THORIUM AND THORIUM COMPOUNDS

1. Introduction

Thorium [7440-29-1] is a naturally occurring radioactive element, atomic number 90, with an atomic mass of 232.0381. Thorium is the second element of the 5*f* actinide series. Discovered in 1828 by J. J. Berzelius in a Norwegian mineral, thorium was named after *Thor*, the Scandinavian god of thunder. Thorium was first isolated in its oxide form (1,2).

The chemistry of thorium is similar to that of the lanthanides and Group 4 (IVB) elements (Ti, Zr, and Hf) and is dominated by the +IV oxidation state. Compounds containing thorium in lower oxidation states are known, but exceedingly rare in contrast to its lanthanide homologue, cerium. Standard potentials of Th(IV) in aqueous solutions have been estimated based on spectroscopic measurements, or determined indirectly from thermodynamic data. The electrochemistry of actinide elements has been reviewed (3–5) and data from different authors spans a wide range. The values most often quoted are those calculated using a modified ionic model to obtain the Gibbs free energy of formation for the Th(IV) aqua ion (6). The predicted standard electrode potential for the $Th^{4+}|Th^{3+}$ couple from this approach is -3.0 V. Wickleder and co-workers argued that the value of -3.7 V is more probable (7). For a full discussion of thorium electrochemistry, the reader is referred to the *Gmelin Handbook* (8). Thorium is generally more acidic than the lanthanides, but less acidic than other light actinides, eg, U, Np, and Pu, as expected based on its larger ionic radius (Th, 1.08 Å).

2. Isotopes

Thirty isotopes of thorium have been observed with masses ranging from 209 to 238 and radioactive half-lives ranging from 0.1 μs for ^{218}Th [33690-62-9] and ^{219}Th [36840-39-8] to 1.405×10^{10} year for ^{232}Th [7440-29-1]. For data on nuclear masses the reader is referred to the compilation by Audi and Wapstra (9), the update by Audi and co-workers (10), and the *Table of Isotopes* (11,12). The light thorium isotopes with masses 209–230, and 232 decay by α particle emission; the heavy thorium isotopes 231 and 233–238 decay by β^- emission. The commonest isotope is ^{232}Th, the predominant isotope in Nature. Five other isotopes occur as members of all three naturally occurring decay chains of the long-lived isotopes, ^{232}Th, ^{235}U, and ^{238}U, as well as the manmade Np series. The ^{232}Th isotope is the progenitor of the $4n$ decay series (Fig. 1), which includes ^{228}Th as a transient. The isotopes ^{234}Th and ^{230}Th ($4n+2$), ^{231}Th and ^{227}Th ($4n+3$), and ^{229}Th ($4n+1$) are daughters in other decay series. The most commonly used isotopes after ^{232}Th include ^{228}Th (1.912 year, α), ^{230}Th (7.538×10^4 year, α), and ^{234}Th (24.10 days, β). The most important thorium isotopes are listed in Table 1.

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3. Atomic Properties

It is customary in discussing the actinide series to only list the electrons in shells outside the radon core. The outermost electrons of the free actinide atoms and ions outside the radon core are found in the $7s$, $7p$, $6d$, and $5f$ shells. For the light actinide elements in the first half of the $5f$ series, there is a small energy difference between $5f^n7s^2$ and $5f^{n-1}6d7s^2$ electronic configurations. Atomic spectra of neutral thorium atoms in the gas phase indicate that the Th $6d$ levels are lower in energy than the $5f$ levels and that neutral thorium atoms have a diamagnetic electronic ground state of $[\mathrm{Rn}]6d^27s^2$ ($^3\mathrm{F}_2$). Identified excited configurations of the neutral thorium atom within the first 2 eV ($\sim$16,000 cm^{-1}) of the ground state include $6d^37s$, $5f6d7s^2$, $6d7s^27p$, $6d^27s7p$, and $5f6d^27s$. The ground state of singly ionized thorium (Th^+) is $6d^27s$ followed by $6d7s^2$, $5f7s^2$, $5f6d7s$, $6d^3$, and $5f6d^2$ within the first 2 eV. For doubly ionized thorium (Th^{2+}) the ground state is $5f6d$, but the $6d^2$ configuration is only 63 cm^{-1} higher in energy. In 1992, Blaise and Wyart published all known energy levels of the actinide elements that had been analyzed up to that time and listed ionization stage, energies, intensities, J values, and level assignments of selected lines (13). The contents of that compilation are available on an updated database at the Laboratoire Aimé Cotton website (www.lac.u-psud.fr). From this discussion, it is easy to see that electronic configurations that include the $5f$ electrons become increasingly stabilized with increasing ionic charge. Since the oxidation state of thorium is generally +IV, it has no $5f$ valence electrons in any of its compounds.

The ionization potential of neutral thorium has been determined by resonance ionization mass spectrometry to be 6.3067(2) eV (14).

4. Occurrence

Thorium has a wide distribution in Nature and is present as a tetravalent oxide in a large number of minerals in minor or trace amounts. Thorium is the most common actinide element, present in the Earth's crust at 7.2 parts per million (ppm), approximately three times more abundant than uranium, and in sea water at a concentration of $< 0.5 \times 10^{-3}$ g/m^3. Thorium refined from ores free of uranium would be almost monoisotopic ^{232}Th, ie, the ^{228}Th from its own decay chain would be 1 part in 10^{10}. The presence of uranium in the ore would introduce infinitesimal amounts of short-lived ^{231}Th and ^{227}Th from the decay of ^{235}U, and ^{234}Th from ^{238}U decay. The isotopes ^{232}Th and ^{228}Th occur in thorianite ($\mathrm{ThO_2}$) and thorite ($\mathrm{ThSiO_4}$); ^{234}Th and ^{230}Th are present in naturally occurring uranium, while ^{231}Th and ^{227}Th occur in uranium minerals as members of the ^{235}U decay chain. The remaining isotopes are formed upon neutron bombardment of those isotopes just discussed, or by charged particle bombardment of various targets.

Thorium isotope concentrations and ratios, with parent and daughter isotope concentrations, are used to date and study the formation and metamorphosis of rocks and sediments. For example, ^{230}Th/^{234}U has been used to date coral reef terraces (15). The ^{238}U/^{230}Th disequilibria and ^{230}Th/^{232}Th ratios are used to determine the source and history of basalts (16). In addition to dating and petrogenetic studies, thorium isotopes are used as magma source tracers (17).

There are only a few minerals where thorium occurs as a significant constituent and besides thorianite (ThO_2) they generally contain mixtures of Th(IV) and trivalent lanthanides. The commercially important ore is the golden-brown lanthanide phosphate, monazite ($LnPO_4$; Ln = Ce, La, Nd), in which thorium is generally present in a 1–15% elemental composition (7,18). Monazite is widely distributed around the world, with some deposits being quite large. Beach sands from Australia and India contain monazite from which concentrates of lanthanides, titanium, zirconium, and thorium are produced (18). The Travancore deposits in India are the most famous, and have been perhaps one of the most significant sources of commercial thorium. Minerals that contain thorium are still being discovered and characterized (19). Significant deposits of thorium are found in Australia, Brazil, Canada, Greenland, India, South Africa, and the United States. Additional information on the occurrence of thorium in minerals can be found in the *Gmelin Handbook* (18), and a review of the mineralogy of thorium is given by Frondel (20).

4.1. Recovery from Ores. Since there are a number of minerals in which thorium is found, a number of fundamental process flow sheets exist for the recovery of thorium from ores (21). The extraction of monazite from sands may be accomplished via the digestion of sand with either strong acid or hot alkali. In the alkali process, the insoluble phosphate is converted to the hydroxide using a 30–45% NaOH solution at 140°C. The hydroxide is then dissolved in acid (HCl or H_2SO_4) and the pH adjusted to pH 5–6 to afford the selective precipitation of thorium hydroxide from the less acidic lanthanides that precipitate at higher pH values (22). The thorium hydroxide is then dissolved in nitric acid and extracted with methyl isobutyl ketone or tributyl phosphate in kerosene to yield $Th(NO_3)_4$ [13823-29-5], which can be isolated from the organic solvent (23). In the acidic process, hot, concentrated sulfuric acid (210–230°C) is used to dissolve the monazite sand. The selective separation of thorium from lanthanides is based on the fact that thorium is almost totally precipitated as a phosphate near pH 1.0 while the lanthanides remain in solution until near pH 2.0. The crude phosphate precipitate can then be treated with alkali to convert to the hydroxide, and then redissolved in nitric acid for solvent extraction as above.

For nuclear fuel applications the purity requirements for thorium are quite demanding, for which solvent extraction techniques have been employed. Once phosphate has been removed via alkaline treatment, the nitrato complexes of thorium, uranium, and lanthanides can be separated and purified by extraction with tributyl phosphate (TBP) in an organic solvent, typically kerosene. An exhaustive compilation of flow sheets covering caustic soda, sulfuric acid, ammonium fluoride, chlorination, and other processes can be found in the *Gmelin Handbook* (21).

5. Economic Aspects

Thorium and its compounds were produced primarily from the mineral monazite, which was recovered as a by-product of processing heavy-mineral sands for tin, titanium, or zirconium minerals. Monazite was recovered primarily for its rare-earth content, and only a small portion of the thorium by-product was consumed. Limited demand for thorium, relative to the rare earths has created a worldwide oversupply of thorium compounds and residues. Excess thorium not designated for commercial use was either disposed of as a radioactive waste or stored for potential use as a nuclear fuel or other application. In 2005, the U.S. government authorized the disposal of 3,220,506 kg of thorium nitrate from the National Defense Stockpile (NDS) classified as excess to goal (24). Total resources of thorium as economically extractable forms were estimated in 2004 to be 1.2 Mtonnes (25). The countries with the greatest reserves include Australia, India, Norway, the United States, and Canada, with 0.3, 0.29, 0.17, 0.16, and 0.10 Mtonnes, respectively. Thorium oxide prices were ~ \$82.50/kg for 99.9% purity in 2004. Thorium nitrate was \$27.00/kg for mantle-grade material (24). Cost estimates for Th-based nuclear fuels have been reported (26). Other economic aspects of thorium are reflected in the industrial processes discussed in the USES section, ie, composite for lantern mantels, catalyst for liquid fuel production, synthesis of high temperature superconductors, and alloy agent for improved structural integrity of airplane parts.

