomimetic approach that proved that hard metal ions, such as actinide(IV) ions, have a preference for oxygen donor ligands [35], Raymond et al. [34] synthesized ligands for actinide sequestration. The authors were interested in thorium(IV) complexes due to it being considered a good analogue for Pu(IV) as a result of its similar radii, coordination number, and oxidation state. [36] With the knowledge that catecholate-based ligands can be used to chelate Fe(III), they sought to design catecholamide-based ligands for binding. The ligand N,N'-diethyl-2,3-dihydroxyterephthalamide (ETAM) was synthesized and coordinated to Th(IV). The authors were able to grow crystals of two thorium(IV) complexes: 1) the 8-coordinate $[\text{Me}_3\text{BnN}]_4[\text{Th}(\text{ETAM})_4]$, **15**, where Me_3BnN = trimethylbenzylammonium and 2) a dimer, **27**, $(\text{NMe}_4)_4[\text{Th}(\text{ETAM})_3\text{MeOH}]_2$, with both metal centers possessing a coordination number of 9 that will be discussed in the later sections. The coordination geometry of complex **15**, Figure 6, was not clear, but it was determined to be between that of an ideal bicapped trigonal prismatic (C_{2v}) and the ideal trigonal dodecahedron, although somewhat closer to geometry of the dodecahedron. The thorium(IV) metal center and the oxygen of complex **15** were found to have a median bond length of 2.414 Å and bite angles that range from 63.9° to 65.06°, with an average bite angle of 64.63°.[34] (Of interest, to date, the structural characterization of the Pu(IV) analog of this complex has not been reported.)

Figure 6.

3.1.7

Another concept has peaked interest in thorium(IV) coordination chemistry, that of its possible use in radiotherapy, in which the α -particle emitter ^{227}Th is complexed to a ligand that can covalently linked to a biomolecule to enable targeted radiation delivery.[37] A high thermodynamic stability and rapid coordination kinetics is required to be appropriate for such a task. Previously proposed macrocycles have either high stability and slow rates or vice-versa, such as the case with 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid, DOTA, and diethylenetriaminepentaacetic acid, DTPA. The structure of these as the Th(IV) complexes have not as yet been reported. Raymond et al. [38] designed and synthesized a novel macrocyclic octadentate ligand that incorporated terephthalamide, 6,19-bis(2-((2,3-Dihydroxy-4-((2-methoxyethyl)carbamoyl)benzoyl)amino)ethyl)-12,13,25,26-tetrahydroxy-2,10,15,23-tetraoxo-3,9,16,22-tetraaza-6,19-diazoniatriacyclo[22.2.2.2^{11,14}]triaconta-1(26),11,13,24,27,29-hexaene dichloride tetrahydrate, (TAM) binding units and chelated it to thorium(IV). The synthesis and structure of the ligand, **16**, can be seen in Figure 7. The ligand incorporates the thermodynamic stability of a macrocycle with the desired rapid kinetics of linear ligands and fulfilling the required coordination number of thorium(IV), 8. The authors were able to crystallize the complex, $\text{ThTAMK}_4 \cdot (\text{DMF})_2 \cdot (\text{MeOH})_2 \cdot \text{THF}$, Figure 8, **17**. This was analyzed and found to have a novel inner coordination environment between the ideal bicapped trigonal prism and an ideal trigonal dodecahedron (D2d). Complex **17** possessed an average Th-O bond length of 2.41 Å that resulted in an average bite angle of 64.95°.

Figure 7.

Figure 8.

3.1.8

The soluble actinide-halide complexes are regularly explored due to them being possible starting materials for other compounds [39] lead Kiplinger et al. to begin developing methods that did not require thorium metal as a starting material.[40] This was done in prior reports [39b] through the reaction of $\text{ThCl}_4(\text{DME})_2$, where DME = 1,2-dimethoxyethane, and trimethylsilyl iodide via complete halide exchange to give $\text{ThI}_4(\text{DME})_2$. The halide exchange product can then react with excess DME to give the dinuclear thorium complex, $\text{Th}_2\text{I}_5[\kappa^2(\text{O},\text{O}')-\mu\text{-O}(\text{CH}_2)_2\text{OCH}_3]_3(\text{DME})$, **18**. During the halide exchange, if the reaction does not go through complete exchange, the production of a mixed-halide compound occurs, yielding $\text{ThCl}_4\text{-}_x\text{I}_x(\text{DME})_2$. This mixed-valent compound then spontaneously reacts with DME in methylene chloride to give the tetranuclear thorium(IV) μ_4 -oxo cluster, $\text{Th}_4(\mu_4\text{-O})(\mu\text{-Cl})_2\text{I}_6[\kappa^2(\text{O},\text{O}')-\mu\text{-O}(\text{CH}_2)_2\text{OCH}_3]_6$, **19**. Figure 9 shows the dinuclear cluster, **18** with its two different thorium(IV) metal ions that are bridged by three alkoxide-ether ligands that are a result of the cleavage of DME C-O bonds. The compound had $\text{Th-O}_{\text{alkoxide}}$ bond lengths that averaged 2.360(7) Å and Th-I bond length was 3.1384(8) Å. The $\text{Th-O}_{\text{ether}}$ and DME coordinated molecule had distances of 2.577(7) Å and 2.538(7) Å, respectively, both of which are representative of dative bonds as supported by literature.[41] The angle between the $\text{Th}_1\text{-O-Th}_2$ atoms was 100.8(3)°, which was similar to the alkoxide bridge in complex **19**.

