CHAPTER THREE

THORIUM

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3.1 HISTORICAL

In 1815 Berzelius analyzed a rare mineral from the Falun district. He assumed that the mineral contained a new element, which he named thorium after the ancient Scandinavian god of thunder and weather, Thor (Weeks and Leicester, 1968).

Unfortunately, 10 years later the mineral turned out to be simply xenotime, e.g. yttrium phosphate. However, in 1828, Berzelius was given a mineral by the Reverend Hans Morten Thrane Esmark. In that mineral Berzelius really discovered a new element and gave it the same name (Berzelius, 1829; Gmelin, 1955, 1986a; Weeks and Leicester, 1968). Consequently, he called the mineral from which he isolated the new element thorite. It is a silicate that contains significant amounts of uranium and should therefore be written as $(Th,U)SiO_4$. Although thorium was discovered in 1828, it virtually had no application until the invention of the incandescent gas mantle in 1885 by C. Auer von Welsbach. Thereafter the application of thorium developed into a wide array of products and processes (Gmelin, 1988b). Besides the above-mentioned incandescent gas mantles, the production of ceramics, carbon arc lamps, and strong alloys may serve as examples. To be mentioned is also its use as coating for tungsten welding rods, because it provides a hotter arc. Furthermore, when added to refractive glass, it allows for smaller and more accurate camera lenses. As minor important applications, the use of ThO_2 in producing more heat-resistant laboratory crucibles and its occasional use as a catalyst for the oxidation of ammonia to nitric acid and other industrial chemical reactions can be mentioned. Nevertheless, during the last decade the demand for thorium in non-nuclear applications has sharply decreased due to environmental concerns related to its radioactivity. The radioactivity of thorium is helpful for the dating of very old materials, e.g. seabeds or mountain ranges. Maybe the largest potential for thorium is its usage in nuclear energy. This is because ^{232}Th can be converted by thermal (slow) neutrons to the fissionable uranium isotope ^{233}U via the following reaction sequence:

$$^{232}\mathrm{Th}(\mathrm{n},\gamma) \rightarrow {}^{233}\mathrm{Th} \xrightarrow{\beta^-} {}^{233}\mathrm{Pa} \xrightarrow{\beta^-} {}^{233}\mathrm{U}$$

Fission of the ^{233}U can provide neutrons to start the cycle again. This cycle of reactions is known as the thorium cycle (Seaborg *et al.*, 1947; Katzin, 1952).

Conversion of ^{232}Th into ^{233}U provides the possibility to gain large amounts of slow-neutron-fissile material, several times the amount of uranium naturally present on Earth, and several hundred times the amount of the naturally occurring fissile uranium isotope ^{235}U (Seaborg and Katzin, 1951).

A number of advantages of thorium-based nuclear fuels exist in comparison with the presently utilized uranium–plutonium fuels (Rand *et al.*, 1975; Trauger, 1978). These include the inherent detectability of ^{233}U, its higher neutron yield, the fact that ^{233}U, unlike ^{239}Pu, can be mixed with ^{238}U so that it cannot directly be used in weapons manufacture, and the superior physical properties of thorium-based fuels that enhance reactor core safety and performance. The disadvantage of the use of thorium-based fuels is that thorium must be irradiated and reprocessed before the advantages of ^{232}Th can be realized. This reprocessing step, requiring more advanced technology than that needed for uranium fuels, and other factors have projected greater costs for thorium fuels. The nuclear technology has nevertheless matured with the development of high-temperature gas-cooled reactors.

3.2 NUCLEAR PROPERTIES

Thorium refined from ores free of uranium would be almost monoisotopic ^{232}Th, with less than one part in 10^{10} of ^{228}Th (radiothorium) produced by its own radioactivity decay chain ($4n$ family). If the ore contains uranium, as is usually the case, practically undetectable concentrations of ^{231}Th (uranium Y) and ^{227}Th (radioactinium) are present, products of the ($4n + 3$) decay chain that starts with ^{235}U. Also present are greater quantities of ^{230}Th (ionium), as well as lesser amounts of ^{234}Th (uranium X_1), which originate from the ($4n + 2$) decay chain whose progenitor is ^{238}U. ^{229}Th is the first product in the ($4n + 1$) decay series (English *et al.*, 1947; Hagemann *et al.*, 1947, 1950) derived from man-made ^{233}U formed as indicated in Section 3.1. The remaining thorium isotopes listed in Table 3.1 (see also Appendix II) are also synthetic, being formed directly by bombardment of lead or bismuth targets with energetic

Table 3.1 *Nuclear properties of thorium isotopes.*[a]

Mass number	*Half-life*	*Mode of decay*	*Main radiations* (MeV)	*Method of production*
209	3.8 ms	α	α 8.080	^{32}S + ^{182}W
210	9 ms	α	α 7.899	^{35}Cl + ^{181}Ta
211	37 ms	α	α 7.792	^{35}Cl + ^{181}Ta
212	30 ms	α	α 7.82	^{176}Hf(^{40}Ar,4n)
213	140 ms	α	α 7.691	^{206}Pb(^{16}O,9n)
214	100 ms	α	α 7.686	^{206}Pb(^{16}O,8n)
215	1.2 s	α	α 7.52 (40%) 7.39 (52%)	^{206}Pb(^{16}O,7n)
216	28 ms	α	α 7.92	^{206}Pb(^{16}O,6n)
217	0.237 ms	α	α 9.261	^{206}Pb(^{16}O,5n)
218	0.109 μs	α	α 9.665	^{206}Pb(^{16}O,4n) ^{209}Bi(^{14}N,5n)
219	1.05 μs	α	α 9.34	^{206}Pb(^{16}O,3n)
220	9.7 μs	α	α 8.79	^{208}Pb(^{16}O,4n)
221	1.68 ms	α	α 8.472 (32%) 8.146 (62%)	^{208}Pb(^{16}O,3n)
222	2.8 ms	α	α 7.98	^{208}Pb(^{16}O,2n)
223	0.60 s	α	α 7.32 (40%) 7.29 (60%)	^{208}Pb(^{18}O,3n)
224	1.05 s	α	α 7.17 (81%) 7.00 (19%) γ 0.177	^{228}U daughter ^{208}Pb(^{22}Ne,α2n)
225	8.0 min	$\alpha \approx 90\%$ EC $\approx 10\%$	α 6.478 (43%) 6.441 (15%) γ 0.321	^{229}U daughter ^{231}Pa(p,α3n)
226	30.57 min	α	α 6.335 (79%) 6.225 (19%) γ 0.1113	^{230}U daughter
227	18.68 d	α	α 6.038 (25%) 5.978 (23%) γ 0.236	nature
228	1.9116 yr	α	α 5.423 (72.7%) 5.341 (26.7%) γ 0.084	nature
229	7.340×10^3 yr	α	α 4.901 (11%) 4.845 (56%) γ 0.194	^{233}U daughter
230	7.538×10^4 yr	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} yr $> 1 \times 10^{21}$ yr	α SF	α 4.016 (77%) 3.957 (23%)	nature

Table 3.1 (*Contd.*)

Mass number	*Half-life*	*Mode of decay*	*Main radiations* (MeV)	*Method of production*
233	22.3 min	β^-	β^- 1.23 γ 0.086	^{232}Th(n,γ)
234	24.10 d	β^-	β^- 0.198 γ 0.093	nature
235	7.1 min	β^-		^{238}U(n,α)
236	37.5 min	β^-	γ 0.111	^{238}U(γ,2p) ^{238}U(p,3p)
237	5.0 min	β^-		^{18}O + ^{238}U
238	9.4 min	β^-		^{18}O + ^{238}U

[a] Appendix II.

multi-nucleon projectiles, by decay of lightweight uranium isotopes, which are themselves synthetic and formed by nuclear bombardment, or by other miscellaneous nuclear reactions. Uranium ores that are relatively thorium-free can be processed to prepare multigram amounts of material with significant proportions of ionium, ^{230}Th. From one unselected ore residue, after removal of uranium, thorium was obtained (Hyde, 1952, 1960) that was 26.4% ionium and 73.6% ^{232}Th (Roll and Dempster, 1952).

3.3 OCCURRENCE OF THORIUM

Two volumes of the *Gmelin Handbook of Inorganic Chemistry* deal with the natural occurrence of thorium and give a comprehensive review of known thorium minerals (Gmelin, 1990a, 1991a). So only the most important features will be emphasized here. Thorium has a much wider distribution than is generally thought. In the Earth's crust it is three times as abundant as Sn, twice as abundant as As, and nearly as abundant as Pb and Mo. It occurs in the tetravalent state in nature and is frequently associated with U(IV), Zr(IV), Hf(IV), and Ce(IV) but also with the trivalent rare earth elements that are relatively close in ionic radii (Cuthbert, 1958; Frondel, 1958; Shannon, 1976).

Due to the isotypism of ThO_2 and UO_2 solid state solutions can be formed and depending on the uranium content the mixtures are named thorianite (75–100 mol% ThO_2), uranothorianite (25–75 mol% ThO_2), thorian uraninite (15–25 mol% ThO_2) and uraninite (0–15 mol% ThO_2). A second mineral with a high thorium content is thorite, $ThSiO_4$, from which the element has originally been discovered. Thorite has the tetragonal zircon-type of structure but also a monoclinic variant of $ThSiO_4$ is known, which is called huttonite (Taylor and

Table 3.2 *Thorium content of various minerals.*

Accessory mineral	*Th* (ppm)
monazite	25000 to 2×10^5
allanite	1000 to 20000
zircon	50 to 4000
titanite	100 to 600
epidote	50 to 500
apatite	20 to 150
magnetite	0.3 to 20
xenotime	Low

Ewing, 1978). In both modifications of $ThSiO_4$, substitution of PO_4^{3-} for SiO_4^{4-} is frequently observed with additional replacement of Th^{4+} by trivalent rare earth ions for charge compensation. SiO_4^{4-} ions may be also replaced by OH^- groups according to $Th(SiO_4)_{1-x}(OH)_{4x}$ leading to a new mineral, thorogummite.

However, in all the minerals given in Table 3.2, Th occurs as the minor constituent. From these minerals, monazite is of significant commercial interest because it is distributed throughout the world, and some of the deposits are very large. Monazite is a phosphate of high specific gravity that is found in the form of yellow to brown sand in nature (monazite sand). The chemical inertness of monazite makes it hard to process.

3.4 THORIUM ORE PROCESSING AND SEPARATION

Monazite can be only attacked by strong acid, which essentially transforms the phosphate ion to $H_2PO_4^-$ and H_3PO_4 and leaves the metal ions as water-soluble salts, or by strong alkali, which transforms the insoluble phosphates to insoluble metal hydroxides that can easily be dissolved in acid after removal from the supernatant solution of alkali phosphates.

Thorium in monazite follows the rare earths in either the acid or the alkali processes. Thorium can be separated from the rare earths in strong sulfuric acid solution (Fig. 3.1) by partial dilution and reduction of acidity (by ammonia addition) to about pH 1.0, at which point hydrated thorium phosphates, containing only small amounts of entrained rare earths, precipitate (Fig. 3.2). The acidity must be reduced to about pH 2.3 to ensure precipitation of the bulk of the rare earths. (Any uranium present in the process solution is separated from the rare earths at this step.) The crude precipitate of thorium phosphate is then treated with alkali to remove undesired sulfate and phosphate anions, and the thorium hydroxide residue may then be dissolved in nitric acid for subsequent

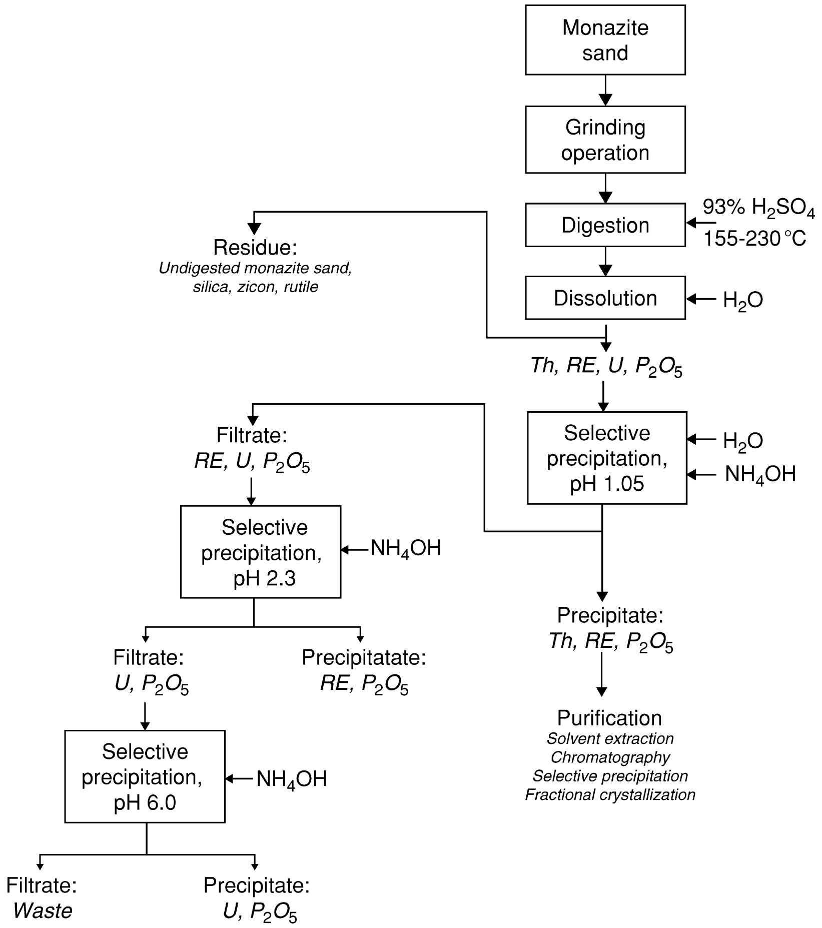

Fig. 3.1 *Simplified schematic diagram of sulfuric acid digestion of monazite sand and recovery of thorium, uranium, and the rare earths.*

purification. Purification is achieved efficiently by solvent extraction of the thorium with tri(*n*-butyl)phosphate (TBP) dissolved in kerosene, a procedure that separates thorium nitrate from rare earths and other non-extractable species. Numerous further extractants have been employed as pointed out in the *Gmelin Handbook* (Gmelin, 1985a).

The solid reaction product of the alkaline digestion of monazite (Fig. 3.3) may be dissolved in acid after separation from the supernatant solution. The solubility of the thorium-containing fraction, however, is a function of the conditions under which the alkaline digestion is performed. Too prolonged

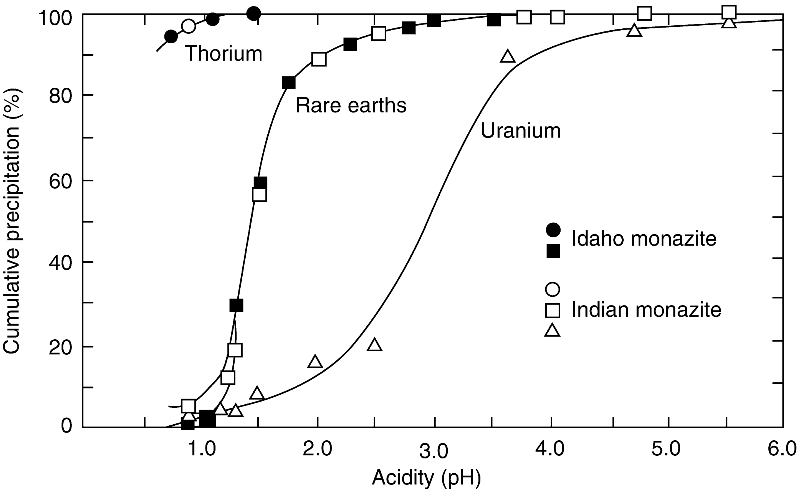

Fig. 3.2 *Effect of acidity on precipitation of thorium, rare earths, and uranium from a monazite–sulfuric acid solution of Idaho and Indian monazite sands: agitation time* 5 min; *dilution ratio,* 45 *to* 50 *parts water per one part monazite sand; digestion ratio of* 93% *sulfuric acid to digestion sands,* 1.77; *neutralizing agent,* 3.1% *ammonium hydroxide* (*Cuthbert,* 1958).

digestion at too high temperature may produce a product in which a large fraction of the thorium will not react readily with the acid used to dissolve the hydroxide cake. Presumably this is a consequence of the formation of ThO_2. Depending on whether hydrochloric, nitric, or sulfuric acid is used to dissolve the hydroxide cake, different procedures may be used in subsequent purification. Assuming the use of hydrochloric acid, which involves the fewest complications, a solution of thorium and rare earth chlorides is obtained. Differential precipitation of thorium from this solution again offers several choices: hydroxide (preferred), peroxide, or phosphate may be used to precipitate the thorium, or precipitation by carbonate may be used to separate the rare earths from thorium (and uranium), which form soluble anionic complexes. Final purification of thorium, again, is preferably made by solvent extraction (Marcus and Kertes, 1969; Gmelin, 1985a), but also chromatographic methods are applied (Kiriyama and Kuroda, 1978; Mayankutty *et al.*, 1982; Gmelin, 1990c, 1991b).

Thorium may also be recovered as a by-product from the treatment of uraninite or uranothorianite to obtain uranium. The thorium remaining in the solution of sulfuric acid after removal of the uranium is extracted into kerosene with the aid of long-chain amines. The thorium is part of a complex sulfate anion, which accompanies the protonated cationic amine into the organic phase. Neutralization of the quaternary ammonium cation precipitates the thorium from the organic phase or allows it to be back-extracted into an aqueous phase.