6. Uses

Thorium is mainly used in commercial lantern mantles, refractory materials, electronic components, alloys utilized for jet engine components, as a catalyst in the chemical industry, in nuclear medicine, and in nuclear reactor fuels (^{232}Th). The oxide finds application in electrodes for arc welding, in the manufacturing of ceramics, and as a minor component in a catalyst for the production of liquid fuel (27). The inherent radioactivity of ^{232}Th (the most important isotope) and the formation of radioactive daughter products are important limiting factors in most industrial uses of thorium (28,29). The radiological protection and necessary permission required by most countries to handle large quantities of thorium, has resulted in a steady decrease in the usage of thorium on an industrial scale.

Gas Mantles. Thorium and thorium compounds, especially oxides, have very high melting temperatures; eg, thoria (ThO_2) has a melting point of 3390°C. By 1891, the Austrian Chemist, C.A. von Welsbach had perfected the thoria gas “mantle” to improve the low luminosity of coal-gas flames then used for lighting. Fabric of the required shape was soaked in an aqueous metal nitrate solution and the fiber burned off converting the nitrates into oxides. A mixture of 99% ThO_2 and 1% CeO_2 was used and has not since been bettered. The CeO_2 catalyzes the combustion of the gas and apparently, because of the poor thermal conductivity of the ThO_2, particles of CeO_2 become hotter making the flame brighter than would otherwise be possible. The commercial success of the gas mantle was immense and produced a worldwide search for thorium. In the process of mining thorium, the lanthanides were found to be more plentiful than had been previously thought and were recovered in large quantities (30).

Catalysis. Thorium is used industrially in the catalytic production of hydrocarbon mixtures for use as liquid motor fuel (31). For direct conversion of synthetic gas to liquid fuels, thorium acts as a promoter in an Al_2O_3 supported catalyst increasing olefin and liquid hydrocarbon production (32). A Ni–ThO_2/Al_2O_3 catalyst was developed for the oxidative cracking of hydrocarbons by steam, and resulted in an increased resistance of the catalyst to inactivation by coking (33). Thorium supported on dehydroxylated γ-alumina is an outstanding heterogeneous catalyst for arene hydrogenation that rivals the most active platinum metal catalysts in activity (34,35).

Alloys and Ceramics. Thorium forms alloys with a wide variety of metals. In particular, thorium is used in magnesium alloys for the aircraft industry to extend the temperature range of important structural properties. Thorium oxide is one of the most refractory materials known, and has been used in crucible materials, and to increase hardness of alloys used for gas turbine blades. For a more detailed discussion on thorium alloys and compounds, the reader is referred to the *Gmelin Handbook* (36), and the treatise by Wickleder and coworkers (7).

Medical Applications. The radioactivity of thorium isotopes make it useful in radiopharmaceutical applications. Alpha particles are of considerable interest for radioimmunotherapy applications since their short range in soft tissue is limited to only a few cell diameters. The delivery of such high energy in such a small volume, or high linear-energy transfer (LET), makes alpha particles especially well suited for targeting micrometastatic disease and single tumor cells, eg, leukemia and other blood-borne disease. Thorium, in the form of ^{229}Th is used to produce ^{225}Ac, which is employed in a ^{225}Ac/^{213}Bi generator system for radioimmunotherapy (37).

Nuclear Fuel. The greatest potential industrial use of thorium is in commercial nuclear fuel cycles due to the ability of "fertile" ^{232}Th to act as a breeder to efficiently produce "fissile" ^{233}U in a thermal neutron reactor (38–40) according the equation:

$$^{232}_{90}\mathrm{Th}\ (\mathrm{n},\gamma) \rightarrow {}^{233}_{90}\mathrm{Th} \xrightarrow[23.3\,\mathrm{m}]{\beta} {}^{233}_{91}\mathrm{Pa} \xrightarrow[27.4\,\mathrm{d}]{\beta} {}^{233}_{92}\mathrm{U}$$

Since natural thorium does not contain any "fissile" isotope, the initial ^{233}U must be produced from thorium in reactors fueled with ^{235}U or ^{239}Pu, or in special accelerator driven systems. Once sufficient amounts of ^{233}U have been produced, the thorium–uranium fuel cycle could become self-sustaining. The feasibility of thorium utilization in high temperature gas cooled reactors (HTGRs), light water reactors (LWRs), pressurized heavy water reactors (PHWRs), liquid metal cooled fast breeder reactors (LMFBRs), and molten salt breeder reactors (MSBRs) has been demonstrated. The reactor may be designed with a core containing a mixture of ^{232}Th and ^{233}U, or with a central core of ^{233}U surrounded by an outer layer (blanket) of ^{232}Th. The fuel material can be a solid matrix, eg, $(Th,U)O_2$ and $(Th,U)C_2$, employed in HTGRs, or $(Th,U)O_2$ in LWRs. Alternatively, the fuel material can be in a liquid matrix as employed in the MSBR tested at Oak Ridge in the 1960s. In the MSBR, UF_4 and ThF_4 were dissolved in an eutectic melt of BeF_2, ZrF_4, and ^{7}LiF. The reactor may be homogeneous with respect to ^{232}Th and ^{233}U, or of the core and blanket design with a graphite moderator (40). Due to the need to control nuclear materials, thorium-based breeder reactor concepts have been modified to be more deliberately proliferation resistant. For example, the central seed region of each fuel assembly could contain uranium enriched to 20% ^{235}U. The thorium “blanket” could contain some ^{238}U such that any uranium chemically separated from it would not be useable for weapons. Plutonium produced in the seed would contain a high proportion of ^{238}Pu, and therefore generate a lot of heat; an additional deterrent is that spent fuel from this design would contain ^{232}U, which decays rapidly and has very gamma-active daughters. Instead of oxide, the seed fuel could be metallic uranium alloy. Since the early 1990s, Russia has had a program to develop a thorium–uranium fuel, which more recently has moved to have a particular emphasis on utilization of weapons-grade plutonium in a thorium–plutonium fuel.

The advantages of a thorium–uranium fuel cycle include the fact that thorium is three to four times more abundant than uranium, intrinsic proliferation resistance due to the formation of ^{232}U (half-life 73.6 year), and the lower quantity of plutonium and long-lived minor actinides that minimize the radiotoxicity associated with the spent fuel (40). The challenges of a thorium–uranium fuel cycle include the presence of hard gamma emitters like ^{232}U that necessitate remote manufacture of ^{233}U fuels in highly shielded environments similar to fabrication of $(U,Pu)O_2$ fuels. The high cost of manufacture is only slightly offset by the avoidance of a uranium enrichment step. Reprocessing of thorium fuels is plagued by both chemical and nuclear difficulties. The decay chain that leads to ^{233}U also forms ^{233}Pa ($t_{1/2} = 27$ days) that generates the need to let spent fuel cool for $\sim$1 year. Even then a considerable amount of long-lived ^{231}Pa still exists that complicates chemical reprocessing. From a proliferation standpoint, ^{233}U is a potential nuclear weapon material with a critical mass in between that of ^{235}U and ^{239}Pu. No full-scale thorium–uranium cycle has yet been demonstrated and reprocessing has only been demonstrated on an experimental scale.

Overall, the $^{232}Th/^{233}U$ cycle is unlikely to be developed in the near future owing to the more advanced state of the $^{238}U/^{239}Pu$ cycle, and the current availability of uranium. An exception to this scenario is the evolving nuclear energy program in India, a country that has vast emerging needs for electricity and abundant thorium resources (41). The Department of Atomic Energy in India is following a course of utilizing Heavy Water Power Reactors (HWPRs) and transitioning to Fast Power Reactors and Thorium reactors.

7. Thorium Metal

7.1. Preparation. Pure thorium metal is very difficult to prepare due to the high reactivity of thorium with H_2, O_2, N_2, and C at the high temperatures necessary for production. Thorium metal can be produced by a variety of reduction techniques (all of which have unique difficulties) including molten salt reduction of $ThCl_4$ [10026-08-1] with Mg or NaHg, or ThO_2 [1314-20-1] with Al, Mg, or Ca (the “Sylvania Process”); fused salt electrolysis of $ThCl_4$ or ThF_4 in a NaCl/KCl eutectic; or the thermal decomposition of ThI_4 [7790-49-0] (7,27). By far, the most advantageous and common method of preparation is the molten salt reduction of ThF_4 [13709-56-6] in a blend of Ca and $ZnCl_2$ in a dolomite-lined reactor at 660°C (7). The highly exothermic reaction produces a massive Th–Zn alloy that settles to the bottom of the slag (CaF_2–$CaCl_2$–ZnF_2). The crude alloy contains 4.1–7.0% Zn with yields of up to 95%. Distillation of the Zn finally leads to the production of a high purity thorium sponge.

7.2. Properties. Pure thorium metal is a dense, bright silvery metal with a very high melting point of 1750°C, and exists in two allotropic modifications under ambient pressure. Thorium adopts a face centered cubic (fcc) structure that transforms to a body centered cubic (bcc) structure >1390°C. Under high pressure, a third phase with a body centered tetragonal structure has been observed (42–44). Thorium is a reactive, soft, and ductile metal that tarnishes slowly on exposure to air (27). Having poor mechanical properties, the metal has no direct structural applications. A survey of the physical properties of thorium, provided by Smith and co-workers (45) and Oetting and co-workers (46) is summarized in Table 2. The magnetic susceptibility of thorium metal increases nearly linearly with increasing temperature to $0.412 \pm 0.001 \times 10^{-6}$ emu/g at 300 K, and is sensitive to the concentration of impurities (47). The metal becomes superconducting between T_c of 1.35–1.40 K, with a critical magnetic field H_c of 159.22 ± 0.10 G for a high purity sample (48).