Figure 9.

3.1.9

Complex **19** contains a rare μ_4 -O atom that coordinates to the four Th(IV) atoms and is one of two tetranuclear μ_4 -oxo complex that has been characterized via X-ray crystallography.[42] The four thorium atoms were found to be a pair of two different thorium metal ions, Figure 10, all of which are bonded to the central oxo-bridge, O1. The Th-Th distances were found to range from 3.6309(9) – 4.1623(5) Å, with the shorter distance being shorter than those reported in literature, 3.7431(9) Å, but the longer distance was longer than the other reported 4.0031(6) Å.[37] The average bond angle for Th₁-O1-Th₁ and Th₂-O1-Th₂ were found to average 98.4(5)°, with the Th₁-O1-Th₂ angle averaging 115.355(13)°. The Th-O bond lengths of 2.391(7) Å for the Th₁-O1 bond and the Th₂-O1 had a bond length of 2.409(7) Å, resulting in a distorted tetrahedral geometry.

Figure 10.

3.1.10

Early reports of thorium (IV) coordination complexes focused on the structural characterization of the synthesized complexes with the stated key goal being structures as archetypes for the improvement of rational design for selective tetravalent actinide extractants. The desire for a highly selective ligand for incorporation into an electronic or chemical sensor is still very relevant today. Wang et al. [43] reported the first thorium open-framework compound with mixed-valent phosphite and pyrophosphate ligands that were found to be highly stable in aqueous solutions

in acidic and basic pH, 1-14. The complex, $[\text{BMMim}]_2\text{-}[\text{Th}_3(\text{PO}_3)_4(\text{H}_2\text{P}_2\text{O}_7)_3]$, ThP-1 (**20**), where BMMim = 1-butyl-2,3-dimethylimidazolium, was found to crystallize in the centrosymmetric cubic space group and adopted a square antiprism coordination, as part of an open-framework resembling metal-organic framework 5 (MOF-5). The crystal structure, Figure 11, shows that the coordination sphere contains four oxygen atoms provided by four different distinct phosphite ligands with the other four oxygen atoms provided by two separate pyrophosphate ligands; however, with each phosphate ligand bridging three adjacent thorium centers a Th_6P_8 cluster is formed resulting in an overall octahedral geometry.[43] The Th-O₁ and Th-O₂ bond lengths were found to be 2.395 and 2.416 Å, respectively. The O₁-Th-O₂ bite angle was found to be 76.8°.

Figure 11.

4.1 9 coordinate

4.1.1

An investigation of the complexes of actinide ions led Viagto et al. to probe the complex of dimethylformamidetetrakis(1-oxo-2-thiopyridinato) Thorium(IV), $\text{Th}(\text{pyOS})_4(\text{dmf})$. [44] Taking advantage of the large ionic radii of Thorium, the authors prepared and structurally characterized the complex, **21**, $\text{Th}(\text{pyOS})_4(\text{dmf})$, producing a nine-coordinated Th(IV). Eight of the donor atoms were from four bidentate ligands and a dimethylformamide solvent molecule, Figure 12, resulting in a distorted monocapped square antiprism. The complex possessed Th-S bonds that averaged 2.965 Å and Th-O bonds that averaged 2.424 Å. These bond lengths resulted in bite angles that averaged 73.0°, 75.26°, and 70.41°, for the O-Th-O, S-Th-S, and O-Th-S bite angles, respectively.

Figure 12.

4.1.2

Raymond et al. [45] prepared and described a nine-coordinate $(C_5H_4NO_2)_4(H_2O)Th$, **22**, between thorium(IV) and bidentate 1-oxy-2-pyridonate ($C_5H_4NO_2^-$) structure.[45] This structure revealed an primary coordination sphere around the thorium(IV) metal center completed with 8 oxygen atoms from the four bidentate 1-oxy-pyridonate ligands and a single coordinated water molecule along the C_2 axis of the metal center. The average bond length between Th^{IV} and the ligand O atoms is 2.44 Å, and that between Th^{IV} and the water O atom is 2.52 Å. This results in an average bite angle of 64.671° and a geometry that resembles a D_{3h} tricapped trigonal prism, but is actually an intermediate C_{2v} symmetry pathway between the C_{4v} monocapped Archimedean antiprism and the D_{3h} tricapped trigonal prism, as you can see in Figure 13. The authors attribute this difference in geometry between this and the 9-coordinate tetrakis(tropolonato)(N,N-dimethylformamide)thorium(IV) complex reported by Day in 1970 [46] as due to an asymmetric charge distribution in the oxypyridinone ligand, as compared with the more symmetric tropolonate.

Figure 13.

4.1.3

Due to its chemical toxicity as a heavy metal, the need to sequester thorium, whether *in vivo* or in the environment, is of concern in applying thorium as nuclear fuel. Ligands containing hydroxypyridinone (HOPO) chelating units have been found effective in animals for the decorporation of Th(IV) and other actinides.[47] To compare and contrast the ability of HOPO-based ligands with Th(IV), [48] three hydroxypyridinone isomers were synthesized and characterized as Th(IV) complexes: **23**) 1-hydroxy-2(1*H*)-pyridinone, **24**) 3-hydroxy-2(1*H*)-pyridinone, **25**) 3-hydroxy-4(1*H*)-pyridinone, abbreviated 1,2-HOPO, 3,2-HOPO, and 3,4-HOPO.[48] All three ligands were synthesized to add an amide linkage to be used as a point of attachment prepare a multidentate ligand.