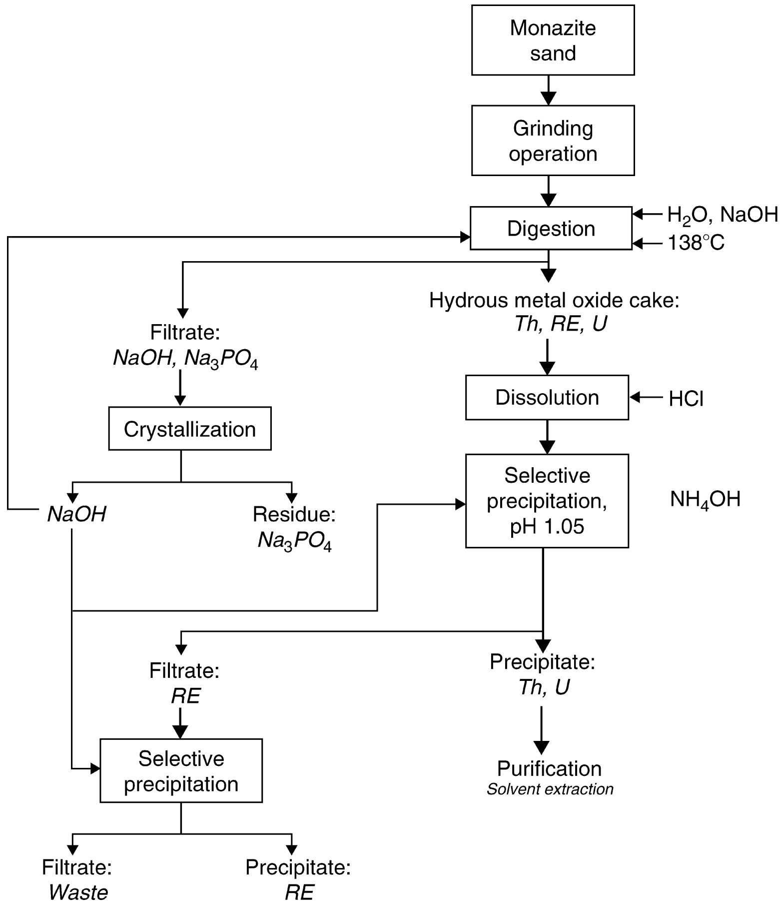

Fig. 3.3 *Simplified schematic diagram of caustic soda digestion of monazite sand and recovery of thorium, uranium, and the rare earths.*

3.5 ATOMIC SPECTROSCOPY OF THORIUM

The atomic spectroscopy of thorium provides not only information about the electronic states of thorium but also clues to the properties expected for elements of higher atomic number. The electronic structure of thorium and the related spectra will be discussed in more detail in Chapter 16 and are only summarized briefly here. Further details are also given in a volume of *Gmelin's Handbook* (Gmelin, 1989).

The four valence electrons of the neutral atom have available to them, in principle, the 5f, 6d, 7s, and 7p orbitals. The stable ground state configuration of the neutral thorium atom turns out to be $6d^27s^2$ ($^3F_2$) (Giacchetti *et al.*, 1974).

The $6d^37s$ ($^5F_1$) level is at higher energy by 5563.143 cm^{-1} and it is only at 7795.270 cm^{-1} that one encounters $5f6d7s^2$ ($^3H_4$). Still higher lie $6d7s^27p$ (10783.153 cm^{-1}), $6d^27s7p$ (14465.220 cm^{-1}), and $5f6d^27s$ (15618.98 cm^{-1}) (Zalubas, 1968).

The ionization potential of neutral Th was recently measured by resonance ionization mass spectrometry (RIMS) (Köhler *et al.*, 1997) as 6.3067(2) eV. The value obtained earlier (Sugar, 1974; Ackermann and Rauh, 1972) by extrapolation of spectroscopic data was 6.08 eV. The ground level of singly ionized Th is d^2s, followed by ds^2 (1859. 938 cm^{-1}), fs^2 (4490.256 cm^{-1}), fds (6168.351 cm^{-1}), d^3 (7001.425 cm^{-1}), and fd^2 (12485.688 cm^{-1}) (Zalubas and Corliss, 1974). It is a major step up in energy to configurations with either p contribution or to configurations that contain paired f-electrons: dsp is at 23372.582 cm^{-1}, followed by f^2s (24381.802 cm^{-1}), fsp (26488.644 cm^{-1}), d^2p (28243.812 cm^{-1}), fdp (30452.723 cm^{-1}), s^2p (31625.680 cm^{-1}), and f^2d (32620.859 cm^{-1}).

The ground state of doubly ionized thorium is 5f6d but the $6d^2$ configuration is only 63.267 cm^{-1} and the 5f7s is 2527.095 cm^{-1} higher (Racah, 1950). These are followed by 6d7s (5523.881 cm^{-1}), $7s^2$ (11961.133 cm^{-1}), $5f^2$ (15148.519 cm^{-1}), 5f7p (33562. 349 cm^{-1}), 6d7p (37280.229 cm^{-1}), and 7s7p (42259.714 cm^{-1}). These trends are continued in the triply ionized form (Klinkenberg and Lang, 1949), in which the ground level is 5f, and 6d is at 9193.245 cm^{-1}, 7s at 23130.75 cm^{-1}, and 7p at 60239.10 cm^{-1}.

Thus, with increasing ionic charge, configurations that include 5f electrons are stabilized with respect to others and the configurations containing 7p electrons become grossly destabilized. Effects in 7s and 6d systems are less but are still significant. The stabilization of the 5f electron in the triply charged ion is not sufficient however to make triply charged thorium a stable chemical species. The stable form is tetrapositive Th^{4+}, in which only the radon core of electrons is present.

Solid metallic thorium with the ground state configuration d^2s^2 has the 5f electrons in a reasonably broad energy band (Koelling and Freeman, 1971), about 5 eV above the Fermi level of 7.5–8.0 eV. This presumably is because the fds^2 level lies so low and interacts with the d^2s^2 level. Electron-binding energies for the various core levels of the atom have been determined (Nordling and Hagström, 1964), and the X-ray transitions have been determined with precision (Bearden, 1967; Bearden and Burr, 1967; Murthy and Redhead, 1974).

3.6 THORIUM METAL

A comprehensive treatment of the physical and chemical properties of thorium metal is given in the *Gmelin Handbook* (Gmelin, 1989, 1997). A brief summary on the most important properties shall be given here.

The preparation of thorium has been done by reducing halides or double halides by sodium, potassium, or calcium (Berzelius, 1829; Chydenius, 1863;

Nilson, 1876; Chauvenet, 1911). Furthermore, $ThCl_4$ can be reduced by sodium or electrolysis can be applied to a melt of thorium chloride or fluoride in sodium chloride or potassium chloride (Matignon and Delepine, 1901; Moissan and Hönigschmid, 1906; von Bolton, 1908; von Wartenberg, 1909; Chauvenet, 1911; Kaplan, 1956). Also, ThO_2 can be used as starting material and various reductants may be used (Ruff and Brintzinger, 1923; Marden and Rentschler, 1927). Care has to be taken when carbon or silicon is used because the formation of carbides and silicides may occur (Berzelius, 1829; Moissan and Étard, 1896, 1897; Hönigschmid, 1906a,b). In the so-called 'Sylvania process' calcium is used as the reducing agent (Dean, 1957; Smith *et al.*, 1975). Other reduction processes involve ThO_2 and aluminum or magnesium (Winkler, 1891; Leber, 1927). Both reactions are preferably carried out in the presence of zinc, making the reduction process thermodynamically favorable due to the formation of the intermetallic compound Th_2Zn_{17} (Spedding *et al.*, 1952). Zinc can easily be removed by vacuum distillation and leaves the metal mainly as a powder (Meyerson, 1956; Fuhrman *et al.*, 1957). Zinc is usually introduced as chloride or fluoride in the process (Briggs and Cavendish, 1971), but attempts have been made to use a zinc–magnesium alloy as reductant (Capocchi, 1971).

Unusual reductions include, for example, the reaction of $ThCl_4$ with $DyCl_2$ (Mikheev *et al.*, 1993). A method leading to high-purity thorium is the thermal decomposition of ThI_4 on a hot tungsten filament, known as the van Arkel–de Boer process (van Arkel and de Boer, 1925). This reaction is also used for the purification of thorium because the iodine formed in the reaction can be used to transport the crude metal from the low-temperature source to the hot wire. Another method to gain very pure thorium is the electrotransport that refines the high-grade thorium from the van Arkel–de Boer process further to a material containing less than 50 ppm impurities in total (Peterson and Schmidt, 1971).

Thorium appears as a bright silvery metal that has the highest melting point among the actinide elements while its density is the lowest one in the series except for Ac. Under ambient conditions, Th adopts the face-centered cubic (fcc) structure of copper that transforms to the body-centered cubic (bcc) structure of tungsten above 1360°C. Under high pressure, a third modification with a body-centered tetragonal lattice has been observed (Bridgman, 1935; Vohra, 1991, 1993; Vohra and Akella, 1991, 1992). Note that the transition conditions between the modifications depend remarkably on the amount of impurities in the metal (Smith *et al.*, 1975; Oetting *et al.*, 1976). The same is true for the properties like melting point, density (James and Straumanis, 1956), resistance, and others shown in Table 3.3, which summarizes selected properties of thorium as reported in two monographs (Smith *et al.*, 1975; Oetting *et al.*, 1976), and in the *Gmelin Handbook* (Gmelin, 1997).

Thorium metal is paramagnetic (ground state $6d^27s^2$) and shows a specific magnetic susceptibility of $0.412 \times 4\pi \times 10^{-9}$ m^3 kg^{-1} at room temperature (Greiner and Smith, 1971). The magnetic susceptibility is nearly

Table 3.3 *Some physical properties of thorium metal.*

melting point	2023 K
crystal structure	
face-centered cubic up to 1633 K	$a = 5.0842$ Å (298 K)
body-centered cubic from 1633–2023 K	$a = 4.11$ Å (1723 K)
body-centered tetragonal at high pressure	$a = 2.282$ Å, c = 4.411 Å (102 GPa)
atomic radius (from fcc structure)	1.798 Å
density	
from X-ray lattice parameters	11.724 g cm^{-3}
bomb reduced, as-cast	11.5–11.6 g cm^{-3}
arc melted, van Arkel metal	11.66 g cm^{-3}
enthalpy of sublimation (298 K)[a]	602 ± 6 kJ mol^{-1}
vapor pressure of the solid (1757–1956 K)	$\log p(\text{atm}) = -28780 \ (\text{T/K})^{-1} + 5.991$
vapor pressure of the liquid (2020–2500 K)	$\log p(\text{atm}) = -(29770 \pm 218) \ (\text{T/K})^{-1} - (6.024 \pm 0.098)$
enthalpy of fusion	14 kJ mol^{-1}
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^{-8} cm^2 N^{-1}
coefficient of thermal expansion (298–1273 K)	12.5×10^{-6} K^{-1}
electric resistivity	
electrorefined metal (298 K)	15.7×10^{-6} Ω cm
temperature coefficient of resistance	3.6×10^{-3} K^{-1}
thermal conductivity (298 K)	0.6 W cm^{-1} K^{-1}
work function	3.49 eV
Hall coefficient (297 K)	-11.2×10^{-5} cm^3 C^{-1}
emissivity (solid, 1600 K)	0.31

[a] Cox *et al.* (1989).

temperature-independent but it depends on the amount of impurities or dopants, respectively (Sereni *et al.*, 1987). Thorium is superconducting at low temperature (Meissner, 1929; de Haas and van Alphen, 1931). The transition temperature T_c is between 1.35 and 1.40 K, the critical magnetic field H_c has been found to be (159.22 ± 0.10) G for a high-purity sample (Decker and Finnemore, 1968). Thorium is an excellent example of a weakly coupled type-I superconductor that exhibits a complete Meissner effect and whose critical field curve $H_c(T)$ has a parabolic temperature dependence and is in good agreement with the predictions of the theory of Bardeen, Cooper, and Schrieffer (Bardeen *et al.*, 1957). The pressure dependence of H_c has been determined (Fertig *et al.*, 1972) and the specific heat discontinuity at T_c has been reported by several authors to be around 8.4 mJ mol^{-1} K^{-1} (Gordon *et al.*, 1966; Satoh and Kumagai, 1971, 1973; Luengo *et al.*, 1972a,b). Calculations on electron–phonon coupling have been also reported (Winter, 1978; Skriver and Mertig, 1985; Allen, 1987; Skriver *et al.*, 1988). The pressure dependence of the critical temperature has been followed up to 20 GPa (Palmy *et al.*, 1971; Rothwarf and Dubeck, 1973). Below 2.5 GPa T_c decreases linearly with pressure. The decrease flattens to a minimum around 7.4 GPa, increases slightly up to 10 GPa, before it smoothly decreases again. The pressure dependence of T_c has also been recently examined theoretically (Rosengren *et al.*, 1975; Mahalingham *et al.*, 1993). Furthermore, the dependence of T_c on impurities has been investigated (Guertin *et al.*, 1980).

The chemical reactivity of thorium is high. It is easily attacked by oxygen, hydrogen (Winkler, 1891; Matignon and Delepine, 1901; Sieverts and Roell, 1926; Nottorf *et al.*, 1952), nitrogen (Matignon, 1900; Kohlschütter, 1901; Matignon and Delepine, 1901), the halogens (Nilson, 1876; Moissan and Étard, 1896, 1897; von Wartenberg, 1909), and sulfur (Berzelius, 1829; Nilson, 1876; von Wartenberg, 1909) at elevated temperatures. Also carbon and phosphorus are known to form binary compounds with thorium (Strotzer *et al.*, 1938; Meisel, 1939; Wilhelm and Chiotti, 1950). Finely divided thorium is even pyrophoric (Raub and Engles, 1947). The reaction of bulky thorium with air under ambient conditions is low, but nevertheless corrosion is observed according to the investigations of several authors. Thorium reacts vigorously with hydrochloric acid. The reaction with hydrochloric acid always leaves a certain amount of a black residue (12 to 15%) behind, which was first thought to be ThO_2 that was originally present in the metal (Matignon and Delepine, 1901; Meyer, 1908; von Wartenberg, 1909). As discussed in Section 3.7.3, other studies have suggested that a lower-valent thorium oxide hydrate, $ThO \cdot H_2O$, is formed but it is much more likely that this compound is in fact an oxide hydride containing hydroxide and chloride ions according to ThO(X)H (X = combination of OH^- and Cl^-) (von Bolton, 1908; Karstens, 1909, Katzin, 1944, 1958; Karabash, 1958; Katzin *et al.*, 1962). This assumption is also supported by mass spectroscopic investigations that show Cl^- to be present in the residue (Ackermann and Rauh, 1973a). The reaction of thorium with other acids occurs slowly, with nitric acid even passivation is observed (Smithells, 1922; Schuler *et al.*, 1952). The latter can be overcome by adding small amounts of fluoride or fluorosilicate ions.

A great number of thorium alloys are known, including those with iron, cobalt, nickel, copper, gold, silver, platinum, molybdenum, tungsten, tantalum, zinc, bismuth, lead, mercury, sodium, beryllium, magnesium, and aluminum. Other systems, like Th/Cr and Th/U, are simply eutectics, and complete miscibility is found in the liquid and solid states with cerium. An overview of thorium alloys with main group metals can be found in the *Gmelin Handbook* (Gmelin, 1992a, 1997).

3.7 IMPORTANT COMPOUNDS

As Chapter 19 is devoted to the thermodynamic properties of the actinides and their compounds, data such as enthalpies of formation or entropies will not be given here, except when needed for the clarity of the discussion.

3.7.1 Hydrides

Reaction of thorium with hydrogen, and formation of two hydrides, ThH_2 and Th_4H_{15}, has been known for more than a century (Winkler, 1891). A substoichiometric dihydride with the fluorite-type of structure was observed by X-ray diffraction (XRD) along with the tetragonal ThH_{2-x} in a preparation of overall composition $ThH_{1.73}$ (Korst, 1962) as well as in dihydrides containing some ThO_2 (Peterson *et al.*, 1959). The well-known dihydride, which can be significantly substoichiometric, has a tetragonal structure (Nottorf *et al.*, 1952; Rundle *et al.*, 1952; Flotow and Osborne, 1978). The compound contains two metal atoms in the unit cell and is isotypic with ZrH_2 (Rundle *et al.*, 1948a; Nottorf *et al.*, 1952). The higher hydride (Matignon and Delepine, 1901; Sieverts and Roell, 1926; Rundle *et al.*, 1948a, 1952; Nottorf *et al.*, 1952; Zachariasen, 1953; Mueller *et al.*, 1977), Th_4H_{15} (= $ThH_{3.75}$), has a unique cubic structure, with the Th atom in 12-fold coordination of hydrogen atoms. The hydrogen atoms are coordinated by three and four thorium atoms as may be expressed by the formula $ThH_{9/3}H_{3/4}$ according to Niggli's formalism. The structure has also been determined for the deuterated analog Th_4D_{15} (Mueller *et al.*, 1977). Th_4H_{15} was the first metal hydride to be found to show superconductivity (Satterthwaite and Toepke, 1970; Satterthwaite and Peterson, 1972; Dietrich *et al.*, 1974). The transition temperature for superconductivity is 7.5–8 K, which is narrow, but not isothermal. Metallic conduction is exhibited at room temperature. Both the hydride and the deuteride are superconducting, with no apparent isotope effect. The existence of another crystalline form, with a 1% tetragonal distortion, that is non-superconducting has been suggested (Caton and Satterthwaite, 1977). The transition temperature is reversibly pressure-sensitive, with a slope of about 42 mK $kbar^{-1}$, up to a pressure of about 28 kbar. The heat capacities of ThH_2 and Th_4H_{15} have been measured from 5 to 350 K (Schmidt and Wolf, 1975; Miller *et al.*, 1976; Flotow and Osborne, 1978). As pointed out in more detail in Chapter 19, experimental values have been extrapolated to 800 K by Flotow *et al.* (1984).

The electronic structure of these binary thorium hydrides has been investigated by photoelectron spectroscopy (Weaver *et al.*, 1977) and nuclear magnetic resonance (NMR) spectroscopy (Schreiber, 1974; Lau *et al.*, 1977; Peretz *et al.*, 1978; Maxim *et al.*, 1979).

Powdered or sintered thorium metal reacts immediately and exothermically with hydrogen at room temperature, whereas massive metal may require heating to 300–400°C before reaction takes place. For the reaction with massive metal, an induction period that is a function of the impurity content of the metal was found (Nottorf *et al.*, 1952). In general, it is taken for granted that a consequence of the reaction of hydrogen on massive metal is a crumbling and powdering of the mass. However, it has been found (Satterwaithe and Peterson, 1972) that, at temperatures around 850°C, massive metal yields massive ThH_2, and then massive Th_4H_{15}, whereas even at 500°C the reaction fractures and cracks the massive metal. It is assumed that at high temperature, there is a sufficiently close match between the crystal structures of the metal and the hydride formed at that temperature that the incorporation of hydrogen can proceed without causing disruption of the solid.