Thorium metal alloys readily with a large number of metals, eg, Fe, Co, Ni, Cu, Au, Ag, B, Pt, Mo, W, Ta, Zn, Bi, Pb, Hg, Na, Be, Mg, Si, Se, and Al. An overview of thorium alloys with main group metals can be found in the *Gmelin Handbook* (49,50). Like many electropositive metals, finely divided thorium metal is pyrophoric in air, and burns to give the oxide. Massive metal, chips, and turnings are stable under ambient conditions, although the surface will darken with time as oxide forms on the surface. Hydrogen, nitrogen, halogens, and sulfur all undergo energetic reactions with thorium at a variety of temperatures.

Most mineral acids react vigorously with thorium metal. Aqueous HCl will attack thorium metal, but dissolution is not complete, and 12–25% of the metal typically remains undissolved. A small amount of fluoride or fluorosilicate is often used to assist in complete dissolution. Nitric acid will passivate the surface of thorium metal, but small amounts of fluoride or fluorosilicate will assist in complete dissolution. Dilute HF, HNO_3, or H_2SO_4, or concentrated $HClO_4$ and H_3PO_4 will slowly dissolve thorium metal with constant hydrogen gas evolution. Thorium metal will not dissolve in alkaline hydroxide solutions.

8. Thorium Compounds

8.1. Hydrides. Reaction of thorium metal with hydrogen forms binary hydrides of general formula ThH_{2-x}, ThH_2, and Th_4H_{15}. The substoichiometric hydride ThH_{2-x} has been identified in both fcc and tetragonal forms. The stoichiometric dihydride ThH_2 has the tetragonal ZrH_2 structure, and can be substantially substoichiometric. The higher hydride of formula Th_4H_{15} has a unique cubic crystal structure. Several excellent reviews have appeared on the synthesis and kinetics (51), the thermodynamics (52), and the physicochemical characteristics of thorium and other actinide hydrides (51,53,54). Thorium hydrides decompose to give pure and finely divided metal. The hydrides are pyrophoric and must be handled in inert atmospheres (He, Ar). The hydrides display metallic conduction.

8.2. Carbides. Binary thorium carbides of formula ThC, Th_2C_3 and ThC_2 are formed by high temperature reaction of ThO_2 with carbon or by the direct fusion of the elements (55–57). Both ThC and ThC_2 are substoichiometric refractory solids with high melting points (2625 ± 25 and 2655 ± 25°C, respectively). The third carbide, Th_2C_3, has been observed at pressures above 33 kbar near 1200°C. The ThC_2 compound is readily oxidized to ThC.

8.3. Pnictides. Thorium nitrides of formula ThN and Th_3N_4 can be obtained by the strong heating of thorium metal in the presence of nitrogen, or by reaction of thorium hydride with nitrogen or ammonia. Reviews of synthesis (58) and structural properties are available (59). The thermally stable nitride is Th_3N_4 as it is the stable product of decomposition of ThN. Golden yellow ThN displays metallic character and adopts the NaCl structure in analogy with all other actinide nitrides. Heavier pnictide analogues, eg, ThP, ThAs, and ThSb, also adopt the cubic NaCl structure (59).

8.4. Oxides. Due to the importance as nuclear fuel material and environmental behavior, actinide oxides have been intensively investigated (60–62). They are very complicated compounds, due to the formation of nonstoichiometric or polymorphic materials. Actinide oxides are very heat resistant and ThO_2 [1314-20-0] is the highest melting (3390°C) of any metal oxide. Thorium dioxide has the cubic fluorite structure with $a_0 = 5.5863(6)$ Å and a density of 10.001 g/cm^3. It can be readily obtained by ignition of thorium hydroxide, oxalate, carbonate, peroxide, nitrate, and other oxoacid salts. Recent X-ray absorption fine structure (XAFS) studies of crystalline ThO_2 are consistent with this structure (63). However, under environmental conditions, small (20 nm) colloidal particles of $ThO_2{\cdot}nH_2O$ can form, and XAFS data reveal that this amorphous solid has a different structure (63). Several binary compounds have been synthesized by fusing the respective thorium and alkali or alkaline earth oxides to form double oxides of the form M_2ThO_3 (M = Na [12058-67-9], K, Rb, Cs, Ba), and $BaThO_3$ [12230-90-9]. Ternary thorium oxides have been reported with lanthanides ((Th,Ce)O_2, (ThCe)O_{2-x} with $x < 0.25$), niobium ($Th_{0.25}NbO_3$), tantalum ($ThTa_2O_7$, $Th_2Ta_2O_9$), molybdenum [$Th(MoO_4)_2$, $ThMo_2O_8$], germanium ($ThGeO_4$), titanium and vanadium. Superconducting properties have been observed in the δ-compound $Nd_{2-x}Th_x\,CuO_4$ at $x = 0.16$. More recently, Busch and co-workers synthesized two new thorium tantalum oxides, $Th_4Ta_{18}O_{53}$ and $Th_2Ta_6O_{19}$, which are representatives of the Jahnberg structural family (64,65). The formula unit $(Th_2O_3)_2(Ta_3O_8)_6$ corresponds to an octahedral layer arrangement of the Th–O coordination polyhedra in $Th_4Ta_{18}O_{53}$. Thorium is eight coordinate, having a trans bicapped octahedral geometry. The quaternary compound, $K_3NaTh_2O_6$, has been synthesized in a Ni bomb at 1300°C from the oxides with single crystals having a monoclinic, space group $C2/c$, and an ordered NaCl-type structure (66).

8.5. Halides and Oxyhalides. The halides and oxyhalides of thorium have been reviewed by Brown (67), by Wickleder and co-workers (7), and in the *Gmelin Handbook* (68).

Fluorides. The compound ThF_4 [13709-59-6] is widely used as a source of elemental thorium through electrochemical reduction. Anhydrous ThF_4 is insoluble in water, and has been isolated a number of ways. One of the first methods involved the dehydration of $ThF_4{\cdot}nH_2O$ at high temperatures with atmospheres of either HF or $CO_2/HF/CCl_4$. Dehydration is inefficient, prompting preparative routes that avoid aqueous media. Anhydrous preparative techniques have employed the reactions of fluorochlorohydrocarbons with ThO_2; F_2 with thorium metal, carbides and tetrahalides; NH_4HF_2 with ThO_2; or HF with thorium hydroxides, oxides, oxalate, carbonates and tetrahalides. The isolated hydrates indicate a stability of ThF_4 against hydrolysis at room temperature, a characteristic that is not shared by other tetrahalides. Pyrohydrolysis does occur at higher temperatures (>700°C) producing first the oxofluoro species, $ThOF_2$ [13597-30-3], and finally ThO_2. The oxyhalo species, $ThOF_2$, has been produced by direct interaction of ThF_4 with O_2, a reactivity that has been exploited to remove O_2 from thorium metal. The ThF_4 has the ZrF_4 crystal structure.

Complex salts of thorium fluorides have been generated by interaction of ThF_4 with fluoride salts of alkali or other univalent cations under molten salt conditions. The general anionic forms of these complexes are: $[ThF_5]^-$ [15891-02-8], $[ThF_6]^{2-}$ [17300-48-0], $[ThF_7]^{3-}$ [56141-64-1], where typical countercations are Li^+, Na^+, K^+, Cs^+, $NH_4{}^+$, and $N_2H_5{}^+$. Additional information on thorium fluorides can be found in the *Gmelin Handbook* (68).

Chlorides. Anhydrous $ThCl_4$ [10026-08-1] has been prepared by direct interaction of thorium metal, hydride, or carbide with chlorine. An alternative to this approach is the reaction of anhydrous HCl or NH_4Cl with the metal or the hydride at elevated temperatures (700–900°C). One of the difficulties of these processes is the production of $ThOCl_2$ [13637-74-6] from either residual H_2O or O_2 in the reactants, but the resulting $ThCl_4$ can be purified by sublimation. The $ThCl_4$ compound melts at 770°C and boils at 921°C.

Complex ions of Th(IV) have been studied and include $M_2[ThCl_6]$ [21493-66-3] ($M = Li{-}Cs$, Me_4N, Et_4N). Under more extreme conditions, ie, molten KCl or vapor phase, $ThCl_5{}^-$ [51340-85-3], $ThCl_7{}^{3-}$ [51340-84-2], $ThCl_8{}^{4-}$ [53565-25-6], and $ThCl_9{}^{5-}$ are known to be important. Additional information on thorium chlorides can be found in the *Gmelin Handbook* (68).

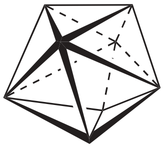
Bromides and Iodides. Anhydrous $ThBr_4$ [13453-49-1] and ThI_4 [7790-49-0] have been prepared in a similar fashion as the chloride, by interaction of thorium metal, hydride, carbide with the elemental halide of choice, or at high temperatures (700–900°C) with HX ($X = Br, I$). Both the tetrabromide and the tetraiodide are light sensitive and are more readily hydrolyzed to $ThOX_2$ ($X = Br$ [13596-00-4], I [13841-21-9]) than the tetrachloride. Two lower iodides, ThI_3 and ThI_2 are known, and may be prepared by reaction of ThI_4 with thorium metal in sealed tantalum tubes (7).

Hydrocarbon soluble $ThX_4(thf)_4$ (thf = tetrahydrofuran; $X = Br$ [140361-04-2], I [140361-05-3]) have been obtained through the interaction of thorium metal turnings with elemental halides in THF (solvent) at 0°C (69). These complexes exhibit distorted dodecahedral coordination geometry. Dissolution of these complexes in the presence of Lewis bases (MeCN, py = pyridine, DME = 1,2-dimethoxyethane) results in substitution of the four thf molecules, producing ThX_4L_y ($X = Br, y = 4, L = py$ [79086-83-2], MeCN [17499-64-8], $y = 2$, $L = DME$ [140361-07-5]; $X = I, y = 4, L = py$ [140361-06-4]) (69). Comparable with the chloride system, complex ions of the form $M_2[ThX_6]$ (X = Br [44490-06-4], M = Me_4N, Et_4N; X = I [44490-18-8], M = Et_4N, Me_3PhN) are known where the metal center is octahedral. Additional information on thorium bromides and iodides can be found in the *Gmelin Handbook* (68).