All three ligands were subjected to solution thermodynamic analysis complexing with Th(IV) and demonstrated to have different optimal binding pH ranges. Reaction of the 3,2-HOPO to prepare a Th(IV) complex produced crystals that were analyzed using XRD. The complex, Th(3,2-HOPO)·H₂O, **26**, was determined to be nine-coordinate, with the ninth coordination spot being occupied by an amide oxygen. This amide oxygen is readily displaced by a water molecule in water and forms an infinite linear coordination polymeric structure with a distorted monocapped square-antiprismatic geometry. The average Th-O_{phenolic} is 2.405(8) Å and the average length of the Th-O_{oxo} bond is 2.524(11) Å, resulting in average bite angle of 63.21°. When compared to the crystal structure of the metal free ligand, the geometry of both structures are nearly identical, leading to the idea that the ligands might serve as metal chelators.[48]

Figure 14.

4.1.4

Work conducted by the Raymond lab in which the ligand N,N'-diethyl-2,3-dihydroxyterephthalamide (ETAM) was coordinated to Th(IV) resulting in the formation of an 8-coordinate complex, **15**, produced an addition structure, the bimetallic complex **27**. [34] This 9-coordinate complex was obtained in the synthesis of the Th[ETAM]₄ where the addition of an excess thorium resulted in a bimetallic species Th₂[ETAM]₆. This structure, shown in Figure 15a, has four complexes per unit cell and crystallizes in *P*2₁/*c*. Two of the three TAM ligands bind to

the thorium(IV) with the catecholate oxygens, while the third TAM ligand binding as a bridge to the second Th(IV) center, with the amide ortho to the oxygen oriented to allow the carbonyl oxygen to bind the second Th(IV) center, Figure 15b. Prior examples of TAM complexes show this amide oxygen pointing away from the metal, allowing the amide proton to hydrogen bond the deprotonated, coordinating catecholate oxygen. The average bond lengths between the thorium metal center and the oxygen atoms was 2.45375 Å, resulting in an average bite angle of 68.125°.[34]

Figure 15.

4.1.5

Another proposed means of actinide sequestration is through the binding of tetravalent actinides with ligands from the aliphatic aminopolycarboxylate family. These have been characterized primarily in solution studies or with uranium.[49] Until Thuéry [50] investigated the ability of aminocarboxylate ligands on chelating thorium(IV) ions, only one metal complex with aminocarboxylate ligands had been structurally characterized and reported.[51] In this investigation, Thuéry complexed Th(IV) with three common ligands: 1) iminodiacetic acid (H_2IDA), which formed a 10-coordinate complex, and two 9-coordinated complexes with 2) nitrilotriacetic acid (H_3NTA), 3) ethylenediaminetetraacetic acid (H_4EDTA). All three complexes were produced under hydrothermal conditions.[50] The 10-coordinate complex, **38**, is discussed in the 10-coordinate section. The first 9-coordinate complex, $[\text{Th}(\text{NTA})(\text{H}_2\text{NTA})(\text{H}_2\text{O})\cdot\text{H}_2\text{O}]$, **28**, has an asymmetric unit that is comprised of two ligands in different states of protonation, Figure 16. One ligand is trianionic and chelates the metal ion through one nitrogen atom, three oxygen atoms, and two carboxylate groups are bridging bidentate. The Th-O bond lengths average 2.41(3) Å, while the Th-N bond distance was

reported at 2.799(2) Å, with average bite angles of 79.51° and 62.24°, respectively. The Th-O_{H₂O} bond length was found to be 2.564(2) Å. The resulting structure is most closely a capped square antiprismatic (D_{4d}) geometry. The second ligand is monoanionic and has two monodentate carboxylate groups coordinated to it, as well as, one uncoordinated carboxylic acid arm, and a central ammonium group.[50]

Figure 16.

The second 9-coordinate complex, **29**, [Th(EDTA)(H₂O)]·H₂O, is the second Th(IV)-EDTA complex to be characterized crystallographically, Figure 17. This complex has an asymmetric unit with the Th(IV) ion coordinated by four oxygen atoms and two nitrogen atoms from the EDTA⁴⁻ anion, two carboxylate oxygen atoms from neighboring molecules, and an aqua ligand to give a capped square antiprismatic (D_{4d}) coordination environment. The Th-O bond length averages 2.41(3) Å and the Th-N bond lengths average 2.727(13) Å. The average O-Th-N bite angle was calculated to 63.208° and the N-Th-N bite angle was found to be 66.95°.

Figure 17.

4.1.6

The ability of Th(IV) to form polynuclear species after undergoing hydrolysis and condensation can have an effect on the transportation of radionuclides in the environment.[52] Forbes et al. [53] took an interest in understanding the effect that condensation and chelation have on each other in the environment when polynuclear clusters are formed. To enhance their

understanding, the group used five polycarboxylates, shown in Figure 18, to form ternary and binary Th(IV) and other metal centered complexes. Four of the synthesized complexes contained 9-coordinate Th(IV) metal centers, while two formed polynuclear complexes.

Figure 18.