At 900°C, in high vacuum, thorium hydride is completely decomposed to its elements. The decomposition product is grey to black, powdered, or in the form of an easily disintegrated mass. When it is desired to prepare thorium metal for some subsequent reaction, formation and decomposition of the hydride is generally used to accomplish this goal. The dissociation pressures of the two hydrides have been reported as (Nottorf *et al.*, 1952):

$$\log p(\text{mmHg}) = -7700\ (T/K)^{-1} + 9.54 \quad (\text{Th/ThH}_2 \text{ system})$$

$$\log p(\text{mmHg}) = -4220\ (T/K)^{-1} + 9.50 \quad (\text{ThH}_2/\text{Th}_4\text{H}_{15} \text{ system})$$

Flotow *et al.* (1984) discuss in greater detail the hydrogen pressures associated with the Th–H_2 system as a function of the hydrogen composition of the solid phases and the temperatures.

Thorium hydride reacts readily with oxygen to form ThO_2. Many hydride preparations are in fact pyrophoric. ThO_2 can also be formed smoothly by reaction of thorium hydride with steam at 100°C. The reactions with oxygen and with steam are typical for the procedures commonly used for the synthesis of binary compounds of thorium. Pure thorium is necessary to prepare thorium hydride that is free of oxygen or moisture. Subsequent manipulation in the absence of air or moisture then assures the formation of pure binary compounds. Thus, in the range of 250–350°C, the hydride reacts smoothly with halogens as well as with hydrogen compounds of the halogens, sulfur, phosphorus, or nitrogen to give the corresponding binary compounds of thorium (Foster, 1945, 1950; Lipkind and Newton, 1952). Methane or carbon dioxide does not react with thorium hydride.

A number of ternary hydrides and deuterides has been reported (Table 3.4). The iron compounds $Th_2Fe_{17}D_x$ are structurally related to the respective alloy Th_2Fe_{17} and show interesting magnetic properties (Isnard *et al.*, 1993). The deuterides $ThZr_2D_x$ can be described as stuffed variant of the cubic Laves phases as it has been shown by neutron diffraction (van Houten and Bartram, 1971; Bartscher *et al.*, 1986). $ThZr_2H_{7+x}$ (and also the hexagonal $ThTi_2H_{6+x}$) combine an extremely large amount of hydrogen per unit volume with relatively low equilibrium vapor pressures of hydrogen at elevated temperatures. Both of

Table 3.4 *Crystallographic data of thorium hydrides and deuterides.*

		Lattice parameters			
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*References*
ThH_2	I4/mmm	4.055		4.965	Flotow and Osborne, 1978[a]
Th_4H_{15}	$I\bar{4}3d$	9.11			Mueller *et al.* (1977)
Th_4D_{15}	$I\bar{4}3d$	9.11			Mueller *et al.* (1977)
$Th_2Fe_{17}D_{4.956}$	$R\bar{3}m$	8.7116		12.624	Isnard *et al.* (1993)
$Th_2Fe_{17}D_{4.668}$	$R\bar{3}m$	8.682		12.56	Isnard *et al.* (1993)
$Th_6Mn_{23}D_{16.2}$	$Fm\bar{3}m$	12.922			Hardman *et al.* (1980)
$Th_6Mn_{23}D_{16}$	$Fm\bar{3}m$	12.921			Hardman *et al.* (1980)
$Th_6Mn_{23}D_{16}$	P4/mmm	9.076		12.961	Hardman-Rhyne *et al.* (1984)
$Th_6Mn_{23}D_{28.5}$	$Fm\bar{3}m$	13.203			Hardman-Rhyne *et al.* (1984)
$ThZr_2D_6$	$Fd\bar{3}m$	9.151			Bartscher *et al.* (1986)
$ThZr_2D_{3.6}$	$Fd\bar{3}m$	9.042			Bartscher *et al.* (1986)
$ThZr_2D_{4.8}$	$Fd\bar{3}m$	9.112			Bartscher *et al.* (1986)
$ThZr_2D_{6.3}$	$Fd\bar{3}m$	9.154			Bartscher *et al.* (1986)
$ThNi_2D_2$	P6/mmm	3.87		3.951	Andresen *et al.* (1984)
$ThNi_2D_{2.6}$	P6/mmm	4.405		4.360	Andresen *et al.* (1984)
Th_2AlD_2	I4/mcm	7.702		6.23	Bergsma *et al.* (1961)
Th_2AlD_3	I4/mcm	7.676		6.383	Bergsma *et al.* (1961)
Th_2AlD_4	I4/mcm	7.629		6.517	Bergsma *et al.* (1961)
$Th_2AlD_{3.71}$	I4/mcm	7.6260		6.5150	Sorby *et al.* (2000)
$Th_2AlD_{2.75}$	$P\bar{4}2m$	7.6796		19.073	Sorby *et al.* (2000)
$Th_2AlD_{2.29}$	I4/mcm	7.7014		6.2816	Sorby *et al.* (2000)

[a] These authors use the F4/mmm setting with a = 5.734 Å. The F-centered cell has the diagonal of the ab-plane as axis, i.e. square root of twice the a axis of the I-centered cell.

these ternary hydrides are apparently stable in air. Unlike thorium hydride itself, the Th–Zr hydride is not superconducting (Satterthwaite and Peterson, 1972). Also the nickel phases $ThNi_2D_x$ are derived from the alloy $ThNi_2$ and show the deuterium atom in tetrahdral interstices of the metal atom network (Andresen *et al.*, 1984). The thorium manganese compounds $Th_6Mn_{23}D_x$ have been investigated frequently with respect to the D atom distribution in the lattice (Hardman *et al.*, 1980, 1982; Jacob, 1981; Carter, 1982; Hardman-Rhyne *et al.*, 1984). Furthermore, the ternary aluminum hydrides Th_2AlD_x have been reported in great detail (Bergsma *et al.*, 1961; Sorby *et al.*, 2000). Other hydrides, for example with cobalt and palladium are known, however not very well characterized in the most cases (Buschow *et al.*, 1975; Oesterreicher *et al.*, 1976).

3.7.2 Borides, carbides, and silicides

Three binary thorium borides are well characterized (du Jassonneix, 1905; Allard, 1932; Stackelberg and Neumann, 1932; Lafferty, 1951; Post *et al.*, 1956; Konrad *et al.*, 1996). ThB_6 contains a network of linked $[B_6]$ octahedra;

in ThB_4, $[B_2]$ dumbbells accompany the octahedra (Brewer *et al.*, 1951; Zalkin and Templeton, 1951; Blum and Bertaut, 1954). Investigations of the thorium–boron system at low boron concentrations showed that non-stoichiometric varieties of ThB_4 can be prepared (Rand *et al.*, 1975; Chiotti *et al.*, 1981). On the other hand, certain impurities (for example ThO_2) have been suggested to be accountable for the non-stoichiometry (Brewer *et al.*, 1951). The third boride, ThB_{12}, is isotypic with UB_{12} (Cannon and Hall, 1977; Cannon and Farnsworth, 1983). Furthermore, the borides ThB_{66} and ThB_{76} have been reported (Naslain *et al.*, 1971; Schwetz *et al.*, 1972), but it was not clear whether they are truly thorium–boron phases or if they are a metal-stabilized form of a boron allotrope.

Various ternary thorium borides have been prepared, especially those containing transition metals. The orthorhombic borides Th_2MB_{10} were obtained from the elements by arc melting and show a structure that is closely related to that of ThB_6 (Konrad and Jeitschko, 1995). Borides of the composition $ThMB_4$ have been recognized for M = V, Mo, W, Re, Cr, and Mo (Pitman and Das, 1960; Rogl and Nowotny, 1974; Konrad *et al.*, 1996). The crystal structures have been determined for M = Cr and Mo, in which the boron atoms form infinite layers with the metal atoms in between similar to MgB_2. The chromium compound $ThCr_2B_6$ is isotypic with $CeCr_2B_6$ and shows metallic conduction and Pauli paramagnetism (Konrad and Jeitschko, 1995). The hexagonal borides $ThIr_3B_2$ and $ThRu_3B_2$ have been characterized magnetically and structurally. They contain discrete boride ions in prismatic coordination of the platin metal atoms (Hiebl *et al.*, 1980; Ku *et al.*, 1980). The magnetic properties have also been also determined for the rather complicated borides $R_{2-x}Th_xFe_{14}B$ (R = Y, Dy, Er) (Pedziwiatr *et al.*, 1986).

Further boron-containing thorium compounds are the borohydrides $Th(BH_4)_4$, $LiTh(BH_4)_5$, and $Li_2Th(BH_4)_6$ (Ehemann and Nöth, 1971). They contain the tetrahedral BH_4^- ion.

Carbides of thorium have been discussed in great detail in the *Gmelin Handbook* (Gmelin, 1992b). Thus only the most important items shall be given here briefly. Binary thorium carbides were obtained by the reaction of ThO_2 with carbon or the direct fusion of the elements (Troost, 1883; Moissan and Étard, 1896, 1897; Wilhelm and Chiotti, 1949, 1950). Three compositions, ThC_2, Th_2C_3, and ThC, are known (Fig. 3.4). ThC_2 occurs in three different modifications. At room temperature, a monoclinic unit cell is found (Jones *et al.*, 1987). Between 1430 and 1480°C, a rotation of the C_2 dumbbells starts, leading to a tetragonal structure that changes to cubic above 1480°C with complete rotational disorder of the C_2 units (Hunt and Rundle, 1951; Gantzel and Baldwin, 1964; Hill and Cavin, 1964; Langer *et al.*, 1964; Bowman *et al.*, 1968). The monocarbide, ThC, has the cubic NaCl structure. Both ThC_2 and ThC are refractory solids with high melting points (2655 ± 25 and 2625 ± 25, respectively). For ThC, the specific heat has been measured from 1.5 to 300 K (Danan, 1975). The third binary thorium carbide, Th_2C_3, has been observed at pressures

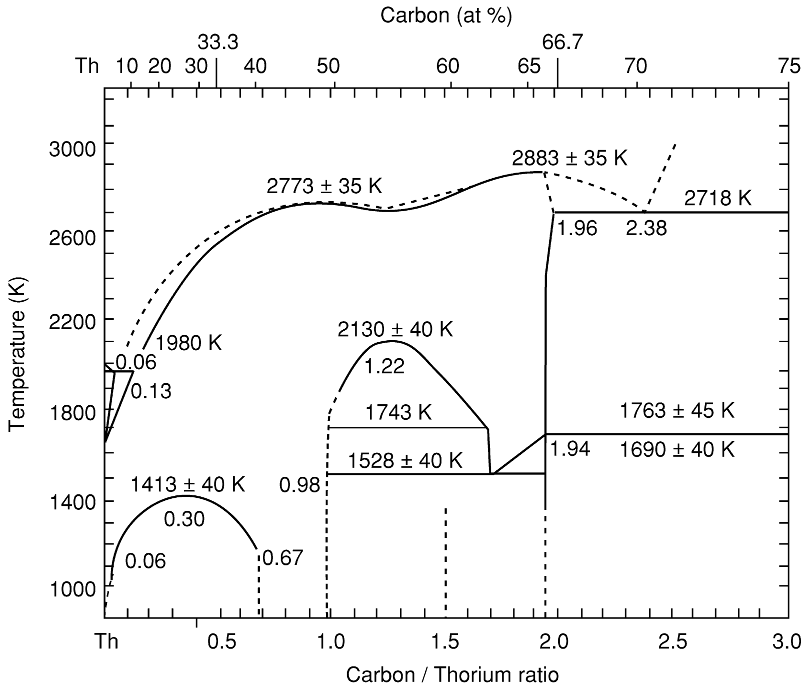

Fig. 3.4 *Phase diagram of the thorium–carbon system* (*Chiotti* et al., 1981).

above 33 kbar in the region of 1200°C (Krupka, 1970). It has the cubic structure of Pu_2C_3 and is a superconductor with T_c decreasing with increasing pressure (Giorgi *et al.*, 1976). Besides these three carbides, several non-stoichiometric phases have been found that can be seen as solid state solutions between α-Th and γ-ThC_2 (Chiotti *et al.*, 1967; Storms, 1967) that have cubic symmetry.

Upon heating ThC_2 to high temperature on a graphite filament, ThC_4^+ ions were observed (Asano *et al.*, 1974). ThC_2 burns in the air to form ThO_2 and reacts with sulfur or selenium vapor (Moissan and Étard, 1896, 1897). Halogens react with the carbide to give anhydrous halides. According to an early study (Lebeau and Damiens, 1913) the hydrolysis of the carbide produces a mixture of almost 60% hydrogen, 3.16% methane, 10.7% ethane, ~15% acetylene, ~3% ethylene, ~8% propylene and propane, and higher products. Other studies on the hydrolysis of ThC and ThC_2 report the formation of methane in the ThC case and the formation of ethane and hydrogen in the ThC_2 case (Kemper and Krikorian, 1962). It seems evident that not only the composition and purity of the carbide but also the actual hydrolysis conditions may be important factors.

A number of ternary carbides have been reported (Table 3.5). The boride carbides have the compositions ThBC, $Th_3B_2C_3$, and ThB_2C (Rogl, 1978, 1979;

Rogl and Fischer, 1989). ThBC and $Th_3B_2C_3$ contain CBBC units; in $Th_3B_2C_3$ additional C atoms are found (Fig. 3.5). For ThB_2C extended layers of connected B and C atoms are found with the thorium atoms located between the layers. In the nitride carbide ThCN (Benz, 1969; Benz and Troxel, 1971), dumbbell-shaped C_2 units and nitride ions are present (Benz *et al.*, 1972).

Several ternary carbide systems have been investigated, Th–M–C, with M being a transition metal element or a lanthanide, and a huge number of compounds are believed to exist (Gmelin, 1992b). However, only a few of them are structurally characterized. Specifically, for ruthenium and nickel, several structure determinations have been performed. In the former case, the compounds $Th_{11}Ru_{12}C_{18}$, $Th_2Ru_6C_5$, and $ThRu_3C$ were investigated (Aksel'rud *et al.*, 1990a,b; Wachtmann *et al.*, 1995). The carbon-rich species contain both C_2 units and single C atoms while $ThRu_3C$ can be regarded as a cubic closest packing of metal atoms with the carbon atoms in octahedral interstices. Two series of thorium iron carbides have been structutrally and magnetically investigated recently. They have the composition $ThFe_{11}C_{1+x}$ $(0 < x < 1)$ and $Th_2Fe_{17}C_x$ $(0 < x < 1)$, respectively (Isnard *et al.*, 1992a,b; Singh Mudher *et al.*, 1995). In the nickel system, three compounds were found: Th_2NiC_2, $Th_3Ni_5C_5$, and $Th_4Ni_3C_6$. According to the structure determination the latter two should be more correctly described as $Th_3Ni_{4.96}C_{4.79}$ and $Th_4Ni_{2.88}C_6$, respectively (Moss and Jeitschko, 1991a,b). Two carbides have been prepared in the system Th–Al–C, namely $Th_2Al_2C_3$ and $ThAl_4C_4$ (Gesing and Jeitschko, 1996). They are both methanides in the sense that they contain isolated carbon atoms. One lanthanide compound that has been structurally characterized is $CeThC_2$ (Stecher *et al.*, 1964).

According to the phase diagram Th–Si (Fig. 3.6) four binary thorium silicides exist (Stecher *et al.*, 1963; Chiotti *et al.*, 1981; Gmelin, 1993b): Th_3Si_5, Th_3Si_2, ThSi, and $ThSi_2$. The latter three are structurally known (Brauer and Mitius, 1942; Jacobson *et al.*, 1956; Brown, 1961). $ThSi_2$ is dimorphic and both the hexagonal (AlB_2 type) and the tetragonal modifications show the thorium atoms in 12-fold coordination of silicon atoms. In ThSi the silicon atoms are linked to zigzag chains (Si—Si distance: 2.49 Å) while Si_2 dumbbells (2.33 Å) are found in Th_3Si_2. Further silicides have been reported, for example Th_6Si_{11} (Brown and Norreys, 1961), but have not be confirmed up to now.

Various ternary silicides of thorium are known (Table 3.5). The largest group among them contains compounds of the composition ThM_2Si_2 with M being a transition metal element. For M = Cr, Mn, Fe, Co, Ni, Cu, and Tc, structure determinations have been performed (Ban and Sikirica, 1965; Leciejewicz *et al.*, 1988; Wastin *et al.*, 1993) and for part of the silicides, magnetic properties are known (Omejec and Ban, 1971; Ban *et al.*, 1975). The compounds are isotypic with each other and have tetragonal symmetry. The stucture consists of layers of edge connected $[ThSi_8]$ cubes that are separated by the transition metal atoms. Other silicides have the composition Th_2MSi_3 (M = M, Fe, Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Pt, Au) and are derived from the two modifications of $ThSi_2$ by substitution of transition metal atoms for silicon atoms (Ban *et al.*, 1975; Wang *et al.*, 1985; Albering *et al.*, 1994). In the same way, the silicides ThMSi (M = Au, Pd, Ni) are derived from the hexagonal form of $ThSi_2$ (Ban *et al.*, 1975; Wang *et al.*, 1985). Two new silicides of thorium have been reported recently with $ThCo_9Si_2$ and $ThRe_4Si_2$ (Albering and Jeitschko, 1995; Moze *et al.*, 1996).

In a few cases, quaternary compounds have also been investigated. For example the silicide–carbides $Th_2Re_{2.086}Si_xC$ ($x = 1.914$ and 1.904), $ThOs_{2.04}Si_{0.96}C$, and $ThOs_{2.284}Si_{0.716}C$ have been reported (Hüfken *et al.*, 1998, 1999), and the two lanthanide nitride carbides CeThNC and DyThNC are known (Ettmayer *et al.*, 1980).