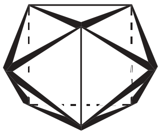
9. Coordination Complexes

The aqueous and nonaqueous coordination chemistry of thorium is dominated by the extremely stable tetravalent ion. Except in a few rare cases in nonaqueous environments where extremely large and sterically demanding ligands are used, and air and moisture are rigorously excluded, lower oxidation states are generally unstable. A rare example of this is with η-$C_5H_3(SiMe_3)_2^-$, which led to the isolation of a genuine molecular Th(III) organothorium complex, $Th[\eta$-$C_5H_3(SiMe_3)_2]_3$ [107040-62-0] (70). Early reports (71) on the synthesis of soluble Th(II) complexes, eg, $ThI_2(NCMe)_2$ [85613-74-7], are suspect (69).

The chemistry of Th(IV) has expanded greatly during the last decade (7,72–74). Being a "hard" metal ion, Th(IV) has the greatest affinity for "hard" donor atoms, eg, N, O, and F. Due to the large ionic radius of tetravalent thorium (1.08 Å), coordination complexes of Th(IV) generally display variable and high coordination numbers, typically 8, 9, 10, or higher. Eight-coordinate complexes are the most common, and the energy differences between the various common eight-coordinate polyhedral geometries are small. Common coordination polyhedra for Th(IV) include dodecahedral, bicapped trigonal prism, and square antisprism, illustrated qualitatively in **1**, **2**, and **3**, respectively.



(1)



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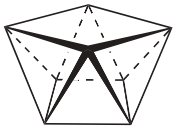


(3)

9.1. Hydration and Hydrolysis in Aqueous Solution.

Under noncomplexing strongly acidic conditions, such as in perchloric or triflic acid solutions, aq. Th(IV) exists as the simple hydrated (or aqua) ion, Th^{4+}, retaining its overall formal charge. Recent X-ray absorption spectroscopic studies reveal that under noncomplexing acid conditions, Th(IV) is coordinated by 9–11 water molecules, with a most probable value of 10 and a molecular formula of $[Th(OH_2)_{10}]^{4+}$ (75). The rate constants and activation parameters for the exchange of solvent and bound water indicate a dissociative exchange mechanism consistent with the formulation $[Th(OH_2)_{10}]^{4+}$ (76).

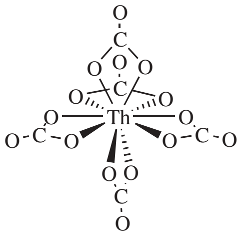
Because of its large size, Th(IV) is generally less resistant to hydrolysis than similarly sized lanthanides, and more resistant to hydrolysis than tetravalent ions of other early actinides (U, Np, Pu). Thorium(IV) hydrolysis has been studied by a number of researchers, and many of these studies indicated stepwise hydrolysis to yield monomeric products of formula $[Th(OH)_n]^{4-n}$ with $n = 1-4$, in addition to a number of polymeric species and colloid formation (77–81). In the most recent critical review, a comprehensive set of hydrolysis constants or the stepwise formation of $[Th(OH)]^{3+}$, $[Th(OH)_2]^{2+}$, $[Th(OH)_3]^{+}$, and $Th(OH)_4$ have been proposed (81). All hydrolyzed solutions are known to contain hydrolysis polymers, and the most reliable models include the presence of dimers $[Th_2(OH)_2]^{6+}$ and $[Th_2(OH)_4]^{4+}$, tetramers $[Th_4(OH)_8]^{8+}$ and $[Th_4(OH)_{12}]^{4+}$, and hexamers $[Th_6(OH)_{14}]^{10+}$ or $[Th_6(OH)_{15}]^{9+}$ (78,80). The solubility products for ThO_2 and $Th(OH)_4$ have also been extensively studied. The solubility product for these compounds depends on the degree of crystallization and solution conditions, and has been reviewed in detail (81–83).

9.2. Oxo Ion Salts. Salts of oxo ions, ie, nitrate, carbonate, sulfate, perchlorate, iodate, phosphate, and oxalate, are very important and readily obtained in aqueous solution. Carbonate, sulfate, and phosphate anions are known to influence the speciation of Th(IV) in natural waters.

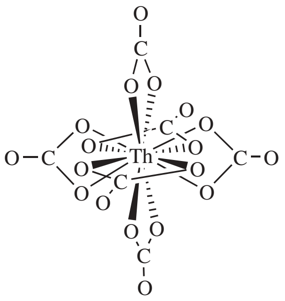
Perchlorate. Thorium perchlorate [16045-17-3] forms upon dissolution of thorium hydroxide in perchloric acid and crystallizes as $Th(ClO_4)_4{\cdot}4H_2O$ (84).

Sulfate. Hydrated thorium sulfate, $Th(SO_4)_2{\cdot}nH_2O$ ($n = 9, 8, 6, 4$), is easily crystallized from thorium and sulfuric acid and can be readily dehydrated by heating to 350–400°C. The crystal structure of the octahydrate has been determined to be a 10-coordinate bicapped square antiprism with two chelating SO_4^{2-} ions, and six coordinated H_2O molecules (85). Various complex salts (and their hydrates), eg, $Na_{12}Th(SO_4)_8$ (86), $K_4Th(SO_4)_4$ (87), and $Rb_2Th(SO_4)_3$ (88), have been reported and reviewed (7).

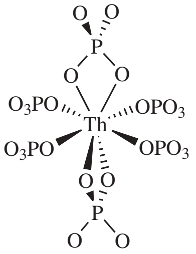
Carbonate. In addition to hydrolysis and colloid formation, complexation of tetravalent actinides by carbonate in one of the most important reactions in aqueous media (89). The carbonato and hydroxo carbonato complexes of redox stable Th(IV) have been of special interest in that they reveal systematic trends across the series of light actinide elements, Th(IV), U(IV), Np(IV), and Pu(IV). The most relevant solution studies for thorium have been reported by Östhols and co-workers (90), Rai and co-workers (91), Felmy and co-workers (92), and Altmaier and co-workers (93). The most recent study by Altmaier and co-workers summarizes the relevant literature in this area, and concludes that at low ionic strength ($I = 0.5\ M$), the mixed hydroxo carbonato complexes $[Th(OH)(CO_3)_4]^{5-}$ [796024-24-3] and $[Th(OH)_2(CO_3)_2]^{2-}$ [796022-26-9] are the most important ternary solution complexes that contribute to Th(IV) solubility. At higher carbonate concentration, the highly charged $[Th(CO_3)_5]^{6-}$ [12364-90-8] is also formed (93). There are literature reports on solids of formula $ThO(CO_3)$ [49741-19-7] and $Th(OH)_2(CO_3){\cdot}2H_2O$ [12538-65-7], but these solids are not well characterized. The pentacarbonato salts of Th(IV) and U(IV) are the best studied of the tetravalent actinide carbonate solids. Salts of the formula $M_6Th(CO_3)_5 \cdot nH_2O$ [12364-90-8] ($M_6 = Na_6$, K_6, Tl_6, $[Co(NH_3)_6]_2$) have all been reported (94–96). It is well established that these hydrated salts contain bidentate carbonate ligands with no water molecules bound directly to the central metal atom. The only single-crystal X-ray diffraction studies are for salts of $[Th(CO_3)_5]^{6-}$ (**4**) [12364-90-8] (97–99) and the mineral tuliokite $Na_6BaTh(CO_3)_6 \cdot 6H_2O$ [128706-42-3] (100), which contains the unusual $[Th(CO_3)_6]^{8-}$ anion shown in **5**.



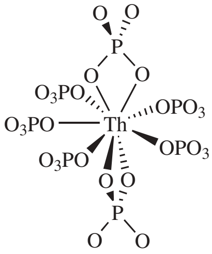
(**4**)



(**5**)



(**6**)



(**7**)

Phosphate. The effects of phosphate on the solubility of ThO_2 in natural waters has been shown to be relatively insignificant (101). Recent experiments have shown that when phosphate concentration is carefully controlled, the thorium phosphate–hydrogenphosphate solid $Th_2(PO_4)_2\ (HPO_4){\cdot}H_2O$ [350506-73-9] precipitates (102), and its solid-state structure has recently been determined (103). Limited data on Th(IV) phosphate complexation in aqueous solution are available (101,104). Due to the low solubility of thorium orthophosphate at neutral pH, complexation studies have been performed in acidic phosphate media and suggest the formation of solution complexes $[ThO(HPO_4)_3(H_2PO_4)]^{5-}$ and $[ThO(HPO_4)_3(H_2PO_4)_2]^{5-}$ (pH 6–7) (105).

Solid thorium phosphates have become the subject of considerable study due to potential applications as radioactive waste forms (106–109) and xerogel thin films for light waveguides (110,111). Binary and ternary thorium compounds have been synthesized with varying ratios of metal, thorium and phosphate. Binary compounds with ThO_2/P_2O_5 ratios of 1:2, 1:1, 3:2, and 3:1 have been reported (112,113). The 3:2 compound, $Th_3(PO_4)_4$ [15578-50-4], has been identified in two allotropic modifications with a transition temperature ~1250°C, and its solubility in low ionic strength waters has been determined (114). Bernard and co-workers reported two distinct thorium types in $Th_4(PO_4)_4(P_2O_7)$ [171845-49-1]: one eight coordinate with oxygen from five phosphate and one diphosphate group around the thorium atom (115). Ternary compounds of the general formula $M(I)Th_2(PO_4)_3$ and $M(II)Th(PO_4)_2$ with M(I) = alkali cation, Tl, Ag, Cu (116,117) and M(II) = Ca, Sr, Cd, Pb (113,118) have been studied. In the solid-state structure of $NaTh_2(PO_4)_3$, each thorium atom is eight coordinate, and the local coordination environment can be described as $[Th(\eta^2\text{-}PO_4)_2(\eta^1\text{-}PO_4)_4]$ (**6**), while for $KTh_2(PO_4)_3$ [15653-56-2] (**7**) each Th(IV) ion is nine coordinate forming a local coordination environment described as $[Th(\eta^2\text{-}PO_4)_2(\eta^1\text{-}PO_4)_5]$ (**7**) with both bridging and bidentate phosphate groups. In $Na_2Th(PO_4)_3$ [56467-86-8], two different thorium atoms are identified with 8 and 10 neighboring oxygen atoms (119).