The first complex, Th_6hedta (with hedta being 2-hydroxyethyl)ethylenediaminetriacetic acid), characterized showed two trimeric Th(IV) cores that were linked via the HEDTA ligand to form a hexameric molecular species with an overall formula of $\text{Na}_4[\text{Th}_6\text{O}_2(\text{hedta})_6] \cdot 28\text{H}_2\text{O}$, Figure 20, **30**, Figure 19 inset. Each of the Th(IV) cations in the trimeric core is coordinated by seven O atoms and two N atoms forming an overall distorted monocapped square antiprismatic (most closely D_{4d}) coordination geometry with Th-O bonds ranging from 2.322(7)-2.516(8) Å. The Th-N bonds were found to be an average of 2.784(7) Å. The O-Th-O bite angle was found to be 68.1(2)° and the bite angle between the thorium atom and the nitrogen atoms was 66.3(3)°. This hexameric species is a result of the free O atom of the carboxylate group on the HEDTA ligand coordinating to the Th(IV) cation of the neighboring trimeric unit. Further analysis showed that there are four unique Na^+ cations present to balance the negative charge of the cluster, $[\text{Th}_6\text{O}_2(\text{hedta})_6]^{4-}$. [53]

Figure 19.

Utilizing the NTP, nitrilipropionic acid, ligand, the second nine-coordinated Th(IV) structure was synthesized and characterized. The complex, **31**, Th(NTP), Figure 20a, was synthesized during the synthesis of a heteronuclear NTP complex with Al(II), however, the intended heteronuclear species was not isolated. Instead, 2-D sheets of $[\text{Th}(\text{C}_9\text{O}_6\text{NH}_{12})-(\text{H}_2\text{O})(\text{NO}_3)] \cdot 2.5\text{H}_2\text{O}$, Figure 20b, resulted. Each Th(IV) cation is coordinated by nine O atoms with bond lengths ranging from 2.337(5)-2.592 Å, resulting in an average bite angle of $66.86(7)^\circ$ and a distorted monocapped square antiprismatic geometry (most closely resembling D_{4d} geometry).

Figure 20.

The primary stated overall goal of this work was the isolation of novel heteronuclear complexes. This was achieved with the third complex, in which the HEIDI ligand (N-(2-hydroxyethyl)iminodiacetic acid) was used to complex both Th(IV) and Al(III), $\text{Th}_2\text{Al}_8\text{HEIDI}$, **32**. This complex was synthesized through the chelation of a hexameric Al(III) core complex and the HEIDI ligand, resulting in two mixed-metal dimeric complexes Figure 21. Specifically, two

ligands can chelate the Th(IV) and Al(III) cations in a tetradentate manner via the carboxylate, hydroxyl, and amine functional groups of the ligand. Additional water adducts were found to coordinate either metal to complete the coordination sphere and are bridged through the deprotonated hydroxyl group. The overall molecular formula for the complex is $[\text{Th}_2\text{Al}_8(\text{OH})_{14}(\text{H}_2\text{O})_{12}(\text{C}_6\text{O}_5\text{NH}_8)_4](\text{NO}_3)_6 \cdot 57\text{H}_2\text{O}$. The Th(IV) metal centers form distorted monocapped antiprismatic coordination spheres with Th-O bond distances ranging from 2.383(3)-2.640(3) Å and elongated Th-N bonds, with Th₁-N possessing a value of 2.776 Å and Th₂-N a value of 2.781 Å.[53] The average N-Th-O bite angle was calculated to be 63.68°.

Figure 21.

These authors also successfully synthesized a Th(IV)/Fe(III) heteronuclear complex, $\text{Th}_2\text{Fe}_2\text{cit}$ (**33**), utilizing the citrate (CIT). The complex resulted in the coordination of Fe(III) cation by six CIT as ligands, with two of the Fe(III) cations being bridged through two central O atoms that are also coordinated to a Th(IV) cation to give a tetramolecular species, Figure 22. The Th(IV) coordination sphere is completed by the chelation of the CIT ligand and an additional water molecule, with the Th-O bond lengths ranging from 2.387(3)-2.563(2) Å, resulting in a bite angle of 66.85°. The overall formula for the complex was found to be $(\text{C}_4\text{N}_2\text{H}_{12})[\text{Th}_2\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_2(\text{C}_6\text{O}_7\text{H}_4)_2(\text{C}_6\text{O}_7\text{H}_5)_2] \cdot 5\text{H}_2\text{O}$.

Figure 22.

4.1.7

The ability of low-valent, i.e. III and IV, actinides and their similarities to the coordination chemistry of lanthanides, in which the geometry is based on the ligand repulsion inspired Wang et al.[54] to synthesize three Th(IV) complexes. Of these, one was crystallized determined structurally to be a nine-coordinate Thorium(IV) complex. The complex was coordinated by 1,3,5-tri(4'-carboxylphenyl) benzoic acid (1,3,5-tCPBA), **34**, Figure 23.

Figure 23.

Single crystal X-ray diffraction of the resulting compound $[\text{C}_7\text{H}_{11}\text{N}_2]_5[\text{Th}_2(1,3,5\text{-tCPBA})_2\text{Cl}_6]\cdot\text{Cl}$, **35**, revealed that the compound crystallizes in the monoclinic $C2/c$ space group. This complex coordination environment was found to be unique in comparison to other nine-coordinate Th(IV) complexes. The compound is comprised of flat layers with a single Th(IV) metal center bonding to three 1,3,5-tCPBA ligand, resulting in a range of 2.435(11)-2.566(9) Å for the Th-O bond distances, Figure 24, resulting in an average bite angle of 52.53° . To satisfy the nine-coordinate sites, three chloride anions are bounded to the Th(IV) and result in three unique bond lengths, 2.787(4), 2.775(5), and 2.856(4) Å.