3.7.3 Oxides, hydroxides, and peroxides

Thorium oxides have received considerable attention in the recent decades. They have been reviewed in the *Gmelin Handbook* (Gmelin, 1976, 1978), but the diverse chemistry of the simple binary oxide of thorium has yielded 435 patents since these days, out of which 53 are related to the catalytic behavior of ThO_2. An recent search of the Chemical Abstract Services database revealed over 540 journal articles and some 50 reports on catalysis. While ThO_2 has been studied as a complement to CeO_2 and HfO_2 in its chemistry, ThO has been postulated as a defect form of the fluorite or a ZnS structure (Katzin, 1958; Ackermann and Rauh, 1973b). Table 3.6 lists the binary oxides and the other chalcogenides (cf. Section 3.7.5) with their lattice constants. Thorium monoxide has been reported to form on the surface of thorium metal exposed to air (Rundle *et al.*, 1948b) but its preparation and isolation as a bulk black suspension was first reported in 1958 by Katzin as a result of the action of 2 to 12 N HCl solutions on thorium metal. The black powder reported appeared later to be a form of low-valent thorium oxide stabilized by HCl and H_2O. XRD studies revealed a cubic phase with a lattice constant of 5.302 Å and a pattern indicative of an fcc lattice – either a defect fluorite or ZnS-type (Ackermann and Rauh, 1973b). However, the 'monoxide' solid state compound appears to be a Th(IV) phase with the formula Th(H)(O)X, where X is a combination of OH^- and Cl^- (Katzin *et al.*, 1962). This seemed to explain the reaction of the black solid upon heating to yield HCl, H_2, H_2O, and ThO_2 under various conditions (Ackermann and Rauh, 1973b). This phase was also reported to be unstable to disproportionation under dynamic vacuum. Until now, however, there is no report on bulk-phase ThO available that is without question. On the other hand, ThO was reported in the vapor phase above a mixture of Th and ThO_2 at high temperatures (Darnell and McCollum, 1961; Ackermann and Rauh, 1973b; Hildenbrand and Murad, 1974a,b; Neubert and Zmbov, 1974).

Thorium dioxide (thoria) is somewhat hygroscopic. Reaction with nitric or hydrochloric acids followed by evaporation yields hydrates that have in the past been thought to resemble the so-called 'metaoxides' of tin and zirconium. The material may be dispersed as a positively charged colloid following evaporation

Table 3.5 *Crystallographic data of thorium borides, carbides, and silicides.*

		Lattice parameters				
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
ThB_4	P4/mbm	7.256		4.113		Zalkin and Templeton (1950, 1953); Konrad *et al.* (1996)
ThB_6	Pm$\bar{3}$m	4.113				Konrad *et al.* (1996), Blum and Bertaut (1954)
ThBC	P4$_1$22	3.762		25.246		Rogl (1978)
ThB_2C	R$\bar{3}$m	6.676		11.376		Rogl and Fischer (1989)
$Th_3B_2C_3$	P2/m	3.703	3.773	9.146	$\beta = 100.06$	Rogl (1979)
$ThB_{66.8}O_{0.36}$	Fm$\bar{3}$c	23.53				Naslain *et al.* (1971)
$Na_{0.77}Th_{0.23}B_6$	Pm$\bar{3}$m	4.151				Blum and Bertaut (1954)
Th_2FeB_{10}	Pbam	5.627		4.183		Konrad and Jeitschko (1995)
Th_2CoB_{10}	Pbam	5.624		4.185		Konrad and Jeitschko (1995)
Th_2NiB_{10}	Pbam	5.646	11.204	4.173		Konrad and Jeitschko (1995)
$ThCrB_4$	Pbam	6.057	11.712	3.640		Konrad *et al.* (1996)
$ThCr_2B_6$	Immm	3.158	6.591	8.364		Konrad *et al.* (1996)
$ThMoB_4$	Cmmm	7.481	9.658	3.771		Rogl and Nowotny (1974)
$ThIr_3B_2$	P6/mmm	5.449		3.230		Ku *et al.* (1980)
$ThRu_3B_2$	P6/mmm	5.528		3.070		Hiebl *et al.* (1980)
ThC	Fm$\bar{3}$m	5.346				Kemper and Krikorian (1962)
ThC_2	C2/c	6.53	4.24	6.56	$\beta =104.0$	Hunt and Rundle (1951)
ThC_2	C2/c	6.684	4.220	6.735	$\beta = 103.91$	Jones *et al.* (1987)
$ThC_{1.97}$	C2/c	6.692	4.223	6.744	$\beta = 103.1$	Bowman *et al.* (1968)
$ThC_{1.97}$	I4/mmm	4.221		5.394		Bowman *et al.* (1968)
$ThC_{1.97}$	Fm$\bar{3}$m	5.806				Bowman *et al.* (1968)
ThCN	C2/m	7.0249	3.9461	7.2763	$\beta = 95.67$	Benz *et al.* (1972)
$Th_2Al_2C_3$	Pnnm	5.406	11.556	3.5201		Gesing and Jeitschko (1996)
$ThAl_4C_4$	I4/m	8.231		3.3273		Gesing and Jeitschko (1996)
$ThFe_{11}C_{1+x}$	I4$_1$/amd	~10.20		~6.61		Isnard *et al.* (1992a)

Table 3.5 (*Contd.*)

		Lattice parameters				
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
$Th_2Fe_{17}C_x$	$R\bar{3}m$	~8.6		~12.5		Isnard *et al.* (1992b)
Th_2NiC_2	I4/mmm	3.758		12.356		Moss and Jeitschko (1991b, 1989b)
$Th_3Ni_{4.96}C_{4.79}$	Cmca	13.961	7.174	7.07		Moss and Jeitschko (1991b, 1989b)
$Th_4Ni_{2.88}C_6$	C2/m	15.369	3.751	7.628	$\beta = 113.29$	Moss and Jeitschko (1991a, 1989a)
$ThRu_3C$	$Pm\bar{3}m$	4.227				Wachtmann *et al.* (1995)
$Th_2Ru_6C_5$	P4/mbm	9.113		4.186		Aksel'rud *et al.* (1990a)
$Th_{11}Ru_{12}C_{18}$	$I4\bar{3}m$	10.764				Aksel'rud *et al.* (1990b)
$Th_2Ru_6C_5$	P4/mbm	9.096		4.177		Wachtmann *et al.* (1995)
$Th_{11}Ru_{12}C_{18}$	$I4\bar{3}m$	10.754				Wachtmann *et al.* (1995)
$ThCeC_2$	$Fm\bar{3}m$	5.280				Stecher *et al.* (1964)
ThSi	Pbnm	5.89	7.88	4.15		Jacobson *et al.* (1956)
$ThSi_2$	P6/mmm	4.136		4.126		Brown (1961)
$ThSi_2$	$I4_1$/amd	4.126		14.346		Brauer and Mitius (1942)
$ThSi_2$	P6/mmm	3.985		4.220		Jacobson *et al.* (1956)
Th_3Si_2	P4/mbm	7.835		4.154		Jacobson *et al.* (1956)

$ThCr_2Si_2$	I4/mmm	4.043		10.577	Ban and Sikirica (1965)
$ThCr_2Si_2$	I4/mmm	4.0414		10.588	Leciejewicz *et al*. (1988)
$ThMn_2Si_2$	I4/mmm	4.021		10.493	Ban and Sikirica (1965)
$ThMn_2Si_2$	I4/mmm	4.0225		10.475	Leciejewicz *et al*. (1988)
$ThMn_2Si_2$	I4/mmm	4.019		10.483	Ban *et al*. (1975)
$ThFe_2Si_2$	I4/mmm	4.038		9.820	Ban and Sikirica (1965)
$ThFe_2Si_2$	I4/mmm	4.038		9.812	Leciejewicz *et al*. (1988)
$Th(Co_{0.5}Si_{1.5})$	P6/mmm	4.043		4.189	Wang *et al*. (1985)
$ThCo_9Si_2$	$I4_1$/amd	9.7914		6.3138	Moze *et al*. (1996)
$ThCo_2Si_2$	I4/mmm	4.015		9.760	Ban and Sikirica (1965)
$ThCo_2Si_2$	I4/mmm	4.0128		9.754	Leciejewicz *et al*. (1988)
$ThNi_2Si_2$	I4/mmm	4.076		9.551	Ban and Sikirica (1965)
$ThNi_2Si_2$	I4/mmm	4.0789		9.555	Leciejewicz *et al*. (1988)
$ThCu_2Si_2$	I4/mmm	4.104		9.864	Ban and Sikirica (1965)
$ThCu_2Si_2$	I4/mmm	4.1031		9.866	Leciejewicz *et al*. (1988)
$ThTc_2Si_2$	I4/mmm	4.184		10.063	Wastin *et al*. (1993)
$ThRe_4Si_2$	Pnnm	7.294	15.500	4.124	Albering and Jeitschko (1995)
ThAuSi	$P\bar{6}m2$	4.260		4.164	Albering *et al*. (1994)

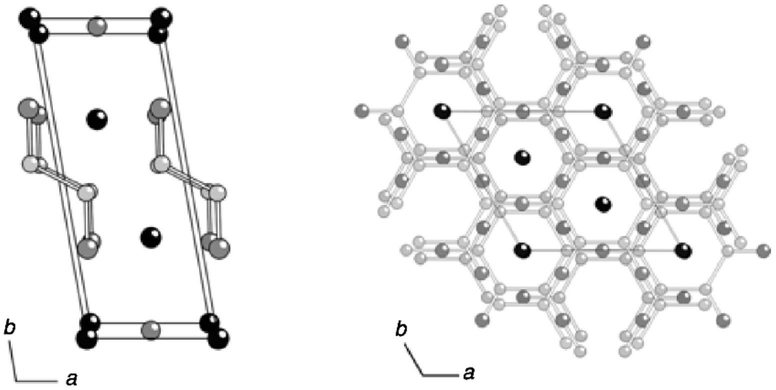

Fig. 3.5 *Crystal structures of $Th_3B_2C_3$ (left) and ThB_2C (right).*

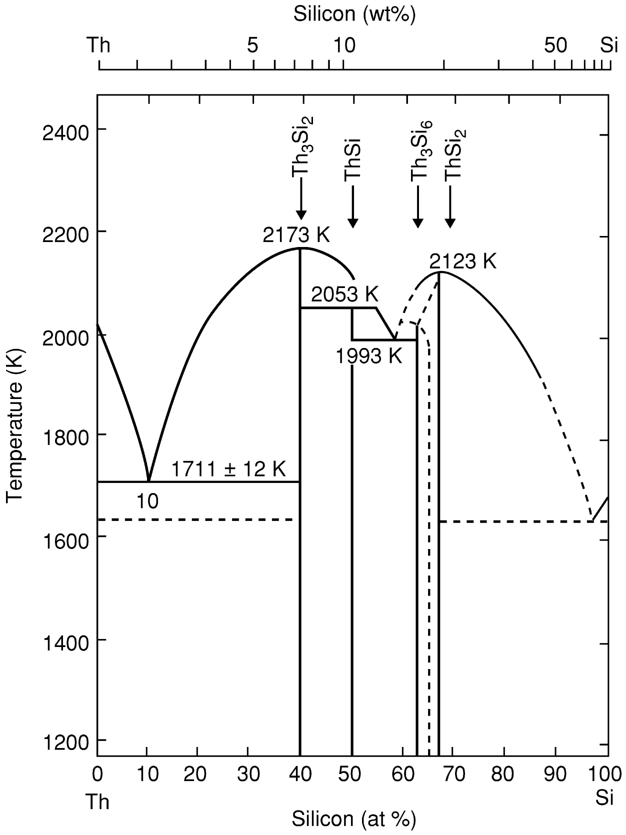

Fig. 3.6 *Phase diagram of the thorium–silicon system* (*Chiotti* et al., 1981).

Table 3.6 *Crystallographic data of thorium chalcogenides.*

		Lattice parameters				
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
ThO	cubic	5.302				Katzin (1958); Ackermann and Rauh (1973b)
ThO_2	Fm$\bar{3}$m	5.592				Gmelin (1976, 1978)
ThOS	P4/nmm	3.963		6.747		Zachariasen (1949c)
ThS	Fm$\bar{3}$m	5.682				Zachariasen (1949c)
Th_2S_3	Pbnm	10.990	10.850	3.960		Zachariasen (1949c)
Th_7S_{12}	P6$_3$/m	11.063		3.991		Zachariasen (1949d)
ThS_2	Pmnb	4.267	7.264	8.617		Zachariasen (1949c)
Th_2S_5	Pcnb	7.623	7.677	10.141		Nöel and Potel (1982)
ThOSe	P4/nmm	4.038		7.019		D'Eye *et al.* (1952)
ThSe	Fm$\bar{3}$m	5.875				D'Eye *et al.* (1952)
Th_2Se_3	Pbnm	11.36	11.59	4.28		D'Eye *et al.* (1952)
Th_7Se_{12}	P6$_3$/m	11.570		4.230		D'Eye (1953)
$ThSe_2$	Pmnb	4.420	7.611	9.065		D'Eye (1953)
Th_2Se_5	Pcnb	7.922	7.937	10.715		Kohlmann and Beck (1999)
$ThSe_3$	P2$_1$/m	5.72	4.21	9.64	$\beta = 97.05$	Nöel (1980)
ThOTe	P4/nmm	4.120		9.563		D'Eye and Sellman (1954)
ThTe	Pm$\bar{3}$m	3.827				D'Eye and Sellman (1954)
Th_2Te_3	hexagonal	12.49		4.35		Graham and McTaggart (1960)
Th_7Te_{12}	P$\bar{6}$	12.300		4.566		Tougait *et al.* (1998)
$ThTe_2$	hexag. (?)	8.49		9.01		Graham and McTaggart (1960)
$ThTe_3$	monoclinic	6.14	10.44	4.31	$\beta = 98.4$	Graham and McTaggart (1960)

and the colloid can be 'salted out' by addition of electrolytes. The ignited oxide or the oxide sintered into larger particles is one of the most refractory substances known, showing limited reactivity with hot sulfuric acid or fusion with potassium hydrogen sulfate. Aqueous nitric acid with a few percentage of HF or sodium fluorosilicate provides a reasonable solution of the oxide (Smithells, 1922). Hot aqueous HF or gaseous HF at 250–750°C converts thoria to ThF_4 (Newton *et al.*, 1952b).

Amorphous thoria is said to crystallize from a suitable flux, for example sodium carbonate, potassium orthophosphate, or borax (Nordenskjöld and Chydenius, 1860; Nordenskjöld, 1861; Chydenius, 1863; Rammelsberg, 1873; Troost and Ouvrard, 1889; Duboin, 1909a,b). However, the use of borax as a flux is questionable, because ThO_2 is known to form ThB_2O_5 in the reaction with B_2O_3 (Baskin *et al.*, 1961).

Thorium dioxide has been studied as an active catalyst because of its reactivity with many gases, in addition to water. Dehydration of alcohols (Frampton, 1979; Siddham and Narayanan, 1979), dehydrogenation of alcohols (Thomke, 1977), and the hydration (Frampton, 1979) and hydrogenation of alkenes (Tanaka *et al.*, 1978) have been demonstrated. Other examples include copper–thorium oxide catalysts studied for the selective hydrogenation of isoprene (Bechara *et al.*, 1990a,b), decomposition of isopropanol (Aboukais *et al.*, 1993), and the oxidative coupling of methane (Zhang *et al.*, 2001). Indeed, the development of mixed-metal rare earth/thorium/copper oxides based on a perovskite parent structure have been shown to decompose NO_x (Gao and Au, 2000), to catalyze the reduction of NO by CO (Wu *et al.*, 2000), and to dehydroxylate phenol (Liu *et al.*, 1997). Lastly, thorium oxide, when heated, produces an intense blue light and mixed with ceria at 1%, produces a more intense white light. It is this property that was the basis for the thoriated gas mantle industry (Mason, 1964; Manske, 1965).

Thorium hydroxide is formed as a gelatinous precipitate when alkali or ammonium hydroxide is added to a solution of a thorium salt. This precipitate dissolves in dilute acids and, when fresh, in ammonium oxalate, alkali carbonates, sodium citrate, or sodium potassium tartrate solutions (Chydenius, 1863; Glaser, 1897; Jannasch and Schilling, 1905; Sollman and Brown, 1907). The hydroxide is also precipitated by the action of sodium nitrate (Baskerville, 1901) or potassium azide (Dennis and Kortright, 1894; Glaser, 1897; Wyrouboff and Verneuil, 1898a). Electrolysis of thorium nitrates is also said to yield a precipitate of hydroxide at the anode (Angelucci, 1907). Material dried at 100°C has been reported to correspond closely in composition to $Th(OH)_4$ (Clève, 1874), but other reports claim to find higher hydrates even at higher temperatures (Wyrouboff and Verneuil, 1905). Two forms of $ThO_2 \cdot 2H_2O$ ($=Th(OH)_4$), from precipitation in basic aqueous solution, have been distinguished, one of which is amorphous (Guymont, 1977). Further studies indicate that $Th(OH)_4$ is stable in the temperature range 260–450°C and is converted to the oxide at temperatures of 470°C and higher (Dupuis and Duval, 1949). Thermal analysis has shown that the decomposition of the hydroxide is a continuous process (Tiwari and Sinha, 1980). Thorium hydroxide absorbs atmospheric carbon dioxide very readily (Chydenius, 1863; Dennis and Kortright, 1894; Chauvenet, 1911). When boiled with thorium nitrate, $Th(OH)_4$ forms a positively charged colloid (Müller, 1906). The colloid formation is also observed if thorium hydroxide is treated with hydrous aluminum chloride, ferric chloride, uranyl nitrate, or hydrochloric acid (Szilard, 1907). The solubility product of $Th(OH)_4$ is discussed in Section 3.8.5.