Nitrate. Thorium nitrate is readily formed by dissolution of $Th(OH)_4$ [13825-36-0] in nitric acid from which, depending on the pH of solution, crystalline $Th(NO_3)_4{\cdot}5H_2O$ [33088-17-4], or $Th(NO_3)_4{\cdot}4H_2O$ [33088-16-3] can be obtained (120) and their solid-state structures have been determined (121,122). Thorium nitrate is very soluble in water and a host of oxygen-containing organic solvents including alcohols, ethers, esters, and ketones. A number of complex thorium nitrate salts of general formula $M_2Th(NO_3)_6$ are known (M = monovalent cation), and these contain the 12-coordinate complex anion of formula $[Th(NO_3)_6]^{2-}$, which has a similar coordination geometry to $[Th(CO_3)_6]^{8-}$ shown in (**5**) (123).

9.3. Nitrogen Donor Ligands. Tetravalent thorium is a relatively strong Lewis acid, and as such, it forms compounds with a wide variety of ligands containing nitrogen donors, ranging from neutral mono-, bi-, and polydentate ligands to anionic ligands, eg, amides and thiocyanates. The most common coordination number is 8; however, some complexes have been observed with coordination numbers as low as 4.

Adducts of $ThCl_4$ [10026-08-1] with NH_3 and primary, secondary, and tertiary amines with coordination numbers ranging from 6 to 8 have been characterized. Examples of these compounds include six-coordinate $ThCl_4(NEt_3)_2$, seven-coordinate $ThCl_4(NH_3)_3$ (124), and eight-coordinate $ThBr_4(EtNH_2)_4$, and $ThCl_4(PhMeNH)_4$. Cationic metal hydrates coordinated with primary, secondary, and tertiary amines have also been isolated with acetylacetonate, nitrate, or oxalate as counter ions. Another common class of ligands for thorium halides are nitriles, RCN (R = alkyl, aryl). These complexes are predominately eight-coordinate species, ie, $ThCl_4(MeCN)_4$ [17499-62-6]; however, six-coordinate isocyanide complexes are also known.

N-Heterocyclic ligands, eg, py, substituted pyridines, quinoline, and isoquinoline bind Th(IV) with typical coordination numbers of 6 and 8. An interesting case is $ThI_4(py)_6$, which instead of the 10-coordinate complex indicated by the formula unit, the compound is actually a salt with formula $[ThI_2(py)_6]I_2$. In some other salts of general formula, $[ThL_x](ClO_4)_4$ ($x = 6$, L = 2-H_2N-, 2,6-Me_2-py; $x = 8$, L = py), the thorium coordination number shows an obvious dependence on the steric bulk of the ligands.

As with the monodentate ligands, a broad spectrum of multidentate ligand–Th(IV) complexes have been isolated and characterized. The simplest bidentate ligands utilized are diaminoalkanes, $H_2N(CH_2)_nNH_2$ ($n = 2$–4), ie, $ThBr_4(H_2N(CH_2)_xNH_2)_y \cdot nH_2O$ ($y = 2$, $x = 3,4$; $y = 4$, $x = 3$). Diaminoarenes, diaminobenzene, benzidine, *o*-tolidine, and *o*-dianisidine, have all been shown to coordinate to Th(IV) halides and nitrates. The chlorides have been isolated with all of the aforementioned ligands in the form, $ThCl_4L_2$, and the nitrates have been identified as complex salts, ie, $[Th(NO_3)_2(1,2\text{-diaminobenzene})_2](NO_3)_2$.

Multidentate *N*-heterocyclic ligands, eg, bipyridyl (bpy), terpyridyl, imidazole, pyrazine, phenanthroline, piperazine (including alkyl and aryl substituted derivatives), and polypyrazol-1-yl-borates (bis, tris, and tetra) have all been found to coordinate Th(IV) chlorides, perchlorates, and nitrates. The tripodal hydrotris(pyrazolyl)borates, $HBPz_3$, have been used to stabilize organometallic complexes, as demonstrated by $(HBPz_3)_2ThX_2$ (X = alkyls, thiolates, alkyl/aryloxides) (125).

Bis(porphyrin) Th(IV) "sandwich" complexes have been synthesized and are formally 8 coordinate. Since thorium is electrochemically inactive, these metal compounds serve as structural models for photosynthetic reaction centers, with particular emphasis on the porphyrin based electrochemistry (126).

Anionic amido species, eg, $[Th(NR_2)_4]_x$ (R = alkyl, silyl), are well known, and the nuclearity is highly dependent on the steric requirements of R. The amides are extremely reactive, readily undergoing protonation to form amines and insertion reactions with CO_2, COS, CS_2, and CSe_2 to form carbamates. Tetravalent thorium thiocyanates have been isolated, however, only as hydrated species, ie, $Th(NCS)_4(H_2O)_4$ [17837-16-0] or as complex salts, ie, $M_4[Th(NCS)_8]{\cdot}xH_2O$ ($M = NH_4$, Rb, Cs).

A tripodal ligand that has recently gained attention is the triamidoamine, $N(CH_2CH_2NSiMe_2)_3$. Thorium complexes with this ligand are dramatically more stable than those using $N(SiMe_3)_2$ due to the combination of the chelate effect and necessarily facial configuration of the ligand. The dimeric chloro species, $[Th(N(CH_2CH_2NSiMe_2)_3)Cl]_2$, has been prepared from the lithium salt of the tris-amide and $ThCl_4$ [10026-08-1]. This complex then served as a convenient starting material for monomeric cyclopentadienyl or solvated tetrahydroborate complexes and dimeric alkoxide or tetrahydroborate complexes (127). Another amido ligand that has the possibility of a tripodal arrangement is $N(CH_2CH_2P{-}i\text{-}Pr_2)_2$, which has been complexed with thorium to produce $\{ThCl_2[N(CH_2CH_2P{-}i\text{-}Pr_2)_2]_2\}$; however, only one of the phosphines from each ligand coordinates with the thorium (128).

9.4. Phosphorous Donor Ligands. Phosphine coordination complexes of thorium are rare ("hard" Th(IV) cation favors "hard" ligand donor types). The only stable thorium–phosphine coordination complexes isolated thus far contain the chelating ligand, dmpe = 1,2-(bis-dimethylphosphino)ethane. The $TlCl_4$(dmpe) and ThI_4(dmpe) complexes have been synthesized directly from the tetrahalides at 80°C and low temperature, respectively. Attempts using other chelating phosphines, ie, dppe = 1,2-(bis-diphenylphosphino)ethane failed to produce the desired coordination complexes. The chemistry of $ThCl_4$(dmpe) in relation to stable thorium–methyl species is discussed further in the organometallic section.

The phosphido complex, $Th(PPP)_4$ [145329-04-0] [$PPP = P(CH_2CH_2PMe_2)_2$], has been prepared and fully characterized (129). This complex was the first actinide complex containing exclusively metal–phosphorous bonds. The X-ray structural analysis indicated three, 3-electron donor phosphides and one, 1-electron phosphide, suggesting the complex is formally 22 electron. Similar to the amido system, this phosphido compound is also reactive toward insertion reactions, especially with CO, which undergoes a double insertion (129,130).

9.5. Oxygen Donor Ligands. A variety of neutral and anionic oxygen-containing organic molecules form complexes with thorium (131). The majority of the complexes have coordination numbers of 6–12, depending mostly on the steric bulk of the ancillary ligands.

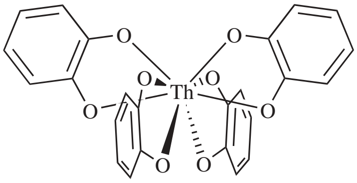
Carboxylates and Oxalates. Complexes of Th(IV) with mono-, di-, tri-, polycarboxylates have been extensively studied. Monocarboxylates, $RCO_2{}^-$, have been complexed with Th(IV), where R can be H, alkyl, or aryl, ie, $Th(RCO_2)_4$ ($R = H$, Me, CCl_3, 2-MeC_6H_4) and $M_xTh(HCO_2)_{4+x}$ ($x = 1$, $M = K$-Cs; $x = 2$, $M = Rb$, Cs, NH_4). The formate complex, $R = H$, has been isolated both as the anhydrous species and as a trihydrate complex. The structural analysis of the trihydrate revealed a bicapped trigonal prism geometry, with eight different bridging formate groups.

The simplest dicarboxylate ligand is oxalate, $C_2O_4{}^{2-}$. Thorium oxalate complexes have been used to produce high density fuel pellets, which improve nuclear fuel processes (132). The stability of oxalate complexes and the relevance to waste disposal have also been recently studied (133). Many thorium oxalate complexes have been isolated, ranging from simple $Th(C_2O_4)_2{\cdot}xH_2O$ to complex salts, ie, $Th(C_2O_4)_n^{2n-4}$ ($n = 4, 5, 6$), where the counterions can be alkali cations, complex transition metal cations, ie, $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, or ammonium ions. Other dicarboxylate thorium complexes have been studied and are of the form, $Th[R(CO_2)_2]_2{\cdot}xH_2O$ ($R =$ methylene units, CHCH, and aryls). The dicarboxylate complex, $Th(pdc)_2{\cdot}xH_2O$ ($x = 0, 4$), $pdc = NC_5H_3$-2,6-$(CO_2)_2$ also has a 10-coordinate bicapped square antiprism geometry about the thorium atom, where the pyridinyl nitrogen atoms occupy the faces and the oxygen atoms of the carboxylates occupy the corners.