Figure 24.

Many published nine-coordinate Th(IV) complexes report a square antiprismatic (D_{4d})(example Figure 19) or trigonal prism geometry (C_{2v}) (example Figure 15) [55], due to each coordination geometry containing a set of three vertices related by a three-fold pseudosymmetry axis. With a set of 5 more vertices related by a collinear pseudosymmetry axis and a vertex sitting on the axis, (See Figure 25), the appropriate geometry for complex **35** can be described as “muffin-

type”, as defined by Alvarez and Ruiz-Martinez.[56] Couple this with the Th(IV) cation sharing the same equatorial plane as the neighboring Th(IV) cation, which is then linked to six more Th(IV) cations via the ligand units results in graphene-like layers that contain hexagonal (6,3)-honeycomb-like motifs.[54]

Figure 25.

4.1.8

The potential applicability of metal-organic frameworks, MOFs, to molecular recognition, gas storage, and catalysis has inspired many research groups to explore the characterization of these.[57] It has been shown that the stability of the MOFs can be heavily influenced by the charge density of the metal cation, and this hypothesis is strongly supported by the fact that the high valent metal based MOFs exhibit high thermal stability and water resistance.[58] With interest in the use of Th²³² nuclear fuels, the need to develop an understanding of the solid state characteristics Th(IV) is vital.[4,59] Albrecht-Schmitt et al. [60] synthesized and characterized two 3D Th(IV) frameworks with tris-(4-carboxylphenyl)phosphineoxide (H₃TPO, Figure 26). The first of these, complex **36**, [C₉H₁₇N₂][Th(TPO)Cl₂]·18H₂O, was synthesized from ionothermal conditions and, the second, **40**, was produced from a solvothermal reaction with Th(NO₃)₄ to give [Th(TPO)(OH)(H₂O)]·8H₂O and will be discussed further later below.

Figure 26.

Complex, **36**, crystallizes in the unusual orthorhombic space group P2₁2₁2. The asymmetric unit has one Th(IV) center, one 1-butyl-2,3-dimethylimidazolium cation, one TPO unit, and two terminal chloride atoms, Figure 27. With six oxygen atoms from the three independent chelating carboxylate groups, which is considered rare, one phosphine oxygen atom, and two terminal chloride atoms, the resulting Th(IV) center is nine-coordinate. The Th-O bond distances range from 2.371 – 2.568(7) Å with an average bite angle of 52.27° and the geometry can be described as an irregular “muffin” shape [56], as might be more typically seen in lanthanide complexes. The Th₂ binuclear subunit come from the two adjacent Th(IV) atoms in the [ab] plane being double-bridged by two TPO units with the coordination sites of the chelating

carboxylate oxygen and phosphine oxygen atoms. These binuclear units connect to four neighboring binuclear units to form a (4, 4) layer in the $[ab]$ plane, which are further bridged by the TPO to form the 3-D framework. The steric bulk of the triphenyl phosphine is likely the source of the irregular geometry.

Figure 27.

5.1 ≥ 10 coordinate

5.1.1

The role of nitrate complexes in the separation chemistry of actinides led Spirlet et al. [61] to synthesize 12-coordinate bis(ammonium)hexanitratothorium(IV). The authors prepared the complex from the reaction of thorium nitrate with ammonium nitrate in stoichiometric proportions in a highly acidic (10 M) nitric acid solution. The resulting complex, **37**, $[\text{NH}_4]_2[\text{Th}(\text{NO}_3)_6]$, possesses 12 coordinated O atoms from six bidentate nitrate ions, with Th-O bond distances ranging from 2.545(6) – 2.608(5) Å. The coordination environment is an irregular icosahedron (C_{2v}). The authors also synthesized the Pu analog of the complex, was found to be isostructural to the Th(IV) complex and can be seen in Figure 2.

Figure 28.

5.1.2

A renewed interest in Th(IV) decorporation led Thuéry to investigate the ability of aminocarboxylate ligands in the coordination of Th(IV) ions.[50] Thuéry complexed Th(IV) with three ligands, two of which were discussed in prior sections and the third was iminodiacetic acid (H_2IDA). All three complexes were produced under hydrothermal conditions. The 10-coordinate complex, $[\text{complex } [\text{Th}(\text{HIDA})_2(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}]$ (HIDA = iminodiacetic acid), **38**, Figure 29, showed that the metal center was coordinated by two carboxylate groups from two HIDA⁻ anions, two oxygen atoms from two different HIDA⁻ anions and two oxalate ligands that were formed *in situ*.

The ten-coordinate environment resulted in a bicapped square antiprismatic geometry. The bond lengths between the thorium center and oxygen atoms of carboxylate atoms are 2.59(3) and 2.411(3) Å. The bridging oxalate ligand forms Th-O bonds with a length of 2.491(6) Å and the average bite angle was calculated to be 60.02°.

Figure 29.