Thorium peroxide had been reportedly known since 1885 as the product of the reaction between hydrogen peroxide and salts of thorium in solution (de Boisbaudran, 1885). The precipitate that forms can be a dense solid or a gelatinous paste. The solid has initially been described in the literature as hydrated thorium peroxide, 'Th_2O_7' (de Boisbaudran, 1885; Pissarsjewski, 1900; Schwarz and Giese, 1928). The existence of peroxide species was confirmed but it was pointed out that the respective anions of the initial thorium salt are part of the solid (Clève, 1885; Wyrouboff and Verneuil, 1898a; Hamaker and Koch, 1952a,b; Johnson *et al.*, 1965; Hasty and Boggs, 1971; Raman and Jere, 1973a,b; Jere and Santhamma, 1977). XRD studies revealed two phases if the precipitation occurs from thorium sulfate solution: $Th(OO)SO_4 \cdot 3H_2O$ precipitated from solutions of high H_2SO_4 concentration and a second phase is obtained from more weakly acidic solutions with a variable sulfate content and 3.0–3.8 peroxide oxygen atoms per thorium atom (Hamaker and Koch, 1952a). A Raman analysis of $Th(OO)SO_4 \cdot 3H_2O$ has been performed (Raman and Jere, 1973a,b) and suggests a formulation of the compound as 'tetraaquo-μ-peroxy-disulfatodithorium(IV)', with two bridging sulfato groups. Raman investigations have been also carried out for the peroxide obtained from a nitrate solution (Raman and Jere, 1973b). According to these measurements thorium peroxide nitrate showed a 'free' (D_{3h}) nitrate anion along with a bridging peroxide molecule between thorium atoms. However, also a nitrate-free peroxide has been obtained from the reaction of a refluxing aqueous solution of $Th(NO_3)_4 \cdot 4H_2O$, urea, and 30% hydrogen peroxide (Gantz and Lambert, 1957). The precipitate, described as a granular light blue-green powder, decomposes at 120°C to yield ThO_2 and water. Chemical analysis revealed a formula of $Th(OH)_3OOH$, equivalent to tin and zirconium analogs. The dried peroxide is insoluble in neutral solutions (aqueous) but is soluble in concentrated mineral acids. Thorium peroxide has also been reported by the action of hydrogen peroxide or sodium hypochlorite on thorium hydroxide, or by anodic oxidation of an alkaline thorium hydroxide suspension containing sodium chloride (Pissarsjewsky, 1902).

Like the double salts of the halides, thorium dioxide will form a similar 'double salt' of oxide with BaO and alkali metal oxides (K_2O, for example) in phases such as $BaThO_3$ and K_2ThO_3 (Brunn and Hoppe, 1977); however, neither the Sr form nor the Li form of these structures have been reported (Hoffmann, 1935; Naray-Szabo, 1951; Scholder *et al.*, 1968; Fava *et al.*, 1971; Nakamura, 1974). No reaction was seen with BeO (Ohta and Sata, 1974) and, although there is solid solution formation with the rare earth oxides, no reaction to form the 'double salt' phase Ln_2ThO_5 has been observed (Diness and Roy, 1969; Sibieude, 1970). Because of the reactivity of ThO_2–CuO mixtures, reactions that have included other transition metal oxides have yielded a number of unique phases including tetragonal perovskite phases such as $La_{1-x}Th_xCoO_3$ (Tabata and Kido, 1987), $La_{1-1.333x}Th_xNiO_3$ (Yu *et al.*, 1992), $Na_{.6667}Th_{.3333}TiO_3$ (Zhu and Hor, 1995), and the Ruddlesden–Popper manganites $Ca_{3-x}Th_xMn_2O_7$ (Lobanov *et al.*, 2003).

3.7.4 Halides

(a) Binary halides

The halides of thorium had been treated comprehensively in 1968 by Brown (1968), and the fluorides in particular have been reviewed by Penneman *et al.* (1973) and Taylor (1976). In addition, a later volume of the *Gmelin Handbook* has discussed thorium halides (Gmelin, 1993a).

The tetrahalides of thorium are known for the whole halogen series (Table 3.7). Thorium fluoride, ThF_4, can be obtained by various procedures (Moissan and Martinsen, 1905; Duboin, 1908a; Chauvenet, 1911; Lipkind and Newton, 1952). Precipitation from aqueous Th^{4+}-containing solutions leads to hydrates of ThF_4 that are, however, not easily dehydrated due to the formation of hydroxide or oxide fluorides (Briggs and Cavendish, 1971). Under careful conditions, for example under streaming HF or F_2 gas, dehydration to pure ThF_4 is possible (Pastor and Arita, 1974). Alternative routes avoiding aqueous media are the reaction of thorium metal or thorium carbide with fluorine (Moissan and Étard, 1896, 1897), or the action of hydrogen fluoride on other thorium halides, thorium oxide or hydroxide, and thorium oxalate or oxide carbonate (Newton *et al.*, 1952a). As mentioned in the Section 3.7.1, the reaction of thorium hydrides with fluorine provides a route to ThF_4 (Lipkind and Newton, 1952). An elegant way to obtain pure ThF_4 is the reaction of ThO_2

Table 3.7 *Crystallographic data of binary thorium halides.*

		Lattice parameters				
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
ThF_4	C2/c	13.049	11.120	8.538	$\beta = 126.31$	Benner and Müller (1990)
β-$ThCl_4$	$I4_1$/amd	8.491		7.483		Brown *et al.* (1973)
α-$ThCl_4$	$I4_1$/a	6.408		12.924		Mason *et al.* (1974a)
β-$ThBr_4$	$I4_1$/amd	8.971		7.912		Madariaga *et al.* (1993)
α-$ThBr_4$	$I4_1$/a	6.737		13.601		Mason *et al.* (1974b)
ThI_4	$P2_1$/n	13.216	8.068	7.766	$\beta = 98.68$	Zalkin *et al.* (1964)
β-ThI_3	Cccm	8.735	20.297	14.661		Beck and Strobel (1982)
β-ThI_2	$P6_3$/mmc	3.97		31.75		Guggenberger and Jacobson (1968)

with NH_4HF_2. Ammonium hydrogen fluoride serves as the fluorinating agent and is much easier to handle than hydrogen fluoride itself. The reaction yields the ternary fluoride NH_4ThF_5 that decomposes above 300°C to the tetrafluoride (Asprey and Haire, 1973). The disadvantage of the method compared to the direct hydrofluorination is that an eight-fold excess of NH_4HF_2 is needed.

The monoclinic crystal structure of ThF_4 is isotypic with those of zirconium and hafnium fluoride and contains Th^{4+} ions in slightly distorted square antiprismatic coordination of fluoride ions (Zachariasen, 1949a; Asprey and Haire, 1973; Benner and Müller, 1990). Each of the fluorine atoms is attached to another thorium ion, leading to a three-dimensional structure according to $^3_\infty[ThF_{8/4}]$. Surprisingly, the thorium fluoride hydrate that can be precipitated from aqueous solution (Berzelius, 1829; Chydenius, 1863) has not been structurally characterized up to now. It is believed to be an octahydrate, which decomposes to a tetrahydrate on further drying and then finally to a dihydrate on heating (Chauvenet, 1911). The only hydrate of ThF_4 that is structurally known is $Th_6F_{24}{\cdot}H_2O$ ($=ThF_4{\cdot}1/6H_2O$) (Cousson *et al.*, 1978). Similarly to the anhydrous fluoride it consists of three-dimensionally connected square antiprisms $[ThF_8]$. Six of these aniprisms are arranged in a way that empty voids are formed in which the water molecule resides having contact to two of the six Th^{4+} ions (Fig. 3.7). It is assumed that this compound can be obtained by

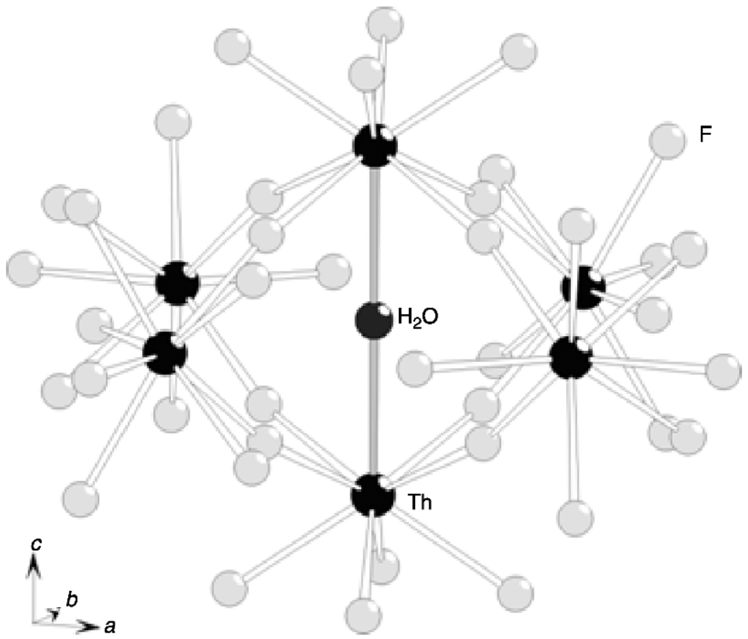

Fig. 3.7 *Detail of the crystal structure of $Th_6F_{24}{\cdot}H_2O$; the H_2O molecule resides in a void formed by six square antiprismatic $[ThF_8]$ polyhedra.*

careful dehydration of higher hydrates but usually hydrolysis is observed yielding $Th(OH)F_3 \cdot H_2O$ and then finally $ThOF_2$ (Marden and Rentschler, 1927; Zachariasen, 1949a; D'Eye, 1958). The structure of neither of the latter two compounds is known without some question. For $ThOF_2$, however, an orthorhombic unit cell has been determined, which has a close relationship to the hexagonal one of LaF_3. Probably the structure can be seen as an ordering variant of the LaF_3-type of structure. The treatment of $ThOF_2$ with steam at 900°C will yield thoria (Chydenius, 1863; Cline *et al.*, 1944).

Thorium tetrachloride, $ThCl_4$, can be crystallized from aqueous solution as an octahydrate, which is easily transformed to basic chlorides upon heating above 100°C (Chauvenet, 1911; Dergunov and Bergman, 1948; Knacke *et al.*, 1972a,b). Dehydration has also been done by refluxing the hydrates with thionyl chloride but the product was hard to get free of $SOCl_2$. Other routes have been employed to produce pure $ThCl_4$ (Chydenius, 1863) including the reaction of ThH_4 with HCl and the action of chlorine on thorium metal (Krüss and Nilson, 1887a; Lipkind and Newton, 1952), ThH_4, or thorium carbide (Nilson, 1876, 1882a,b, 1883; Moissan and Étard, 1896, 1897; von Wartenberg, 1909). Furthermore mixtures of chlorine and carbon or S_2Cl_2 were used for the chlorination of ThO_2 (Matignon and Bourion, 1904; Meyer and Gumperz, 1905; Bourion, 1909; von Wartenberg, 1909; Yen *et al.*, 1963), and also carbon tetrachloride (Matignon and Delepine, 1901; von Bolton, 1908; Knacke *et al.*, 1972a), phosgene (Baskerville, 1901; Karabasch, 1958), and phosphorus pentachloride (Smith and Harris, 1895; Matignon, 1908) were applied as chlorinating agents and mixtures of chlorine and CO or CO_2 for the chlorination of thorium oxalate and nitrate, respectively (Dean and Chandler, 1957). A facile synthesis of $ThCl_4$ is provided in the reaction of thorium metal with NH_4Cl in sealed tubes (Schleid *et al.*, 1987). Purification of $ThCl_4$ can be achieved by sublimation. $ThCl_4$ melts at 770°C (Moissan and Martinsen, 1905; Fischer *et al.*, 1939) and boils at 921°C. The results of vapor pressure measurements as a function of the temperature have been compiled (Fuger *et al.*, 1983).

$ThCl_4$ is dimorphic and exhibits a phase transition at 405°C (Mooney, 1949; Mucker *et al.*, 1969; Mason *et al.*, 1974a). The phase transition can only be observed under special conditions and in very pure samples. Usually the high-temperature phase β-$ThCl_4$ remains even at temperatures below 405°C as a metastable compound. Both the low-temperature phase α-$ThCl_4$ and the high-temperature phase β-$ThCl_4$ are tetragonal and show eight-fold coordinated Th^{4+} ions. The coordination polyhedra are slightly distorted dodecahedra that are connected via four edges to a three-dimensional structure. Thus, each of the chloride ligands are connected to two Th^{4+} ions. The difference in the two polymorphs results from small differences in the orientation of the $[ThCl_8]$ polyhedra with respect to each other (Fig. 3.8). The symmetry decreases from $I4_1/amd$ for β-$ThCl_4$ to $I4_1/a$ for α-$ThCl_4$. The two modifications of $ThCl_4$ are related in much the same way as are zicon ($ZrSiO_4$) and scheelite ($CaWO_4$).

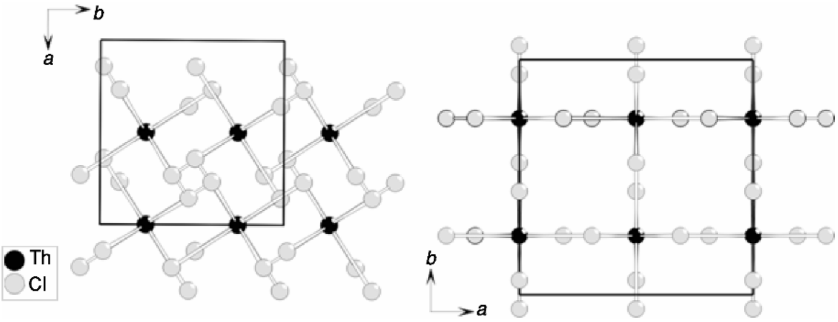

Fig. 3.8 *Projections of the crystal structures of* α*-ThCl*$_4$ (*right*) *and* β*-ThCl*$_4$ (*left*) *onto* (001).

In fact the structures of $ThCl_4$ result if the atoms in the tetrahedral centers (Si and W, respectively) are removed in the oxo-compounds. More recent investigations gave some evidence that there is a third modification of $ThCl_4$ below 70 K that has a complicated incommensurate structure related to that of α-$ThCl_4$ (Khan Malek *et al.*, 1982; Bernard *et al.*, 1983; Krupa *et al.*, 1987).

Structural data of $ThCl_4$ hydrates are not known up to now but the enthalpies of formation of the di-, tetra-, hepta- and octahydrates have been evaluated (Fuger *et al.*, 1983) from enthalpy of solution measurements (Chauvenet, 1911). Also the basic chlorides that are frequently observed as the products of the thermal treatment of the hydrates are poorly investigated (Bagnall *et al.*, 1968). It is only for the oxychloride $ThOCl_2$ that lattice parameters have been calculated from powder diffraction data based on the data given for $PaOCl_2$ (Bagnall *et al.*, 1968). The heat of formation of $ThOCl_2$ has been reported several times (Yen *et al.*, 1963; Korshunov and Drobot, 1971; Knacke *et al.*, 1972b; Fuger *et al.*, 1983) and will be discussed in proper context in Chapter 19. Chlorides of lower-valent thorium have been reported to form by electrochemical reduction of a $ThCl_4$/KCl melt (Chiotti and Dock, 1975) but these observations are still in need of confirmation.

Analogous to the tetrachloride, $ThBr_4$ can be obtained from aqueous solution, for example, by adding $Th(OH)_4$ to aqueous HBr. Depending on the drying conditions various hydrates may form. The main disadvantage of the wet route for preparing $ThBr_4$ is the contamination of the product with hydrolysis products like $ThOBr_2$. Dry routes to $ThBr_4$ include the action of bromine on thorium metal, ThH_4, ThC, or on mixtures of ThO_2 and C (Nilson, 1876; Troost and Ouvrard, 1889; Moissan and Étard, 1896, 1897; Matthews, 1898; Moissan and Martinsen, 1905; Fischer *et al.*, 1939; Young and Fletcher, 1939; Lipkind and Newton, 1952). Moreover, the reaction of gaseous HBr with ThH_4 (Lipkind and Newton, 1952) and of a mixture of S_2Cl_2 and gaseous HBr with ThO_2 have been employed (Bourion, 1907). Sublimation above 600°C in vacuum should be applied for purification. The temperature dependence of the vapor pressure has been investigated (Fischer *et al.*, 1939) and melting (679°C) and boiling (857°C) points have been reported (Fischer *et al.*, 1939; Mason *et al.*, 1974b).

As found for the tetrachloride, $ThBr_4$ is also dimorphic (D'Eye, 1950; Brown *et al.*, 1973; Fuger and Brown, 1973; Mason *et al.*, 1974b; Guillaumont, 1983). Both modifications, β-$ThBr_4$ and α-$ThBr_4$, are isotypic to the respective chlorides. The transition temperature is slightly higher compared to $ThCl_4$ and is determined to be 426°C. Again, the β-phase is found to remain metastable even below 426°C. The phase transition has been investigated in detail by means of nuclear quadrupolar resonance (NQR) on the ^{79}Br isotope (Kravchenko *et al.*, 1975). According to these experiments, the time to achieve complete conversion is strongly dependent on the previous treatment of the sample and is reduced after one conversion cycle has passed. Analogous to $ThCl_4$ another phase transition is found at lower temperature. According to NQR and electron paramagnetic resonance (EPR) measurements as well as neutron and X-ray diffractions, the transition is second order and occurs at 92 K (Kravchenko *et al.*, 1975). It is only observed in β-$ThBr_4$ and can be described as a continuous modulation of the bromide ions along the *c*-axis, leading to a complicated incommensurate structure (Madariaga *et al.*, 1993). The incommensurate low-temperature modifications of $ThBr_4$ and $ThCl_4$ have also been investigated spectroscopically on U^{4+}-doped samples (Krupa *et al.*, 1995).

There are two reports on the low-valent thorium bromides, $ThBr_3$ and $ThBr_2$ (Hayek and Rehner, 1949; Shchukarev *et al.*, 1956). They have been prepared from the elements in the desired molar ratio or, in the case of $ThBr_3$, by reduction of $ThBr_4$ with hydrogen. These bromides are highly reactive and show disproportionation at higher temperatures. Unfortunately no structural data are known. More recently the molecular species, $ThBr_3$, $ThBr_2$ and ThBr, have been identified by mass spectrometry in the bromination of thorium between 1500 and 2000 K (Hildenbrand and Lau, 1990).