Polycarboxylates have been studied with the most well known being the tetracarboxylic acid, edta, ethylenediaminetetraacetic acid, $(HO_2CCH_2)_2NCH_2{-}CH_2N(CH_2CO_2H)_2$, which coordinates in a hexadentate fashion. Representative examples of isolated thorium complexes with EDTA consist of $Th(edta){\cdot}xH_2O$, $[Th(edta)(OH)]^-$, and $[Th(edta)F_3]^{3-}$. The structure $(CN_3H_6)_3[Th(edta)F_3]$ is based on a nine-coordinate distorted capped tetragonal antiprism geometry, with three F atoms, four O atoms (one from each of the carboxylate groups), and two N atoms (one in the capping position). Two other polycarboxylate ligands, which complex thorium, are dota (1,4,7,10-tetraazacyclodocedcane-N, N', N'', N'''-tetraacetic acid, which coordinates in an octadentate fashion, and HEHA (1, 4, 7, 10, 13, 16-hexaazacyclooctadecane-N, N', N'', N''', N'''', N'''''-hexaacetic acid), which can form 12-coordinate complexes (134). For both complexes, Th(dota) and $Th(HEHA)^{2-}$, detailed nuclear magnetic resonance (nmr) studies lead to the assignment of an icosahedral geometry.

Actinide Sequestering Agents. A considerable amount of research has gone into development of sequestering agents for tetravalent plutonium, and thorium has often been employed as a surrogate (72). This involves complex ligand design and chemical synthesis. A number of important chelating subunits have been found in siderophores, and include catechols, hydroxamic acids, hydroxypyridinones, and terephthalamides. Thorium complexes have been studied with all of these ligand types, and a number of solid-state structures have been determined. Complexes of Th(IV) with these ligand types all display high coordination numbers.

Catecholate-type thorium complexes include the following ligands: catechol (1,2-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), hydroquinone (1,4-dihydroxybenzene), orcinol (2,5-dihydroxytoluene), and phloroglucinol (1,3,5-trihydroxybenzene). For the ligands other than catechol, the only complexes that have been isolated are $ThCl_2L$. Studies of the catecholates have led to the isolation of $ThCl_2(C_6H_4O_2)$, $[Th(C_6H_4O_2)_n]^{2n-4}{\cdot}xH_2O$ ($n = 3,4$) and $[Th_3(C_6H_4O_2)_7]^{2-}$. A structural determination of $Na_4[Th(C_6H_4O_2)_4]{\cdot}21H_2O$ revealed a trigonal faced dodecahedral geometry about the thorium atom with the water molecules producing a hydrogen bonding network. The $[Th(C_6H_4O_2)_4]^{4-}$ ion is illustrated qualitatively in **8**. The use of polycatecholates as sequestering agents for the actinides has also been studied (135).



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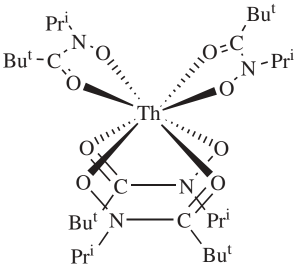
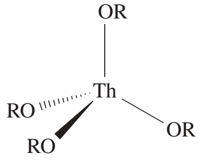


(**9**)

Hydroxamic acid complexes of formula Th[*i*-PrN(O)C(O)*t*-Bu]$_4$ and Th[*i*-PrN(O)C(O)CH$_2$*t*-Bu]$_4$ have been prepared and characterized. The *tert*-butyl substituted hydroxamate adopted a distorted cubic geometry (**9**), while the neopentyl substituted derivative adopted a more typical dodecahedral geometry (136). The third chelating subunit found in siderophores, hydroxypyridinone (HOPO), also forms stable complexes with Th(IV) (137). The crystal structure of $(C_5H_4NO_2)_4(H_2O)Th{\cdot}2H_2O$ revealed a one-dimensional coordination polymer with nine-coordinate trigonal prismatic coordination about Th(IV).

Alkoxides and Aryloxides. Alkoxide and aryloxide ligands have been studied extensively in transition-metal chemistry, and more recently these studies have been extended to thorium. These studies have focused on determining which ligand systems yield crystalline compounds and provide useful starting materials. Oligomerization in thorium alkoxide complexes, as well as many of their solution properties, are highly dependent on the steric requirements of the alkoxide ligands. In the case of the sterically demanding ligand O-2,6-*t*-Bu$_2$C$_6$H$_3$, monomeric Th(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_4$ (**10**) can be readily isolated (138). As the steric bulk of the alkoxide ligand decreases, dimers, Th$_2$(OCH$-$*i*-Pr$_2$)$_8$ (**11**) [140684-41-9] (139), Th$_2$(O$-$*t*-Bu)$_8$L, (**12**) (140), trimers, Th$_3$O(O$-$*t*-Bu)$_{10}$ (**13**) [147361-65-7], (140), and tetramers, Th$_4$(O$-$*i*-Pr)$_{16}$(py)$_2$ [157440-79-4], etc, are observed (141).



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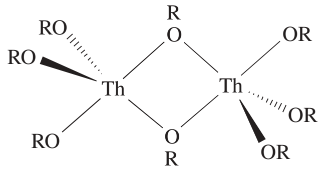

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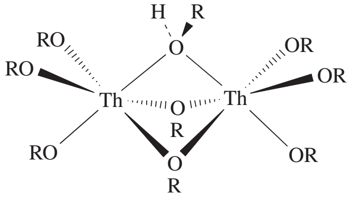

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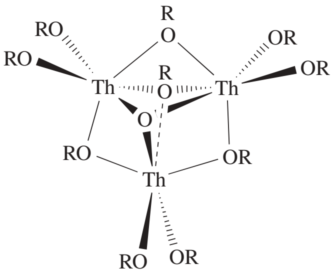


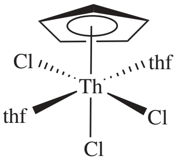
(13)

10. Organometallic Complexes

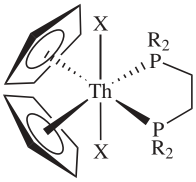
The organometallic chemistry of thorium has been widely studied due to potential utility in homogeneous and heterogeneous catalysis (73,74), with activities ranging from the hydrogenation and polymerization of olefins to the selective activation of alkanes (34). While there are no examples of thorium carbonyl complexes, hydrocarbyls, allyls, arenes, cyclooctatetraenyl, and a host of cyclopentadienyl-based ligand complexes have been reported.

10.1. Cyclopentadienyl and Substituted Cyclopentadienyl Complexes. Thorium complexes containing cyclopentadienyl rings, $Cp = C_5H_5^-$, and its modified analogues, Cp* ($C_5Me_5^-$), $Cp^\dagger$ ($Me_3SiC_5H_4^-$), $Cp^\ddagger$ [$(Me_3Si)_2C_5H_3^-$], Cp′ ($MeC_5H_4^-$) are among the most common organothorium complexes known. Electron-deficient compounds of the type (η-Ring)ThX_3 (X = halogen) are not stable and have only been isolated as Lewis base adducts, eg, $CpThX_3L_n$ (**14**) ($n = 2$, X = Cl, Br, L = thf, DME, amides, organonitriles; $n = 3$, X = Cl, L = MeCN eCN [91947-79-4]) or Cp*ThX_3L_2 (X = Cl, Br; L = Ph_3PO, thf, and organonitriles). Mono-ring complexes can be stabilized through the use of sterically demanding ancillary ligands, as in the case of Cp*$ThBr_{3-x}(OAr)_x$ ($x = 1,2$), and serve as starting materials for the synthesis of thorium alkyl complexes (142). Three-legged piano stool complexes of the form (η-Ring)ThR_3 can also be stabilized by ligands capable of π-donation to the metal center, eg, amides, allyl, or benzyl ligands, to form complexes of the type $CpTh(NEt_2)_3$ [108187-12-8], Cp*$Th(C_3H_5)_3$, or Cp*$Th(C_7H_7)_3$ [82511-73-7]. It is noteworthy that the benzyl analogue exists in a rapid $\eta^1-\eta^3$ equilibrium in solution, indicating the preference for higher coordination environments.

While Cp_2MX_2 compounds are ubiquitous in early transition-metal organometallic chemistry, the thorium analogues are rather unstable. The Cp_2ThX_2 compounds have been stabilized against ligand redistribution by adding ancillary ligands, such as the chelating phosphine 1,2-bis(dimethylphosphino)ethane, dmpe, to form Cp_2ThX_2(dmpe) (**15**) for X = Cl [108089-88-9], Me [108089-89-0], CH_2Ph [108678-62-3]. Stabilization against redistribution has also been achieved through the use of Cp*, sterically demanding X groups, or ligands capable of both σ and π donation to the actinide metal center, thereby saturating the metal coordination sphere. For example, treatment of $Cp_2An(NEt_2)_2$ with bulky acidic ligands gives a variety of stable Cp_2ThX_2 complexes for X = OC*t*-Bu_3, O-2,6-$Me_2C_6H_3$, etc. The reaction of $Cp^*{}_2ThCl_2$ [67506-88-1] with dialkylphosphido lithium reagents yields stable $Cp^*{}_2Th(PR_2)_2$ complexes for R = Ph [93943-04-5], Cy [98720-32-2], and Et [98720-31-1]. X-ray analysis suggested that there is no Th−P multiple bond character. Complexes of the form, $Cp^*{}_2ThR_2$ (R = Cl, alkoxide, amide, phosphide, acyls, alkyl, thiolate, vinyl, phosphorylide, butadiene, etc) have been synthesized and fully characterized. The syntheses of $Cp^*{}_2Th(Ph)_2$ [79301-39-6] and $Cp^*{}_2ThCl$(aryl) have recently been improved; and the first examples of mixed alkyl−aryl complexes, $Cp^*{}_2Th$(Me)(aryl) (aryl = tolyl [156956-31-9], xylyl [156956-32-0]) have been isolated (143). These compounds exhibit a host of interesting properties and reactivities including C−H activation and migratory insertion reactions. A hydride complex has also been isolated, $[Cp^*{}_2ThH_2]_2$ [79735-38-9], and engages in alkene insertion and migration. Double insertion of CO to produce the first metalloxy ketene complex has been observed for a mixed chloro−silyl complex, $Cp^*{}_2ThCl(Si{-}t\text{-}BuPh_2)$ [163851-90-9] (144).