5.1.3

The diverse nature of Th(IV) coordination ability coupled with a need for a greater understanding of it led Biros and co-workers [62] to study complexes containing Th(IV) coordinated to a rigid, bidentate phosphine oxide ligand. Such ligands have been proposed previously in solution-solution extractions for actinides with trivalent actinides.[63] The authors used the same cis-ethylenebis-diphenylphosphine oxide, DPO, ligand to study seven different Th(IV) complexes that are all 10 or more in coordination number. The different complexes arise from the different crystal growing environments.[62]

The first complex, $\text{Th}(\text{NO}_3)_2\text{-DPO}\cdot(\text{NO}_3)_2$, **39a**, was grown via slow vapor diffusion of benzene into a concentrated solution of the complex dissolved in methanol resulted in a 10-coordinated, asymmetric Th(IV) complex that crystallized in the triclinic space group P1. The unit, Figure 30, is comprised of 1:3 $\text{Th}(\text{NO}_3)_2$ -ligand complex with two outer sphere nitrate anions and resembles a distorted bicapped square antiprism with the bidentate nitrato groups in the apical positions, with Th-O bonds ranging from 2.394 – 2.641 Å.[62] The average bite angle associated with thorium atoms bound to oxygen atoms of the nitrate anions was found to be 48.42° and those phosphine oxide ligand was calculated to average 70.02°.

Figure 30.

Obtaining crystals from the vapor diffusion of carbon tetrachloride into a concentrate solution of the complex in non-coordinating chloroform resulted **39b** shown in Figure 31, this complex crystallized in the monoclinic space group P21/n. Like **39a**, this complex is a 10-coordinate 1:3 Th(NO₃)₂-ligand complex with two outer sphere nitrate anions, however, there is a carbon tetrachloride solvent molecule. The Th-O bond distances range from 2.3857 to 2.6497 Å, these distances form an average bond angle of 48.62° for the oxygen atoms on the nitrate groups and 68.95° for oxygen atoms on the phosphine oxide molecules.[62]

Figure 31.

Probing the other metal-ligand stoichiometries and solution behavior of the aforementioned complex (**39b**) resulted in the complexation of one 12-coordinate and one 10-coordinate complexes. To do this, the authors prepared a concentrated mixture of Th(NO₃)₄ hydrate and DPO in methanol in a 1:1 stoichiometric ratio and placed the mixture in methanol in the refrigerator for 72 hours. The structure was solved in the orthorhombic space group *Pbca* and the asymmetric unit, **39c**, showed both the 10- and 12-coordinate Th(IV) complexes, Figure 32, along with two ordered molecules of methanol. The 1:2 metal-ligand complex is the ten coordinate environment and bears three bidentate nitrate groups that results in the an overall charge of +1, with Th-O bond distances ranging from 2.342 – 2.627 Å. The 1:1 complex is twelve coordinate and bears five bidentate nitrate groups, which results in an overall charge of -1, with Th-O bond distances ranging from 2.360 – 2.656 Å. In both complexes, all eight counter-ions are bound directly to the Th(IV) center. With an average bite angle between Th₁ and the nitrate oxygens calculated to be 49.06° and those on the phosphine oxide average 73.00°, giving the 1:2 complex a distorted bicapped square antiprism (D_{4d}) geometry. The average bite angle between the Th₂ atom and the nitrate oxygens is 48.66° and the oxygen atoms of the phosphine oxide form a bite angle of 68.22°, resulting in an icosahedron geometry.

Figure 32.

Crystallizing complex **39d** in methanol via vapor diffusion in diisopropylether resulted in a 1:3 metal-ligand complex that crystallized in the triclinic space group P1 and has an epoxide in place of the alkene, Figure 33.[62] There are three ligands and two nitrato groups bound in a bidentate manner to the 10-coordinate Th(IV). The complex resembles a distorted bicapped square antiprism (D4d) geometry with the inner sphere nitrato groups occupying the apical positions and the three ligands occupy the equatorial positions. The epoxide bearing ligand is bound with the oxygen atoms perpendicular to the nitrates, which is assumed to be stabilized by the electrostatic interactions between the epoxide oxygen and the nitrato nitrogen. The Th-O bond distances range from 2.377(3) – 2.642 (3) Å, resulting in average bite angles of 48.86° and 69.76° between the nitrato oxygens and the thorium atom, as well as, the phosphine oxide oxygen atoms, respectively.

Figure 33.

Three additional complexes came from efforts to reproduce the epoxide bearing complex, **39d**, by dissolving **39** in methanol and increasing stepwise the amount of epoxidation occurring in the solution. In each case, 1, 2, or 3 equivalents of *t*-BuOOH was added to the mixture, before stirring for one hour at room temperature and vapor diffusion in benzene or *i*Pr₂O. The *t*BuOOH did not result in epoxides on any of the bound ligands, but did result in two 1:3 metal-ligand complexes. These polymorphs differed only in the amount and location of the solvent in the

crystal lattice. The Th-O bond distances in the ten coordinate structures range from 2.413(4) – 2.700(4) Å for **39e** and 2.391(3) – 2.663 Å for **39f**. [62] The packing of the two complexes reveals the difference between the two complexes, although both bear three bidentate ligands and two bidentate nitrato groups. Complex **39e** has one outer sphere nitrate ion, three methanol molecules, and one water molecule, whereas, **39f** has one ordered outer sphere nitrate ion and two methanol molecules. The third complex showed that there were two different Th(IV)-ligand complexes in one asymmetric unit, which was solved in the triclinic space group P1. The first complex the thorium(IV) is bound to two bidentate nitrato atoms, two bidentate ligands, one monodentate ligand, and one water molecule. In the second complex with a 1:3 metal-ligand ratio, the Th(IV) is similar to that of complex **39a**. The first Th(IV) metal center is ten-coordinate in a distorted antiprism geometry.