None of the various hydrates of $ThBr_4$ that have been reported to contain 12, 10, 8, and 7 molecules of water, respectively (Lesinsky and Gundlich, 1897; Rosenheim and Schilling, 1900; Rosenheim *et al.*, 1903; Moissan and Martinsen, 1905; Chauvenet, 1911), are well characterized to date. The heat of solution has been determined in some cases and the thermal decomposition of the hydrates is known to lead to $Th(OH)Br_3$ and finally to $ThOBr_2$ (Chauvenet, 1911). The powder diffraction pattern of the oxybromide shows that this compound is not isotypic with $ThOCl_2$ but seems to have a lower symmetry (Bagnall *et al.*, 1968). $ThBr_4$ is also known to form solvates with amines (Rosenheim and Schilling, 1900; Rosenheim *et al.*, 1903), acetonitrile (Young, 1935), and trimethylphosphine (Al-Kazzaz and Louis, 1978).

Thorium tetraiodide (ThI_4) is most conveniently prepared by the reaction of the elements in sealed silica ampoules (Nilson, 1876; Moissan and Étard, 1896, 1897; Zalkin *et al.*, 1964). It is very important to exclude any traces of water or oxygen during the reaction to avoid contamination of the product with $ThOI_2$ or even ThO_2. Alternative procedures involve the reactions between ThH_4 and HI, and between thorium metal and a H_2/I_2 mixture (Lipkind and Newton, 1952). If only small amounts of ThI_4 are needed, the action of AlI_3 on ThO_2 might also be appropriate (Chaigneau, 1957). In the temperature range from 500 to 550°C, ThI_4 can be sublimed for purification under dynamic vacuum yielding yellow crystals. Knudsen cell effusion studies of ThI_4 have suggested dissociation through ThI_3, ThI_2, and ThI to thorium metal (Knacke *et al.*, 1978). On heating, ThI_4 reacts with ThO_2 to form the basic iodide $ThOI_2$ (Scaife *et al.*, 1965; Corbett *et al.*, 1969).

ThI_4 is not isotypic with the other tetrahalides. It has monoclinic symmetry and contains eight-fold coordinated Th^{4+} ions (Zalkin *et al.*, 1964). The coordination polyhedron can be seen as a distorted square antiprism. The polyhedra are linked in chains via two triangular faces leading to Th–Th distances of 4.48 Å. The chains are further connected via the two remaining iodine ligands into layers. The connectivity may be formulated as ${}^{2}_{\infty}[ThI^{f}_{6/2}I^{e}_{2/2}]$ (f = face; e = edge). These layers are held together only by van der Waals interactions (Fig. 3.9).

Two lower-valent thorium iodides, ThI_3 and ThI_2, are known. Both can be obtained by reduction reactions of ThI_4 with appropriate amounts of thorium metal in sealed tantalum tubes (Anderson and D'Eye, 1949; Hayek and Rehner, 1949; Hayek *et al.*, 1951; Clark and Corbett, 1963; Scaife and Wylie, 1964; Guggenberger and Jacobson, 1968). If hydrogen is used as the reducing reagent, the formation of iodide hydrides is observed (Struss and Corbett, 1978).

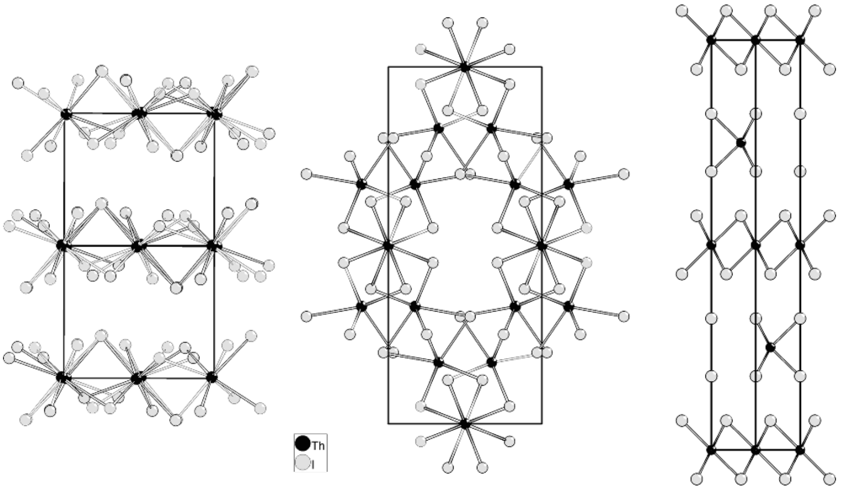

Fig. 3.9 *Crystal structures of the thorium iodides* ThI_4 (*left, as a projection onto the* (101) *plane*), β-ThI_3 (*middle, as a projection onto the* (001) *plane*), *and* β-ThI_2 (*right, as a projection onto the* (110) *plane*).

For the preparation of ThI_2, another route has been developed. The electrolysis of thorium metal in a solution of iodine and tetraethyl ammonium perchlorate in acetonitrile affords $ThI_2 \cdot 2CH_3CN$ that can be decomposed into ThI_2 *in vacuuo* (Kumar and Tuck, 1983).

Depending on the time, the reaction of ThI_4 and Th leads to two modifications of ThI_3 (Beck and Strobel, 1982). After a short period of 2–3 days, thin shiny rods of α-ThI_3 were obtained while long heating times led to compact crystals of β-ThI_3 that show a slight green to brass-colored luster. For α-ThI_3 only the lattice constants are known while a complete structure determination has been performed for β-ThI_3 (Beck and Strobel, 1982). It shows three crystallographically different thorium atoms in the unit cell, each of them in an eightfold coordination of iodide ions. Two of the $[ThI_8]$ polyhedra are square antiprismatic, the third one is a slightly elongated cube. The $[ThI_8]$ cubes are connected via four rectangular faces to $[ThI_8]$ square antiprisms (Fig. 3.9). One half of the square antiprisms is further connected to other cubes and, the second half to other square antiprisms, leading to a three-dimensional network. The Th–I bond distances suggest that thorium is in the tetravalent state in ThI_3 and has to be formulated according to $Th^{4+}(I^-)_3(e^-)$ with the electrons delocalized or involved in metal–metal bonds. The latter assumption is supported by the relatively short Th–Th distances of 3.46 to 3.80 Å.

ThI_2 is also found to adopt two different crystal structures (Clark and Corbett, 1963; Scaife and Wylie, 1964). Lustrous gold crystals of β-ThI_2 are obtained at 700 to 850°C while α-ThI_2 forms at 600°C. Both compounds are hexagonal but a structure determination has been performed only for β-ThI_2 (Guggenberger and Jacobson, 1968). The structure can be seen as a stacking variant of the CdI_2 structure (Fig. 3.9). It has a remarkable long *c*-axis (31 Å) and the stacking sequence of the iodide ions is ...ABCCBA... with the thorium atoms in octahedral and trigonal prismatic sites (Fig. 3.9). Judging from the Th–I bond distances, Th^{4+} is present in the structure and the free electrons, according to $Th^{4+}(I^-)_2(e^-)_2$, should be responsible for the electrical conductivity of the compound. The metal–metal distances, however, are remarkably longer than those found in ThI_3. Both subiodides, ThI_3 and ThI_2, exhibit peritectic decomposition above 850°C caused by disproportionations to ThI_4 and ThI_2 or ThI_4 and Th, respectively (Scaife and Wylie, 1964).

The formation of pseudo-halides of thorium (such as thiocyanate or selenocyanate) in organic solvents has been reported, but up to now, no binary compound is known (Golub and Kalibabchuk, 1967; Laubscher and Fouché, 1971; Golub *et al.*, 1974).

(b) Polynary halides

The systems AF/ThF_4, where A is an alkali or another monovalent metal ion, have been widely investigated (Brunton *et al.*, 1965). Phase diagrams of the

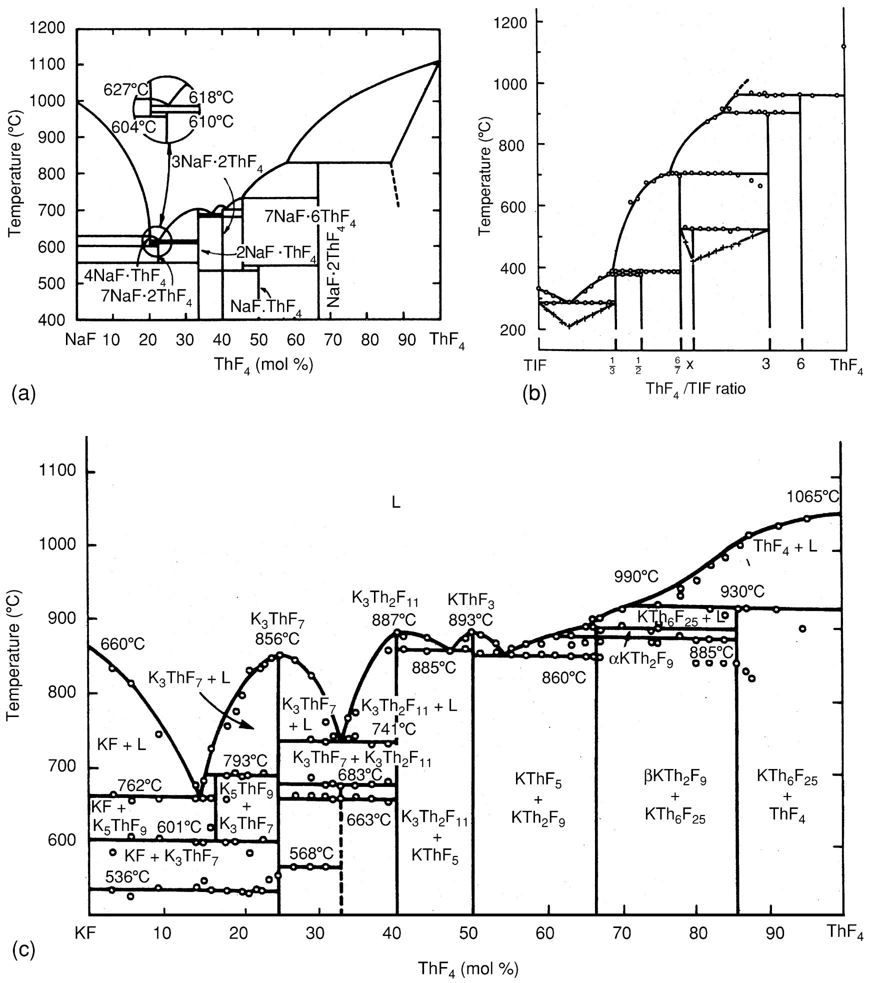

Fig. 3.10 *Phase diagrams of three AF/ThF$_4$ systems.* (*a*) *NaF/ThF$_4$* (*Thoma,* 1972). (*b*) *TlF/ThF$_4$* (*Avignant and Cousseins,* 1970). (*c*) *KF/ThF$_4$* (*Kaplan,* 1956).

systems NaF/ThF$_4$ (Thoma, 1972), KF/ThF$_4$ (Kaplan, 1956), and TlF/ThF$_4$ (Avignant and Cousseins, 1970) are given as examples in Fig. 3.10. Furthermore, the binary and also some ternary phase diagrams of ThF$_4$ with several other fluorides were determined. Table 3.8 surveys the phases that are reported to exist along with those found in the other halide systems. Unfortunately, only very few of these phases have been carefully characterized. In some cases lattice parameters of the compounds were determined by powder diffraction; moreover,

Table 3.8 *Detected phases in the systems with* ThX_4 ($X = F, Cl, Br$).

System	*Compounds*	*References*
$LiF–ThF_4$	Li_3ThF_7, $LiThF_5$, $LiTh_2F_9$, $LiTh_4F_{17}$	Thoma and Carlton (1961)
$NaF–ThF_4$	Na_4ThF_8, Na_3ThF_7, Na_2ThF_6, $Na_3Th_2F_{11}$, $Na_7Th_6F_{31}$, $NaThF_5$, $NaTh_2F_9$	Thoma and Carlton (1961); Thoma (1972); Brunton *et al.* (1965)
$KF–ThF_4$	K_5ThF_9, K_2ThF_6, $K_7Th_6F_{31}$, $KThF_5$, KTh_2F_9, KTh_6F_{25}	Thoma and Carlton (1961); Dergunov and Bergman (1948); Harris (1960)
$RbF–ThF_4$	Rb_3ThF_7, Rb_2ThF_6, $Rb_7Th_6F_{31}$ $RbTh_3F_{13}$, $RbTh_6F_{25}$	Thoma and Carlton (1961); Dergunov and Bergman (1948)
$CsF–ThF_4$	Cs_3ThF_7, Cs_2ThF_6, $CsThF_5$, $Cs_2Th_3F_{14}$, $CsTh_2F_9$, $CsTh_3F_{13}$, $CsTh_6F_{25}$	Thoma and Carlton (1961); Brunton *et al.* (1965)
$NH_4F–ThF_4$	$(NH_4)_4ThF_8$, $(NH_4)_3ThF_7$, $(NH_4)_2ThF_6$	Ryan *et al.* (1969); Penneman *et al.* (1971, 1976, 1968)
$N_2H_5F–ThF_4$	$(N_2H_5)_3ThF_7$, $(N_2H_5)ThF_5$	Glavic *et al.* (1973); Sahoo and Patnaik (1961)
$NH_3OH–ThF_4$	$(NH_3OH)ThF_4$	Satpathy and Sahoo (1968); Rai and Sahoo (1974)
$TlF–ThF_4$	Tl_3ThF_7, Tl_2ThF_6, $Tl_7Th_6F_{31}$, $TlThF_5$, $TlTh_3F_{13}$, $TlTh_6F_{25}$	Avignant and Cousseins (1970); Keller and Salzer (1967)
$LiCl–ThCl_4$	Li_4ThCl_8	Vdovenko *et al.* (1974)
$NaCl–ThCl_4$	$NaThCl_5$	Vdovenko *et al.* (1974)
$KCl–ThCl_4$	K_3ThCl_7, K_2ThCl_6, $KThCl_5$	Gershanovich and Suglobova (1980)
$RbCl–ThCl_4$	Rb_3ThCl_7, Rb_2ThCl_6, $RbThCl_5$, $RbTh_{1.6}Cl_{5.6}$	Gershanovich and Suglobova (1980)
$CsCl–ThCl_4$	Cs_3ThCl_7, Cs_2ThCl_6, $CsThCl_5$, $CsTh_3Cl_{13}$	Gershanovich and Suglobova (1980)
$BaCl_2–ThCl_4$	Ba_3ThCl_{10}, $Ba_3Th_2Cl_{14}$	Gorbunov *et al.* (1974)
$NaBr–ThBr_4$	$NaThBr_5$	Gershanovich and Suglobova (1981)
$KBr–ThBr_4$	K_2ThBr_6	Gershanovich and Suglobova (1981)
$RbBr–ThBr_4$	Rb_2ThBr_6	Gershanovich and Suglobova (1981)
$CsBr–ThBr_4$	Cs_2ThBr_6	Gershanovich and Suglobova (1981)

careful structure determinations remain scarce. Known crystallographic data are summarized in Table 3.9.

In the system LiF/ThF_4 four compounds are known to exist (Brown, 1968; Cousson *et al.*, 1977; Penneman *et al.*, 1973; Taylor, 1976), namely Li_3ThF_7, $LiThF_5$, $LiTh_2F_9$, and $LiTh_4F_{17}$. A complete structure analysis has been done for only one of these phases, namely Li_3ThF_7 (Cousson *et al.*, 1978;

Table 3.9 *Crystallographic data of polynary thorium halides (in italics: powder data).*

		Lattice parameters				
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
Li_3ThF_7	Ccca	8.788	8.768	12.958		Laligant *et al.* (1989)
Li_3ThF_7	$P4/ncc$	6.206		12.940		Cousson *et al.* (1978); Laligant *et al.* (1992)
$\mathit{LiThF_5}$	$\mathit{I4_1/a}$	*15.10*		*6.60*		Keenan (1966)
$\mathit{LiTh_2F_9}$	*tetragonal*	*11.307*		*6.399*		Harris *et al.* (1959)
$\alpha\text{-}(Na_2ThF_6)_{1.333}$	$Fm\bar{3}m$	5.687				Zachariasen (1949a)
$\beta_2\text{-}Na_2ThF_6$	P321	5.989		3.835		Zachariasen (1948a)
$\delta\text{-}\mathit{Na_2ThF_6}$	*hexagonal*	*6.14*		*7.36*		Zachariasen (1948b)
$NaTh_2F_9$	$I\bar{4}3m$	8.722				Zachariasen (1948a, 1949b)
$\mathit{Na_4ThF_8}$	*cubic*	*12.706*				Zachariasen (1948b)
$\mathit{Na_7Th_6F_{31}}$	$\mathit{R\bar{3}}$	*14.96*		*9.912*		Keenan (1966)
$Na_3Li_4Th_6F_{31}$	P3c1	9.906		13.282		Brunton and Sears (1969)
$Na_3BeTh_{10}F_{45}$	$P4_2/ncm$	11.803		23.420		Brunton (1973)
$Na_3ZnTh_6F_{29}$	P321	10.166		13.255		Cousson *et al.* (1979b)
Li_2CaThF_8	$I\bar{4}m2$	5.109		11.013		Vedrine *et al.* (1973)
$KNaThF_6$	$P\bar{3}$	6.307		7.891		Brunton (1970)
$\alpha\text{-}(K_2ThF_6)_{1.333}$	$Fm\bar{3}m$	5.994				Zachariasen (1948b, 1949a)
$\beta\text{-}K_2ThF_6$	$P\bar{6}2m$	6.578		3.822		Zachariasen (1948a)
K_5ThF_9	$Cmc2_1$	7.848	10.840	12.785		Ryan and Penneman (1971)
$K_7Th_6F_{31}$	$R\bar{3}$	15.293		10.449		Brunton (1971a)
KTh_6F_{25}	$R\bar{3}m$	8.313		25.262		Brunton (1972)
$RbTh_3F_{13}$	$P2_1ma$	8.649	8.176	7.445		Brunton (1971b)
$\mathit{Rb_3ThF_7}$	$\mathit{Fm\bar{3}m}$	*9.62*				Dergunov and Bergman (1948)
$\mathit{Rb_2ThF_6}$	$\mathit{P\bar{6}2m}$	*6.85*		*3.83*		Harris (1960)
$\mathit{Rb_7Th_6F_{31}}$	$\mathit{R\bar{3}}$	*9.58*			$\alpha = 106.9^{a}$	Brunton *et al.* (1965)
$\mathit{RbTh_6F_{25}}$	$\mathit{R\bar{3}m}$	*8.330*		*25.40*		Brunton *et al.* (1965)
$\mathit{Cs_3ThF_7}$	$\mathit{Fm\bar{3}m}$	*10.04*				Brunton *et al.* (1965)
$\mathit{CsTh_6F_{25}}$	$\mathit{P6_3/mmc}$	*8.31*		*16.91*		Brunton *et al.* (1965)