(**14**)



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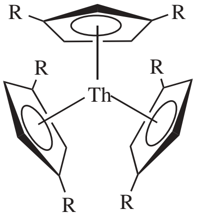

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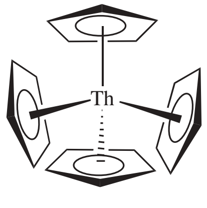


(**17**)

Similar stability and reactivity have also been observed for bridged-Cp* systems with the synthesis of catalytically active $Me_2Si(C_5Me_4)_2ThR_2$ (R = Cl [89597-06-8], alkyl, Bz [89597-10-4], aryls, H [89597-11-5]). Similar to Group 4 (IVB) transition-metal Zeigler-Natta catalysts, stable cationic Th(IV) species, ie, $[Cp^*{}_2ThMe]^+$ [108834-69-1], have been isolated with a host of noncoordinating/nonreactive anions. Metallacycle formation has also been shown to stabilize bis−Cp complexes, ie, $Cp'_2Th(CH_2SiMe_2CH_2)$ (145). These complexes are structurally similar to the Group 4 (IVB) and 6 (VIB) transition-metal acycle complexes, but show a dramatically reduced reactivity.

In contrast to the instability of simple mono- and bis–Cp complexes, simple systems of the form, (η-Ring)$_3$ThX (Ring = Cp, X = F [61288-97-9], Cl [1284-82-8], alkyls, allyls; Ring = Ind or alkyl-substituted Ind, X = Cl [11133-05-4], Br [57034-55-6], I [66775-24-4]) are well known. Recently, [(RC$_5$H$_4$)$_3$Th]BPh$_4$ (R = SiMe$_3$ [168024-92-8], *t*-Bu [168024-95-1]) have been prepared. These compounds react with alkyl lithium reagents to produce stable (η-Ring)$_3$ThH species (146). A tris-Indenyl Th(IV) monohydride species has also been prepared, utilizing the sterically bulky trimethylsilylindenyl ligand.

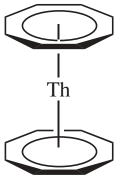
The synthesis of the first stable Th(III) organometallic complex, Cp$^{‡}_3$Th [107040-62-0] (**16**) [Cp‡ = 1,3-C$_5$H$_3$(SiMe$_3$)$_2$], was achieved via reduction of Cp$^{‡}_2$ThCl$_2$ [87654-17-9] (147). This air-sensitive complex is electron paramagnetic resonance (epr) active, having a $6d^1$ ground-state configuration as opposed to a $5f^1$ ground state (148).

There is little known chemistry of tetrakis–Cp thorium complexes. Pseudotetrahedral molecules, (η-Ring)$_4$Th (**17**) (Ring = Cp [1298-75-5], Ind [11133-17-6]) have a measurable dipole, resulting from deviation of T_d symmetry (149). Differing coordination environments, ie, η^3 in the Ind system and η^5 in the Cp system, appears to indicate great steric crowding about the thorium center, which probably limits the reactivity and synthetic derivatization of these complexes.

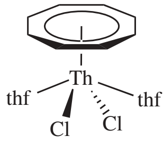
10.2. Cyclooctatetraenyl Compounds. Sandwich-type complexes of cyclooctatetraene (COT = $C_8H_8^{2-}$) are well known. The chemistry of thorium–COT complexes is similar to that of its Cp analogues in steric number and electronic configurations. Thorocene, COT$_2$Th [12702-09-9] (**18**), the simplest of the COT derivatives has been prepared by the interaction of ThCl$_4$ [10026-08-1] with 2 equiv of K$_2$C$_8$H$_8$. Thorocene derivatives with alkyl, silyl, and aryl substituted COT ligands have also been described. These compounds are thermally stable and air sensitive.

Mono-COT compounds have been studied including: (COT)ThX$_2$(thf)$_2$ (**19**) (X = Cl [73652-04-7], BH$_4$ [73643-98-8]), (COT)Th[N(SiMe$_3$)$_2$]$_2$ [117097-70-8], and Cp*(COT)ThCl(thf) [119390-83-9]. The chloro complexes have been used to generate mixed-ring Cp*/COT complexes, ie, Cp*(COT)ThX (X = N(SiMe$_3$)$_2$ [119390-81-7], CH(SiMe$_3$)$_2$ [119390-80-6], as well as organo–COT complexes (150). The unsaturated complex, Cp*(COT)Th(CH$_2$SiMe$_3$) (**20**), is an example of an organo derivative stabilized by an agostic interaction with one of the methyl groups of the trimethylsilylmethyl ligand.

Another C$_8$ system, the pentalene dianion ($C_8H_6^{2-}$), has been far less studied than the cyclooctatetraenyl ligand. This ligand may be considered to be derived from $C_8H_8^{2-}$ by removal of two hydrogen atoms with generation of a C–C bond to yield two fused five-membered rings. A substituted derivative of the pentalene ligand, [1,5-(*i*-Pr$_3$Si)$_2$C$_8$H$_4$]$^{2-}$, has been employed to generate the neutral bis(ligand) [1,5-(*i*-Pr$_3$Si)$_2$C$_8$H$_4$]$_2$Th [194298-31-2] (**21**), which is rare examples of η^8-coordinated pentalene ligands (151).



(18)



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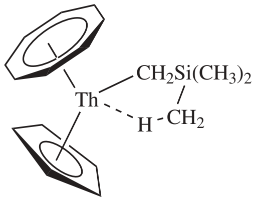

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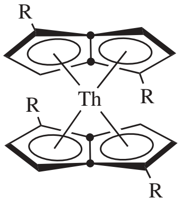

(21)

Allyl Complexes. Allyl complexes of thorium have been known for ~30 years and are usually stabilized by cyclopentadienyl ligands. Allyl complexes can be accessed via the interaction of a thorium halide and an allyl grignard. This synthetic method was utilized to obtain a rare example of a "naked" allyl complex, $Th(\eta^3\text{-}C_3H_5)_4$ [144564-74-9], which decomposes at 0°C. The $Th(\eta^3\text{-}C_3H_5)_4$ complex supported on dehydroxylated γ-alumina is an outstanding heterogeneous catalyst for arene hydrogenation that rivals the most active platinum metal catalysts in activity (34,35). Quite recently, Hanusa and co-workers isolated the bulky allyl complexes $[(Me_3Si)_nC_3H_{5-n}]_4Th$ ($n = 1,2$) from the reaction of $ThBr_4(thf)_4$ and 4 equiv of $K[(Me_3Si)_nC_3H_{5-n}]$ in THF at −78°C. The isolated complexes are stable up to 90°C ($n = 1$) or 124°C ($n = 2$) and are the first structurally authenticated homoleptic Th–allyl complexes (152).

Hydrocarbyl Complexes. Stable homoleptic and heteroleptic thorium hydrocarbyl complexes have been synthesized. Two common homoleptic species are $[Li\text{-}TMEDA]_3[Th(Me)_7]$ [92366-18-2] and $Th(Bz)_4$ [54008-63-8]. The benzylic complex has been synthesized at low temperatures and may owe its stability to possible multihapto coordination, $\eta^1\text{-}\eta^3$, of the benzyl ligand. The methyl complex is stable even up to room temperature. Six of the methyl groups are hydrogen bonded to the Li atom, stabilizing this highly charged species. As might be expected, this compound is very reactive with H_2 and CO. However, there is no concrete structural data for the final products of such reactions.

Comparable to the homoleptic complexes, the heteroleptic systems are dominated by methyl and benzyl groups. Examples of these materials are $ThR_3R'(dmpe)$ ($R = Bz$, $R' = Me$; $R = R' = Me$, Bz) and $ThX_2(pyr)_2$ (X = Cl, 2,6-di-*tert*-butylphenoxide), pyr = 2-(6-methylpyridyl). Interestingly, these compounds coordinate "soft" chelating phosphine ligands, a rarity for the "hard" Th(IV) atom.

Another class of heteroleptic complexes contains π-donors and is of the form, $ThR[N(SiMe_3)_2]_3$ (R = Me [69517-43-7], H [70605-07-1], BH_4 [69532-06-5]). The methyl compound has exhibited insertion reactivity, including: aldehydes, ketones, nitriles, and isocyanides (73). Stable metallacycle compounds are also known, ie, $[(Me_3Si)_2N]_2\overline{Th(CH_2Si(Me_2)N}SiMe_3)$, and can be obtained by pyrolysis triamido-hydrido–thorium complexes (153).

Bimetallic Complexes. There are two types of bimetallic organometallic thorium complexes, those with, and those without metal–metal interactions. Examples of species containing metal–metal bonds are complexes with Fe or Ru carbonyl fragments. $Cp^*{}_2ThX(CpRu(CO)_2)$ (X = Cl, I) and $Cp'_3Th(CpM(CO)_2)$ ($Cp' = C_5H_4Me$; M = Fe, Ru) have been prepared by interaction of $Cp^*{}_2ThX_2$ or

Cp'_3ThCl [62156-90-5], respectively, with the anionic metal carbonyl fragment. These complexes contain very polar metal–metal bonds that can be cleaved by alcohols.

The chemistry of nonmetal–metal bonded species is more extensive, especially with the use of bridging ligands, eg, phosphido, polyoxo, or σ-bonded ferrocenyl groups. Phosphides have been found to bridge thorium fragments with nickel and platinum. The two examples are $Cp^*_2Th(\mu\text{-}PPh_2)Ni(CO)_2$ and $Cp^*_2Th(\mu\text{-}PPh_2)Pt(PMe_3)$. The polyoxoanions are represented by $[N\text{-}n\text{-}Bu_4][Cp_3Th(MW_5O_{19})_2]$ (M = Nb, Ta); compounds of this type are also known for uranium. A thorium σ-bonded ferrocenyl complex, $Th(acac)_3(FcN)$ [143687-88-1] FcN = (dimethylaminomethyl)ferrocenyl, has been isolated. This complex is eight-coordinate with six oxygens from the acac ligands and two nitrogens from the ferrocenyl group.