5.1.4

In one unusual case, the applicability of metal-organic-frameworks to the fields of molecular recognition and gas storage, inspired Albrecht-Schmitt et al. explore the three-dimensional Th(IV) frameworks in reference 60. One of the complexes they synthesized, **40**, crystallized in the centrosymmetric triclinic space group of P1 with a 3-D framework of dimers the $[\text{Th}_2\text{O}_{18}]$, the thorium-oxygen subunit. The asymmetric unit contains one crystallographically independent, ten-coordinate Th(IV) ion, as shown in Figure 36. Two μ_2 -bridging oxygen atoms from two bridging hydroxyl groups, two oxygen atoms from two bidentate bridging carboxylate groups, four oxygen atoms form two chelating carboxylate groups, one phosphine oxygen atom, and one terminal oxygen atom as a water molecule complete the inner coordination sphere. This complex, Figure 34, adopts a coordination geometry that can be described as a spherical sphenocorona, as described by Ruiz-Martinez and Alvarez [64] in 2009. There are two planes, with a square plane defined by O1, O2, O3 and O6. The second plane is a pentagonal plane defined by O4, O5, O7, O8, and O9. Overall, the resulting 12 coordinate polyhedron contains 22 edges and 14 faces of 12 triangles and 2 squares. The Th-O bond distances range from 2.34 – 2.69 Å and the complex has a bite angle of 69.0(4)°. [60]

Figure 34.

6.1 Conclusion

The aforementioned complexes are examples that show the complex nature of Th(IV) and the binding geometries it can obtain. The ability of thorium to coordinate in different geometries and a wide-range of coordination numbers results in the difficulty to predict its preferred geometry and convolutes efforts to model it via computational methods. Even with the difficulties associated with predicting their geometry, Th(IV) complexes afford untapped possibilities of catalysis, MOF's that can be used for molecular recognition and magnetic molecules, and a potential means to sequester a fuel source, which would lead one to believe that delving further into this underexplored area would be beneficial. To our knowledge, this is the first review of its kind that was prepared comparing coordination numbers and metal center environment rather than a specific type of ligand binding Th(IV). [65]

7.1 Acknowledgements

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Tables

Table 1. The Th(IV) complexes in this review.

Schemes

Scheme 1. Synthesis of 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxantheneligand, [XA₂], reported by Emslie et al.

Scheme 2. Synthesis of Thorium complexes **3-7**.

Scheme 3. A) The synthesis of complex **8**, {N[o-NCH₂PⁱPr₂)C₆H₄]₃}Th[Co(CO)₃]. B) Seven coordinate complex **8** illustrating the Co-Th bond. Both images are generated from reference 16 and the Cambridge Crystallographic Database.

Figures

Figure 1. A) Complex **10** (Na₄[Th(C₆H₄O₂)₄·21H₂O]). B) Schematic diagram of the Th(IV) catecholate coordination geometries with the average bond distances and angles. Both images generated from the Cambridge Crystallographic Database based on reference 24.

Figure 2. The spectroscopic picture of the tetrakis(thenoyltrifluoroacetato)thorium(IV) molecule **11**, Th(TTA)₄. Image generated from the Cambridge Crystallographic Database based on reference 25.

Figure 3. The geometry of the two independent TTA ligands from **11**. Image generated based on reference 25.

Figure 4. A) Complex Th[(CH₃)₂CHN(O)O(O)C(CH₃)₃]₄ **12** with hydrogen atoms omitted for clarity. B) A view of complex Th[(CH₃)₂CHN(O)O(O)CH₂C(CH₃)₃]₄ **13**. Both images generated from the Cambridge Crystallographic Database based on reference 27.

Figure 5. The two ThA₄ molecules of **14**. The image was generated from the Cambridge Crystallographic Database based on reference 32.

Figure 6. a) The OLEX diagram of [Me₃BnN]₄[Th(N,N'-diethyl-2,3-dihydroxyterephthalamide)₄] **15**. b) The isolated coordination geometry of the 8-coordinate Th(IV) ion in **15**. Both images generated from the Cambridge Crystallographic Database based on reference 34.

Figure 7. Macrochelate TAM derived ligand **16**. Image generated based on reference 38.

Figure 8. Complex **17** with potassium ions, solvent molecules, and hydrogens omitted for clarity. The image was generated from the Cambridge Crystallographic Database based on reference 38.

Figure 9. Complex **18**, Th₂I₅[κ²(O,O')-μ-O(CH₂)₂OCH₃]₃(DME). The image was generated from the Cambridge Crystallographic Database based on reference 40.

Figure 10. Complex **19**, the μ₄-oxo tetranuclear complex, μ₄-oxo cluster, Th₄(μ₄-O)(μ-Cl)₂I₆[κ²(O,O')-μ-O(CH₂)₂OCH₃]₆. The image was generated from the Cambridge Crystallographic Database based on reference 40.

Figure 11. a) The Th(IV) cation of **20** - [1-butyl-2,3-dimethylimidazolium]₂-[Th₃(PO₃)₄(H₂P₂O₇)₃]. b) The hexanuclear clusters achieved by the phosphite ligands. The green is the thorium, the red the coordinating oxygens and the purple the phosphate bridges. Both images generated from the Cambridge Crystallographic Database based on reference 43.