Table 3.9 (*Contd.*)

Compound	*Space group*	*Lattice parameters* *a* (Å)	 *b* (Å)	 *c* (Å)	 *Angles* (°)	*References*
$(NH_4)_4ThF_8$	$P\bar{1}$	8.477	8.364	7.308	$\alpha = 88.38$ $\beta = 96.08$ $\gamma = 106.33$	Ryan *et al.* (1969)
$(NH_4)_3ThF_7$	Pnma	13.944	7.928	7.041		Penneman *et al.* (1971)
$(NH_4)_7Th_2F_{15}\cdot H_2O$	$P2_13$	12.573				Penneman *et al.* (1968)
Tl_3ThF_7	$P2_1/m$	9.793	8.464	10.712	$\beta = 117.20$	Gaumet *et al.* (1995)
$\mathit{Tl_7Th_6F_{31}}$	$R\bar{3}$	*15.60*		*10.84*		Avignant and Cousseins (1970)
$\mathit{TlTh_6F_{25}}$	$P6_3/mmc$	*8.31*		16.86		Avignant and Cousseins (1970)
$(SmTh_2F_{11})_{1.333}$	Pnma	8.610	4.137	7.225		Abaouz *et al.* (1997)
Zr_2ThF_{12}	I2/m	9.895	10.488	7.856		Taoudi *et al.* (1996)
$\mathit{CaThF_6}$		*6.994*		*7.171*		Keller and Salzer (1967); Salzer (1966)
$\mathit{SrThF_6}$		*7.150*		*7.313*		Keller and Salzer (1967); Salzer (1966)
$\mathit{BaThF_6}$		*7.419*		*7.516*		Keller and Salzer (1967); Salzer (1966)
$\mathit{CdThF_6}$		*6.963*		*7.109*		Keller and Salzer (1967); Salzer (1966)
$\mathit{PbThF_6}$		*7.245*		*7.355*		Keller and Salzer (1967); Salzer (1966)
$\mathit{EuThF_6}$		*7.124*		*7.360*		Keller and Salzer (1967); Salzer (1966)
Cs_2ThCl_6	$P\bar{3}m1$	7.614		6.038		Siegel (1956)
$\mathit{K_2ThCl_6}$	*Orthorh.*	*8.16*	*14.13*	*8.62*		Gershanovich and Suglobova (1981)
$\mathit{Rb_2ThCl_6}$	*Orthorh.*	*8.31*	*14.39*	*8.74*		Gershanovich and Suglobova (1981)
In_2ThBr_6	C2/c	8.791	14.670	9.046	$\beta = 91.15$	Dronskowski (1995)
$\mathit{K_2ThBr_6}$	*trigonal*	*7.52*		*11.80*		Siegel (1956); Gershanovich *et al.* (1981);
	tetragonal	*11.478*		*7.94*		Brunton *et al.* (1965)
$\mathit{Rb_2ThBr_6}$	trigonal	*7.58*		*12.24*		Gershanovich and Suglobova (1981)

Cs_2ThBr_6	*tetragonal*	*11.37*		*10.69*	Siegel (1956); Gershanovich and Suglobava (1981)
	trigonal	*9.537*		*8.10*	Brunton *et al.* (1965)
$\mathrm{CaThBr_6}$	Pmma	9.764	4.109	12.104	Beck and Kühn (1995)
$\mathrm{SrThBr_6}$	Pmma	9.878	4.286	12.255	Beck and Kühn (1995)
$\mathrm{BaThBr_6}$	Pmma	9.992	4.490	12.526	Beck and Kühn (1995)
$SnThBr_6$	*Pmma*	*9.143*	*4.209*	*12.716*	Beck *et al.* (1993)
$PbThBr_6$	*Pmma*	*9.191*	*4.228*	*12.68*	Beck *et al.* (1993)
$\mathrm{FeTh_6Br_{15}}$	Im$\bar{3}$m	11.488			Böttcher *et al.* (1991a)
$\mathrm{CoTh_6Br_{15}}$	Im$\bar{3}$m	11.507			Böttcher *et al.* (1991a)
$\mathrm{NaFeTh_6Br_{15}}$	Im$\bar{3}$m	11.605			Böttcher *et al.* (1991a)
$\mathrm{Th_6Br_{15}H_7}$	Im$\bar{3}$m	11.390			Böttcher *et al.* (1991a)
$\mathrm{Th_6Br_{15}D_7}$	Im$\bar{3}$m	11.376			Böttcher *et al.* (1991a)
$\mathrm{Th_6H_7Br_{15}}$	Im$\bar{3}$m	11.470			Böttcher *et al.* (1991b)
$\mathrm{Th_6D_7Br_{15}}$	Im$\bar{3}$m	11.376			Böttcher *et al.* (1991b)
$\mathrm{Th_6Br_{14}C}$	Cmca	15.764	14.160	13.123	Böttcher *et al.* (1991)
$\mathrm{K(Th_{12}N_6Br_{29})}$	Pnnm	17.524	11.943	14.031	Braun *et al.* (1995)
ThNI	P4/nmm	4.107		9.242	Juza and Sievers (1968)
$\beta\text{-}\mathrm{PbThI_6}$	P$\bar{3}$1c	7.748		13.789	Beck *et al.* (1993)
$\gamma\text{-}\mathrm{PbThI_6}$	Cmcm	4.387	13.956	10.005	Beck *et al.* (1993)
$\beta\text{-}\mathrm{SnThI_6}$	P$\bar{3}$1c	7.748		13.789	Beck *et al.* (1993)
$\beta\text{-}PbGeI_6$	*P*$\bar{3}$*1c*	*7.526*		*13.783*	Beck *et al.* (1993)
$\beta\text{-}CaThI_6$	*P*$\bar{3}$*1c*	*7.697*		*13.959*	Beck *et al.* (1993)
$\gamma\text{-}GeThI_6$	*Cmcm*	*4.248*	*13.92*	*9.991*	Beck *et al.* (1993)
$\gamma\text{-}SnThI_6$	*Cmcm*	*4.376*	*13.937*	*9.995*	Beck *et al.* (1993)
$\gamma\text{-}CaThI_6$	*Cmcm*	*4.278*	*14.02*	*10.10*	Beck *et al.* (1993)
$\gamma\text{-}SrThI_6$	*Cmcm*	*4.455*	*13.991*	*10.052*	Beck *et al.* (1993)
$\gamma\text{-}BaThI_6$	*Cmcm*	*4.685*	*13.76*	*10.015*	Beck *et al.* (1993)
$\gamma\text{-}EuThI_6$	*Cmcm*	*4.420*	*13.964*	*10.038*	Beck *et al.* (1993)

[a] rhombohedral setting.

Laligant *et al.*, 1989; Pulcinelli and de Almeida Santos, 1989). It is dimorphic but the linkage of the monocapped square antiprisms [ThF_9] is the same in the two modifications. They are connected via two common edges to layers according to the formulation $^{2}_{\infty}[ThF^{e}_{4/2}F^{t}_{5/1}]$ (e = edge, t = terminal). The layers are stacked along the *c*-axis. The different symmetry of the two modifications arises from the different positions of the Li^+ ions in the interlayer spacings, and their positions are temperature-dependent, making the compound a good ionic conductor (Laligant *et al.*, 1992). According to powder diffraction measurements, $LiThF_5$ is isotypic with $LiUF_5$ and contains a three-dimensional network of vertex-connected monocapped square antiprisms [ThF_9] that incorporate the Li^+ in a six-fold coordination (Keenan, 1966). The lattice parameter of the other two fluorides have been obtained by powder XRD (Harris *et al.*, 1959; Cousson *et al.*, 1978).

The system NaF/ThF_4 shows the formation of seven compounds (Table 3.8) (Rosenheim *et al.*, 1903; Dergunov and Bergman, 1948; Brunton *et al.*, 1965; Kaplan, 1956; Ryan and Penneman, 1971; Thoma, 1972). Na_2ThF_6 may either be cubic (α-Na_2ThF_6) or trigonal (β_2-Na_2ThF_6) (Table 3.9). The cubic modification is a variant of the CaF_2-type of structure with Na^+ and Th^{4+} occupying Ca^{2+} sites in a disordered fashion (Zachariasen, 1949b). The trigonal structure of Na_2ThF_6 is very similar to the structure of LaF_3 and contains both the Na^+ and the Th^{4+} ions in tricapped trigonal prismatic coordination of fluoride anions (Zachariasen, 1948b). The polyhedra are connected via triangular faces in the [001] direction and via common edges in the (001) plane. A third modification, δ-Na_2ThF_6, has been reported to be also trigonal but has not been proved yet (Zachariasen, 1948c; Penneman *et al.*, 1973). In $NaTh_2F_9$ the Th^{4+} are nine-fold coordinated by F^- ions. The polyhedra are connected via vertices according to $^{3}_{\infty}[ThF_{9/2}]^{-0.5}$ to a three-dimensional network with the Na^+ ions incorporated for charge compensation (Zachariasen, 1948b, 1949a). In the complex structure of $Na_7Th_6F_{31}$ nine- and ten-fold coordinated Th^{4+} ions are present (Keenan, 1966; Penneman *et al.*, 1973).

An X-ray structure analysis is available for all of the six compounds that exist in the KF/ThF_4 system (Kaplan, 1956), except for $KThF_5$ (Table 3.9). α_1-K_2ThF_6 is isotypic with the respective sodium compound, while a slight difference is found between β_1-K_2ThF_6 and β_1-Na_2ThF_6 (Zachariasen, 1948c; Ryan and Penneman, 1971). The Th/F sublattice is the same in the two compounds, however, in the former the K^+ ions are located in tricapped trigonal prismatic voids, in the latter, Na^+ occupies octahedral sites. The complex fluoride $K_7Th_6F_{31}$ (Zachariasen, 1948c; Brunton, 1971a) shows isotypism to the sodium compound. K_5ThF_9, which has also been prepared from aqueous media (Wells and Willis, 1901), consists of monomeric distorted square antiprismatic $[ThF_8]^{4-}$ anions that are connected via K^+ ions (Ryan and Penneman, 1971). Furthermore there are isolated F^- ions in the structure that are not bonded to Th^{4+}. The structure of KTh_6F_{25} is a polymorph of the CsU_6F_{25}-type with the Th^{4+} ions in nine-fold coordination by fluoride ions (Brunton, 1972).

The tricapped trigonal prismatic polyhedra are linked via shared edges and vertices. The resulting three-dimensional network incorporates the K^+ ions in voids. Finally, a mixed sodium potassium fluoride is known: $NaKThF_6$ (Brunton, 1970).

Among the compounds found in the RbF/ThF_4 system (Dergunov and Bergman, 1948; Thoma and Carlton, 1961), Rb_2ThF_6, $Rb_7Th_6F_{31}$ and $RbTh_6F_{25}$ are isotypic to their respective potassium fluorides (Harris, 1960; Penneman *et al.*, 1973). Rb_3ThF_7 has the same cubic structure as K_3UF_7 and shows a highly disordered fluoride sublattice (Dergunov and Bergman, 1948).

The same is true for Cs_3ThF_7, which is one of the seven phases that are known to exist in the CsF/ThF_4 system (Thoma and Carlton, 1961; Penneman *et al.*, 1973). Unfortunately, lattice parameters are only available for one additional compound, $CsTh_6F_{25}$. It is isotypic to CsU_6F_{25} and can be seen as a polymorph of the KTh_6F_{25}-type wherein the Th^{4+} ions are in nine-fold and the Cs^+ ions in 12-fold coordination by fluoride ions (Brunton, 1971b; Penneman *et al.*, 1973).

Although the size of the ammonium ion is comparable to the radii of K^+ and Rb^+, the NH_4F/ThF_4 system contains only a few phases, namely $(NH_4)_2ThF_6$, $(NH_4)_3ThF_7$, and $(NH_4)_4ThF_8$ (Ryan *et al.*, 1969; Penneman *et al.*, 1971). The latter two have been structurally characterized. $(NH_4)_3ThF_7$ is not isotypic with the respective potassium or cesium compounds but crystallizes with orthorhombic symmetry (Penneman *et al.*, 1971). It contains chains of edge-sharing $[ThF_9]$ polyhedra with the formulation $^1_\infty[ThF_{4/2}F_{5/1}]$ that are separated by the NH_4^+ ions. Similar chains are found in the unique crystal structure of $(NH_4)_4ThF_8$. This latter compound contains, however, an additional fluoride ion that is not coordinated to any Th^{4+} so that it should be formulated as $(NH_4)_4[ThF_7]F$ (Ryan *et al.*, 1969).

As far as structural data are known, the compounds found in the TlF/ThF_4 system show a close relationship to the respective fluorides of the larger alkali metal ions (Avignant and Cousseins, 1970). Slight deviations may be observed as can be seen from the structure of Tl_3ThF_7 and are usually attributed to the stereochemical activity of the lone electron pair on Tl^+ (Gaumet *et al.*, 1995).

Several other systems with ThF_4 have been investigated with unusual components like N_2H_5F or even NH_3OH (Table 3.8) (Sahoo and Patnaik, 1961; Satpathy and Sahoo, 1968; Glavic *et al.*, 1973; Rai and Sahoo, 1974). Single crystal structures are not known in these cases. In addition, compounds with higher valent ions have been investigated. With divalent cations, a number of compounds are known that have essentially the LaF_3 structure type, wherein the La^{3+} positions are filled by Th^{4+} and the divalent cation, respectively (Zachariasen, 1949a; Keller and Salzer, 1967; Brunton, 1973). Anion-rich fluorides can be obtained when a small amount of Th^{4+} is doped in the CaF_2 lattice and complicated phases with severe disorder in the cation and anion lattice are described for lanthanide-containing compounds like $SmTh_2F_{11}$ (Abaouz *et al.*, 1997). Finally, the zirconium thorium fluoride $ThZr_2F_{12}$ is completely ordered and contains layers of vertex-shared $[ZrF_8]$ polyhedra that alternate with layers of Th^{4+} ions in nine-fold coordination by F^- ions (Taoudi *et al.*, 1996).

A few hydrates of ternary thorium fluorides are known. Probably the most remarkable hydrate has the composition $(NH_4)_7Th_2F_{15} \cdot H_2O$ (Penneman *et al.*, 1968, 1976) and contains the dimeric anion $[Th_2F_{15}(H_2O)]^{7-}$ in which the Th^{4+} ions are linked via three fluoride ions. Furthermore the lanthanide-containing phases $LaTh_4F_{19} \cdot H_2O$ and $ThEr_2F_{10} \cdot H_2O$ have been reported in which the lanthanide and the Th^{4+} ions occupy the same sites (Guery *et al.*, 1994; Le Berre *et al.*, 2000). Finally, the fluoride hydroxide $Li_3Th_5F_{22}OH$ should be mentioned, which incorporates the Li^+ ions in a three-dimensional network of $[ThF_9]$ and $[ThF_8OH]$ polyhedra (Cousson *et al.*, 1979a).

Polynary thorium fluorides with more than one additional cation have been rarely characterized (Table 3.9). Structural data are available for $Na_3Li_4Th_6F_{31}$ (Brunton and Sears, 1969), $KNaThF_6$ (Brunton, 1970), Li_2CaThF_8 (Vedrine *et al.*, 1973), $Na_3BeTh_{10}F_{45}$ (Brunton, 1973), and $Na_3ZnTh_6F_{29}$ (Cousson *et al.*, 1979b). $Na_3Li_4Th_6F_{31}$ has the same structure as $Na_7Th_6F_{31}$, with some of the Na^+ ions being substituted by Li^+. Similarly, the structure of $KNaThF_6$ is closely related to the structure of the potassium-only compound. Li_2CaThF_8 adopts the structure of $CaWO_4$, even if the symmetry is slightly different. The Li^+ ions occupy the tetrahedral positions of the tungsten atoms, while both Ca^{2+} and Th^{4+} are found on the calcium sites of $CaWO_4$. $Na_3BeTh_{10}F_{45}$ and $Na_3ZnTh_6F_{29}$ (Fig. 3.11) have crystal structures wherein the Th^{4+} ions are found mainly in an eight-fold coordination of fluoride ions (Brunton, 1973). The thorium polyhedra are linked in complicated three-dimensional networks

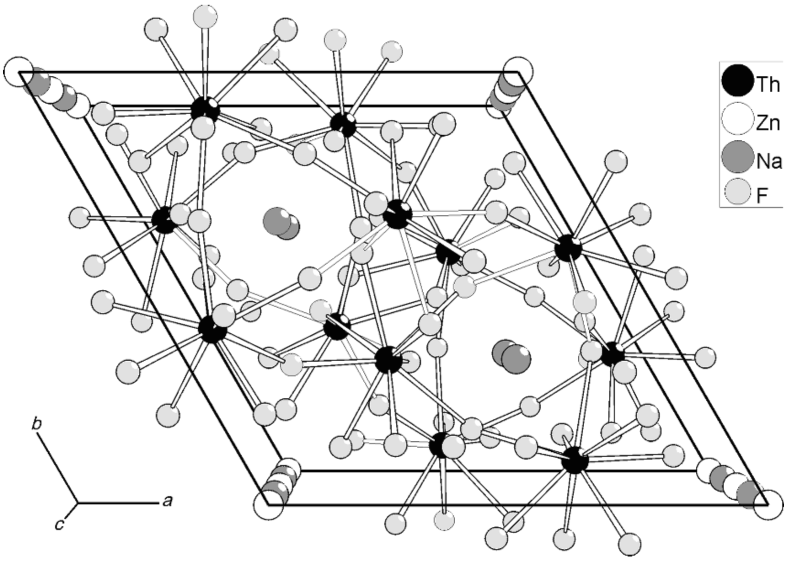

Fig. 3.11 *Crystal structure of the polynary* $Na_3ZnTh_6F_{29}$.

that incorporate the Na^+, Be^{2+}, and Zn^{2+} ions, respectively. The coordination number of the sodium ions range from six to eight. Be^{2+} is tetrahedrally coordinated, and Zn^{2+} is in the center of an octahedron.