11. Analytical Chemistry

The analytical chemistry of thorium has been extensively reviewed (154), and the general analytical techniques have been described in detail (155–157). The majority of analytical chemistry techniques for thorium determination have been developed for detecting thorium under environmental concentrations. Most methods employ preconcentration, coprecipitation, solvent extraction, and/or ion exchange separation steps prior to conducting the analytical measurement (157,158). Once the preconcentration has been accomplished, then thorium can be measured using alpha-spectrometry (159), gamma-spectrometry (160), liquid scintillation (161), photon electron rejecting alpha liquid scintillation (PERALS) (162), neutron activation analysis (NAA) (163–165), electrospray mass spectrometry (166), inductively coupled plasma mass spectrometry (ICP–MS) or atomic emission spectrometry (ICP–AES) (167). The majority of thorium analyses are currently performed by alpha and gamma spectrometry, NAA, liquid scintillation spectrometry, ICP–MS and ICP–AES.

11.1. Alpha and Gamma Spectrometry.

Alpha spectrometry is based on the measurement of specific alpha particle emission energies from decay of thorium isotopes, and typically determines the activity of ^{232}Th, ^{230}Th, and ^{228}Th. Sample preparation generally involves pretreatment, solubilization and extraction, chemical separation of thorium from the matrix, thin source preparation, and alpha particle counting (159). A tracer of ^{229}Th is generally added to the sample for accuracy determination. The number of alpha particles detected per second is related to the activity of the isotope, measured in units of becquerels (1 Bq = 1 disintegration per second). Alpha spectrometry is one of the most suitable techniques for detecting short-lived isotopes ^{228}Th and ^{230}Th down to 0.2 mBq, which corresponds to quantities of 10^{-17} g (^{228}Th) and 10^{-13} g (^{230}Th) (158). Thorium can be detected by passive gamma spectrometry, wherein only total thorium is determined based on the indirect quantification of ^{232}Th. The technique measures γ-rays of specific energies produced by decay of daughter product nuclides using high sensitivity germanium detectors. It is a nondestructive technique with low detection limits.

11.2. Neutron Activation Analysis. In the technique of neutron activation analysis, a sample is activated in the neutron flux of a nuclear reactor to produce ^{233}Th from ^{232}Th. Thorium is then quantitatively determined by measuring the gamma emission from decay of ^{233}Th to ^{233}Pa, or more commonly, the decay of ^{233}Pa to ^{233}U (168).

11.3. Inductively Coupled Plasma Techniques. These techniques are normally employed for samples in solution. The solution is nebulized and the aerosol introduced into an argon plasma where the constituent atoms are ionized. In ICP–MS, the ions are separated according to their mass/charge in a mass spectrometer. In ICP–AES the excited ions are detected by light emission (167).

11.4. Energy Dispersive X-Ray Techniques. For samples that contain bulk concentrations of thorium, eg, thorium containing nuclear fuels, the thorium content may be analyzed using energy-dispersive X-ray techniques, eg, K-edge densitometry and K-edge X-ray fluorescence (169). These techniques are particularly well suited for rapid thorium determination at elevated thorium concentrations.

12. Health and Safety Factors

Thorium is potentially hazardous in a few ways. Finely divided thorium metal and hydrides can be explosive or inflammatory hazards with respect to oxygen and halogens. Finely divided ThO_2 [1314-20-1] and other inorganic salts also present an inhalation and irritation hazard. Generally, the use of standard precautions, skin covering, and a conventional dust respirator should be sufficient.

The long half-life of ^{232}Th makes it a minimal radiation hazard. External radiological hazards are generally not of concern since the γ-rays from thorium daughter products have low abundance and many are in the X-ray range, ie, < 85 keV, where they will be absorbed in the source material. There are some residuals in the 240 and 727-keV energy ranges that can lead to radiation effects from tonnage amounts of materials. Such sources merit safety precautions in terms of distance and shielding.

When inhaled, ingested, or adsorbed through the skin thorium isotopes are potentially harmful both due to ionizing radiation and chemical toxicity. If Th(IV) is injected as the soluble nitrate form, it can cause hemolysis. Thorium is generally insoluble in the presence of organic complexing agents and mainly retained in the bones, lungs, lymph nodes, and parenchymatous tissues. In animal experiments, not $>10^{-4}\%$ of thorium was absorbed from the gastrointestinal tract (170). Prolonged retention of thorium, particularly in a fixed location, allows the possibility of radiation damage by the energetic alpha particles of some of the short-lived daughter members of the decay chain, of which there are five for every thorium alpha.

Thorotrast (colloidal ThO_2) was once used as a radiopaque agent in medicine (171–173). Its injection in a dose of 2.0–15.0 g caused rises in body temperature, nausea, and injury to tissues at the injection site, followed by anemia, leukopenia, and impairment of the reticuloendothelial system. After intravenous administration, thorotrast particles are taken up by reticuloendothelial cells of the liver and spleen. Thorotrast is virtually not eliminated from the body (170). Between 1947 and 1961, 33 cases of cancer of the liver, larynx, and bronchi and sarcoma of the kidneys, developing 6–24 years after thorotrast administering, were described in the literature (174). These cases probably contributed to stopping the medical use of a radiopaque material based on thorium.

Thorium compounds are legally classified as source materials for nuclear energy and thus are regulated by various government agencies, eg, the NRC. The relevant regulations cover licensing and safety aspects.

13. Acknowledgments

The authors acknowledge Los Alamos National Laboratory, and the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy for their support of actinide chemistry research at Los Alamos National Laboratory.

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David L. Clark
Mary P. Neu
Wolfgang Runde
Los Alamos National Laboratory
D. Webster Keogh
Applied Marine Technology International

Table 1. **Radioactive Decay Properties of Selected Thorium Isotopes**[a]

Mass number	Half-life	Mode of decay	Main radiations, MeV	Method of production
227	18.68 days	α	α 6.038 (25%) 5.978 (23%) γ 0.236	nature
228	1.9116 year	α	α 5.423 (72.7%) 5.341 (26.7%) γ 0.084	nature
229	7.340×10^3 year	α	α 4.901 (11%) 4.845 (56%) γ 0.194	^{233}U daughter
230	7.538×10^4 year	α	α 4.687 (76.3%) 4.621 (23.4%) γ 0.068	nature
231	25.52 h	β^-	β^- 0.302 γ 0.084	nature ^{230}Th (n,γ)
232	1.405×10^{10} year $> 1 \times 10^{21}$ year	α SF	α 4.016 (77%) 3.957 (23%)	nature
234	24.10 days	β^-	β^- 0.198 γ 0.093	nature

[a] Refs. 11,12.

Table 2. **Some Physical Properties of Thorium Metal**[a]

crystal structure	
fcc to 1633 K	$a_0 = 5.0842$ Å (298 K)
density	11.724 g/cm^3
atoms per unit cell (Z)	4
bcc, 1633–2023 K	$a_0 = 4.11$ Å (1723 K)
density	11.10 g/cm^3
atoms per unit cell (Z)	2
body centered tetragonal (bct), high pressure	$a = 2.282$ Å, $c = 4.411$ Å (102 GPa)
melting point, K	2023
boiling point, K	$\sim$4073
enthalpy of sublimation (298 K)	602 ± 6 kJ/mol
enthalpy of fusion	14 kJ/mol
vapor pressure of the solid (1757–1956 K)	$\log(p/\text{atm}) = -28{,}780\,(T/\text{K})^{-1} + 5.991$
vapor pressure of the liquid (2020–2500 K)	$\log(p/\text{atm}) = -(29{,}770 \pm 218)\,(T/\text{K})^{-1} - 6.024 \pm 0.098$
thermal conductivity (298 K)	0.6 W/cm K
work function	3.49 eV
Hall coefficient (297 K)	-11.2×10^{-5} cm^3/C
emissivity of solid (1600 K)	0.31
elastic constants	
Young's modulus	7.2×10^{7} kPa
shear modulus	2.8×10^{7} kPa
Poisson's ratio	0.265
compressibility	17.3×10^{-13} cm^2/dyn
coefficient of thermal expansion (298–1273 K)	12.5×10^{-6}/K
electrical resistivity (electrorefined metal, 298 K)	15.7×10^{-6} Ω·cm

[a] Data compiled from Refs. 45 and 46.

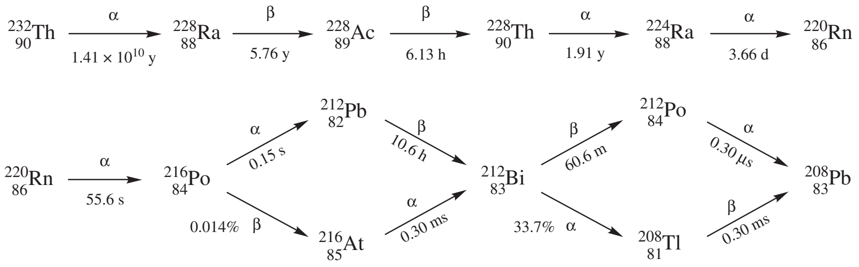
232 90 Th
α
1.41 × 10^10 y
228 88 Ra
β
5.76 y
228 89 Ac
β
6.13 h
228 90 Th
α
1.91 y
224 88 Ra
α
3.66 d
220 86 Rn
220 86 Rn
α
55.6 s
216 84 Po
α
0.15 s
212 82 Pb
β
10.6 h
0.014% β
216 85 At
α
0.30 ms
212 83 Bi
β
60.6 m
212 84 Po
α
0.30 μs
33.7% α
208 81 Tl
β
0.30 ms
208 83 Pb

Fig. 1. The thorium (4*n*) decay series.