Figure 12. Complex **21**, Th(pyOS)₄(dmf). Image generated from the Cambridge Crystallographic Database based on reference 44.

Figure 13. The nine-coordinate complex (C₅H₄NO₂)₄(H₂O)Th -**22** with the view normal to the plane along the pseudo-C₃ axis. The image is generated from data in the Cambridge Crystallographic Database based on reference 45.

Figure 14. Structure of complex **26** Th(3-hydroxy-2(1*H*)-pyridinonate)₄, view is down from the cap of the monocapped square antiprism, C_{2v} geometry. The image was generated from the Cambridge Crystallographic Database based on reference 48.

Figure 15. a) The ORTEP diagram of complex **27** - (Th₂(N,N'-diethyl-2,3-dihydroxyterephthalamidate)₆). b) The coordination geometry of the Th(IV) metal centers as seen in complex **27**. Both images have been generated from the Cambridge Crystallographic Database based on reference 34.

Figure 16. Structure of complex [Th(NTA)(H₂NTA)(H₂O)·H₂O], **28** with the carbon-bound hydrogens omitted. This image generated from the Cambridge Crystallographic Database based on reference 50.

Figure 17. Structure of complex **29** - [Th(EDTA)(H₂O)]·H₂O, with the carbon-bound hydrogens omitted for clarity. The figure has been generated from the Cambridge Crystallographic Database based on reference 50.

Figure 18. Ligands used to complex Th(IV) in reference 53.

Figure 19. Inset: The trimeric unit of complex **30** - Na₄[Th₆O₂(hedta)₆]·28H₂O. The H₂O molecules have been omitted for clarity. The hexameric form of complex **30** - Na₄[Th₆O₂(hedta)₆]·28H₂O. The H₂O molecules have been omitted for clarity. Both images generated from the Cambridge Crystallographic Database based on reference 53.

Figure 20. a) One NTP ligand and one nitrate anion bonding to the Th(IV) ion in complex **31**-[Th(C₉O₆NH₁₂)-(H₂O)(NO₃)]·2.5H₂O. The 2D sheets of complex **31** - [Th(C₉O₆NH₁₂)-(H₂O)(NO₃)]·2.5H₂O. Both images generated from the Cambridge Crystallographic Database based on reference 53.

Figure 21. The Al atoms forming the central core of complex **32** ([Th₂Al₈(OH)₁₄(H₂O)₁₂(C₆O₅NH₈)₄](NO₃)₆·57H₂O). This image generated from the Cambridge Crystallographic Database based on reference 53.

Figure 22. Structure of complex **33**. The image was generated from the Cambridge Crystallographic Database based on reference 53.

Figure 23. The 1,3,5-tri(4'-carboxylphenyl) benzoic acid (1,3,5-tCPBA) ligand (**34**) used by Wang et al. Image reconstructed from reference 54.

Figure 24. The flat layers of the single Th(IV) metal center from complex **35**, [C₇H₁₁N₂]₅[Th₂(1,3,5-tCPBA)₂Cl₆]·Cl. This image generated from the Cambridge Crystallographic Database based on reference 54.

Figure 25. The “muffin type” coordination environment of complex **35**, $[\text{C}_7\text{H}_{11}\text{N}_2]_5[\text{Th}_2(1,3,5\text{-tCPBA})_2\text{Cl}_6]\cdot\text{Cl}$. Defined as such as it does not fit into a clearly defined Archimedean geometry. This figure has been generated from the Cambridge Crystallographic Database based on reference 54.

Figure 26. The structure of H_3TPO . Image constructed from reference 60.

Figure 27. The coordination environment of complex **36**. Image constructed from the Cambridge Crystallographic Database based on reference 60.

Figure 28. The reported isostructural Pu(IV) complex $([\text{NH}_4]_2[\text{Pu}(\text{NO}_3)])$ is analogous to complex **37** $[\text{NH}_4]_2[\text{Th}(\text{NO}_3)]$. Image constructed based off image found in reference 61.

Figure 29. Structure of complex $[\text{Th}(\text{HIDA})_2(\text{C}_2\text{O}_4)]\cdot\text{H}_2\text{O}$ **38**. Image constructed from the Cambridge Crystallographic Database and based on reference 50.

Figure 30. Coordination environment of complex **39a** $\text{Th}(\text{NO}_3)_2\text{-DPO}\cdot(\text{NO}_3)_2$, where DPO is cis-ethylenebis-diphenylphosphine oxide ($\text{C}_{26}\text{H}_{22}\text{P}_2\text{O}_2$), grown via slow vapor diffusion of benzene. Image constructed from the Cambridge Crystallographic Database and based on reference 62.

Figure 31. Coordination environment of complex **39b** prepared from thorium nitrate and the tetraphenyl bis diphenylphosphine oxide (Figure 31) and grown from the vapor diffusion of carbon tetrachloride into the solution of complex in chloroform.. Image constructed from the Cambridge Crystallographic Database and reference 62.

Figure 32. The coordination environment of complex **39d**. Image constructed from the Cambridge Crystallographic Database and based on reference 62.

Figure 33. The A) 10- and B) 12-coordinate environments of complex **39c**. Image constructed from the Cambridge Crystallographic Database and based on reference 62.

Figure 33. The coordination environment of complex **39d**. Image constructed from the Cambridge Crystallographic Database and based on reference 62.

Figure 34. The coordination environment of complex **40**. Image taken from reference 60.