Mixed chloride–fluorides, namely $LiThClF_4$, $CsTh_2ClF_8$, $SrThCl_2F_4$, and $BaThCl_2F_8$, have been reported but these compounds are in need of further characterization (Gudaitis *et al.*, 1972; Desyatnik *et al.*, 1974a,b).

Compared to the respective fluorides the number of well-characterized polynary thorium chlorides, bromides, or iodides is quite limited. According to phase diagram investigations containing $ThCl_4$, the compounds included in Table 3.8 are known to exist (Vdovenko *et al.*, 1974; Gershanovich and Suglobova, 1980). However, additional chlorides, which were not found in their respective phase diagrams, have been prepared by several authors (Rosenheim and Schilling, 1900; Rosenheim *et al.*, 1903; Chauvenet, 1911; Siegel, 1956; Ferraro, 1957; Adams *et al.*, 1963; Brown, 1966; Vokhmyakov *et al.*, 1973; Gorbunov *et al.*, 1974; Desyatnik and Emel'yanov, 1975). Unfortunately, the structure of only a few chlorides is known, all of them being exclusively hexachlorothorates containing the octahedral $[ThCl_6]^{2-}$ anion. Alkaline metal ions, Tl^+ and Cu^+, as well as divalent ions, for example Ba^{2+} or Pb^{2+}, may serve as counter-ions (Binnewies and Schäfer, 1973, 1974; Gorbunov *et al.*, 1974; Westland and Tarafder, 1983). Furthermore, alkyl ammonium ions can be used to crystallize the hexachlorothorate (Brown, 1966; Woodward and Ware, 1968). Occasionally, complex $[ThCl_5]^-$ and $[ThCl_7]^{3-}$ ions have been mentioned in the literature (Oyamada and Yoshida, 1975; Yoshida *et al.*, 1978). The enthalpies of formation of several thorium–alkali metal ternary chlorides have been reported. Experimental data on these chlorides, together with those on other actinide ternary halides are assembled and briefly discussed in Chapter 19.

Chloro compounds of thorium in which one or more chloride ions in $ThCl_4$ are replaced by other ligands have been prepared. These ligands can be trimethysilylamide, benzaldehyde, and methylsalicylate, for example (Bradley *et al.*, 1974).

The phase diagrams of $ThBr_4$ and the alkali metal bromides NaBr–CsBr show one compound to exist in each case (Ribas Bernat and Ramos Alonso, 1976; Ribas Bernat *et al.*, 1977; Gershanovich and Suglobova, 1981). For sodium, $NaThBr_5$ melts incongruently, and for the remaining alkali metals, the bromides A_2ThBr_6 ($A = K - Cs$) melt congruently. The structure of the equivalent sodium compound is not known, but for the compounds with heavier alkali metals, the lattice parameters have been derived from powder diffraction data. Although the data are not in entire agreement, it seems very likely that these compounds are (nearly) isotypic with the respective iodides and thus contain the octahedral $[ThBr_6]^{2-}$ anion. The same anion also occurs in the family of bromides, $AThBr_6$, with A being a divalent cation (cf. Table 3.9) (Beck and Kühn, 1995). An interesting exception is the unique crystal structure of In_2ThBr_6. It contains square antiprismatic $[ThBr_8]$ polyhedra that are linked in

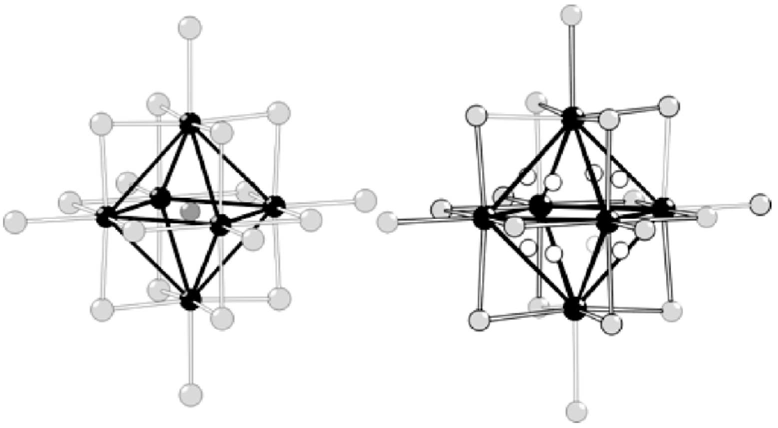

Fig. 3.12 *Octahedral [Th_6] cluster in the crystal structures of $Th_6Br_{15}Co$ and $Th_6Br_{14}H_7$, respectively. The cobalt atom as well as the hydrogen atoms are stabilizing the cluster, which are surrounded by* 18 *Br^-* ions. *The hydrogen position are only occupied to* 7/8.

chains along [001] according to the formula $^1_\infty[ThBrF_{4/2}Br_{4/1}]$ via shared edges. The chains are held together by nine-fold coordinated In^+ ions (Dronskowski, 1995).

A series of reduced thorium bromides containing octahedral [Th_6] clusters has been described recently. They have been prepared from $ThBr_4$ and thorium metal in the presence of either hydrogen, carbon, or a transition metal, leading to the compounds: MTh_6Br_{15} (M = Mn, Fe, Co, Ni), $Th_6Br_{14}C$, and $Th_6Br_{15}H_7$ (Böttcher *et al.*, 1991a,b). The transition metal and the carbon atom act as a stabilizing interstitial atom within the octahedron whereas the hydrogen atoms are located above the triangular faces of the empty octahedra. In each case, the [Th_6] core is surrounded by 12 Br^- ions that are bridging the edges of the octahedron, and six additional anions attached to the vertices. The linkage of the [$(Th_6Br_{12})Br_6$] units is different in $Th_6Br_{14}C$ compared to the metal-centered cubic phases, causing the slightly higher Th/Br ratio (Fig. 3.12). Another unique cluster compound is $KTh_{12}N_6Br_{29}$. It shows a core of six [NTh_4] tetrahedra that are connected by sharing edges (Fig. 3.13) (Braun *et al.*, 1995).

Ternary iodides containing the octahedral $[ThI_6]^{2-}$ anion have been prepared with a number of different counter-cations, for example alkali metal ions, tetraalkyl ammonium ions, or $[As(C_6H_5)_4]^+$ (Bagnall *et al.*, 1965; Brown *et al.*, 1970a, 1976; Brendel *et al.*, 1985). The ThI_4/AI_2 systems with A being Ca, Sr, Sn, or Pb, have been investigated and for selected examples crystal structures have even been determined (Beck *et al.*, 1993). Ternary iodides have also been synthesized by the fusion of the binary iodides at elevated temperature with other divalent cations (Beck *et al.*, 1993). Finally, the mercury iodides $Hg_2ThI_8 \cdot 12H_2O$ and $Hg_5ThI_{14} \cdot 18H_2O$ have been reported (Duboin, 1909a).

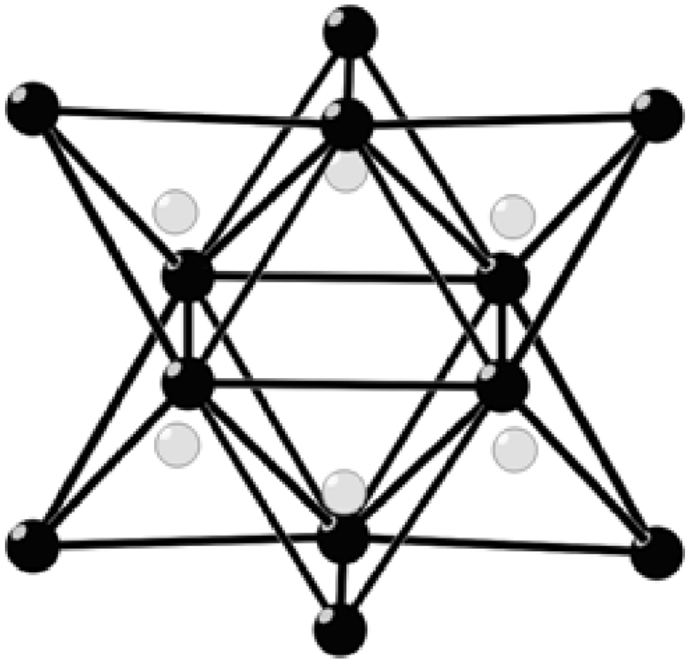

Fig. 3.13 [*Th*$_{12}$*N*$_6$] *core in the crystal structure of KTh*$_{12}$*N*$_6$*Br*$_{29}$. The unit consists of six linked [*NTh*$_4$] *tetrahedra. It might also be seen as an* [*Th*$_6$] *octahedron whith four of the six triangular faces capped by an additional thorium atom.*

3.7.5 Chalcogenides

The heavier analogs of oxides, the chalcogenides S, Se, and Te, all form compounds with thorium (Table 3.6). While some are based on simple crystal structures such as fluorite or NaCl, the richness of the electronic structures of sulfur, selenium, and tellurium lend themselves to forming more complex structures than the oxides. Binary thorium sulfur compounds can be prepared by the action of H_2S on the metal (Berzelius, 1829; Nilson, 1876; Moissan and Étard, 1896, 1897), the metal halide (Krüss and Volck, 1894; Duboin, 1908b), the metal hydride (Eastman *et al.*, 1950; Lipkind and Newton, 1952), or on thoria itself in the presence of carbon (Eastman *et al.*, 1950). Sulfur will react at elevated temperatures with the metal or thorium carbide and CS_2 with thoria will also form the binary sulfides. There are six generally recognized structurally characterized sulfides (including ThOS, which is not isostructural with ThS_2 or ThO_2) listed in Table 3.6 (Shalek, 1963). The sulfide with the lowest sulfur content (Khan and Peterson, 1976), ThS, stands out against ThO as not being like ZnS but rather forming the NaCl structure type (Zachariasen, 1949c). However, as mentioned earlier, the characterization of ThO remains a puzzle. ThS is metallic in appearance with a density of 9.56 g cm^{-3}. The compound sinters above 1950°C with no appreciable vapor pressure above its melting point (2200°C). The compound can be machined or polished and becomes superconducting near 0.5 K (Moodenbaugh *et al.*, 1978). The disulfide of thorium, ThS_2, is a purple-brown solid with the $PbCl_2$ structure and a density of 7.36 g cm^{-3}. It is reported to melt at 1905°C with considerable decomposition starting at 1500°C (Eastman *et al.*, 1950, 1951). Heating the disulfide in vacuum will yield a black phase, Th_7S_{12}, which melts around 1770°C (Zachariasen, 1949d; Eastman *et al.*, 1950, 1951). This compound has been mislabeled as Th_4S_7. The sesquisulfide is a brown-metallic phase, isotypic with stibnite, Sb_2S_3 (Zachariasen, 1949c). This phase also melts with no appreciable vapor pressure at high temperatures (2000°C), making it a useful high-temperature crucible material. An orange-brown material has been prepared via a lower-temperature reaction (400°C) between thorium metal and sulfur or between the hydride and excess H_2S. A 'polysulfide' phase was first identified as Th_3S_7 (Strotzer and Zumbusch, 1941) and later found (Graham and McTaggart, 1960) to evolve sulfur around 150°C to yield Th_2S_5, of tetragonal structure, although more recent studies found that it is correctly reported in the orthorhombic cell (Noël and Potel, 1982). ThOS, a yellow phase prepared from the action of thoria and CS_2 or thoria and sulfur (Krüss, 1894; Heindl and Loriers, 1974), forms in the PbFCl structure type, analogous with the rare earth series of compounds (Zachariasen, 1949c). ThOS hydrolyzes in acid solutions as do all the other binary sulfides of thorium (Dubrovskaya, 1971).

Selenium and tellurium form a series of compounds with thorium that are homologs of the sulfides. These compounds, listed in Table 3.6, are ThOSe, ThSe, Th_7Se_{12}, Th_2Se_3, $ThSe_2$, Th_2Se_5, and $ThSe_3$ (D'Eye *et al.*, 1952; D'Eye, 1953; Graham and McTaggart, 1960; Noël, 1980; Kohlmann and Beck, 1999). These phases have all been obtained by the reaction of selenium on thorium metal (D'Eye *et al.*, 1952) on the carbide, the halide, or the silicide of thorium (Moissan and Martinsen, 1905). Thorium selenides have also been produced by the reaction of hydrogen selenide gas on thorium bromide (Moissan and Martinsen, 1905). It has been reported that ThSe becomes superconducting at 1.6 K (Moodenbaugh, 1978), in contrast to earlier observations (Bucher and Staundenmann, 1968). A selenium analog to the polysulfide phase may be Th_7Se_{12} (D'Eye, 1953) or Th_2Se_5 (Graham and McTaggart, 1960). Another reported polyselenide is $ThSe_3$ (Noël and Potel, 1982), which is isotypic with USe_3 (Ben Salem *et al.*, 1984). Finally, the reaction of selenium with thoria yields ThOSe (D'Eye, 1953).

The tellurides of thorium exist in phases of similar stoichiometry but with slightly differing structures from those of the sulfides or selenides. For example, ThTe is found in the CsCl structure rather than the NaCl-type (D'Eye and Sellman, 1954). Several conflicting reports exist about the identity of a higher telluride, Th_3Te_8, although it has been confirmed to be $ThTe_3$, in a structure type analogous to the low-dimensional $ZrSe_3$-type (Graham and McTaggart, 1960). This same report also suggests that $ThTe_2$ is hexagonal rather than orthorhombic as in the $PbCl_2$-type found for $ThSe_2$. Recently, the missing link in the series, Th_7Te_{12}, was prepared and characterized as isostructural with the selenide (Tougait *et al.*, 1998). An early report on 'Th_3Te' has not been confirmed up to now and seems to be not very reliable (Montignie, 1947).

During the past decade, a series of interesting ternary and quaternary thorium chalcogenide phases have been prepared (Cody and Ibers, 1996; Wu *et al.*, 1997; Tougait *et al.*, 1998; Narducci and Ibers, 1998a,b, 2000; Choi *et al.*, 1998; Briggs-Piccoli *et al.*, 2000, 2001, 2002; Hess *et al.*, 2001). The series of layered tellurides and selenides of thorium, ATh_2Te_6, are based on the sesquiselenide or telluride structure type that has been, in effect, pried apart, reduced, and intercalated by an alkali metal (Cody and Ibers, 1996; Wu *et al.*, 1997; Tougait *et al.*, 1998). The review by Narducci and Ibers describes these reactions in detail (1998a). Indeed, a series of related transition metal compounds such as $KCuThSe_3$, $CuTh_2Te_6$, and $SrTh_2Se_5$ have been prepared from the action of tellurium or selenium, or their alkali metal salts, on thorium metal (Narducci and Ibers, 1998a, 2000).

Attempts were also made to prepare chalcophosphate analogs of the thorium phosphates discussed in Section 3.7.7e. The unique chemistry of thiophosphates and selenophosphates provided a rich set of compounds from homoleptic clusters of $[Th_2(PS_4)_6]^{10-}$ (Briggs-Piccoli *et al.*, 2002) to complex three-dimensional phases with a unique $(P_2Se_9)^{6-}$ anion building block in $Cs_4Th_4P_4Se_{26}$ (Briggs-Piccoli *et al.*, 2001).

3.7.6 Pnictides

The nitride of thorium, Th_3N_4, can be prepared by a variety of methods (Gmelin, 1987). One is the strong heating of the metal in the presence of N_2. At the turn of the last century, there was significant debate about the composition and color (chestnut, citron yellow, maroon, and black) of the thorium nitride that could be obtained by heating the metal in presence of N_2 (Matignon and Delepine, 1907; Düsing and Hüniger, 1931). The debate lingered into the 1960s and the variations in color have been attributed to vacancies in nitrogen and oxygen impurities. Indeed, the tan-colored Th_2N_3 is actually Th_2N_2O (Aronson and Auskern, 1966; Benz and Zachariasen, 1966). The golden yellow ThN (Chiotti, 1952; Olson and Mulford, 1965) may likely be seen as a thin layer on the surface of Th_3N_4 as it is the thermally stable product of all decomposition reactions of the other thorium nitrides (Aronson and Auskern, 1966). ThN displays metallic character when prepared as a thin film (Gouder *et al.*, 2002). The ThN phase is isotypic with all other actinide mononitrides and has the NaCl fcc structure (Auskern and Aronson, 1967; Benz *et al.*, 1967). ThN is a superconductor at low temperatures with an inverse dependence of pressure on the critical temperature (Dietrich, 1974).

The synthesis of the binary nitrides listed in Table 3.10 can be achieved most easily by the action of ammonia or nitrogen on heated thorium hydride

Table 3.10 *Crystallographic data of thorium pnictides.*

		Lattice parameters				
Compound	*Lattice symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
ThN	cubic	5.180				Evans and Raynor (1959)
Th_3N_4	rhombohedral	3.87		27.38		Bowman and Arnold (1971)
Th_2N_3	rhombohedral	3.883		6.187		Zachariasen (1949a)
ThP	cubic	5.840				Gingerich and Wilson (1965)
Th_3P_4	cubic	8.600				Meisel (1939); Zumbusch (1941)
Th_2P_{11}	monoclinic	17.384	10.104	19.193	$\beta = 117.62$	von Schnering *et al.* (1980)
ThP_7	orthorhombic	10.218	10.401	5.671		von Schnering and Vu (1986)
ThAs	cubic	5.978				Ferro (1955)
Th_3As_4	cubic	8.843				Ferro (1955)
$ThAs_2$	tetragonal	4.086		8.575		Ferro (1955); Pearson (1985)
ThSb	cubic	6.318				Ferro (1956)
Th_3Sb_4	cubic	9.371				Ferro (1956)
$ThSb_2$	tetragonal	4.352		9.172		Ferro (1956)
$ThBi_2$	tetragonal	4.492		9.298		Pearson (1985)

(Katzin, 1983). Metal powder heated in nitrogen will yield the nitrides; in the presence of ammonia, a hydride intermediate can be formed (Juza and Gerke, 1968). These hydrogen-containing species might be nitride-imides, nitride-amides, or pure amides of thorium, as investigations of the system Th–N–H have shown. Thoria treated with carbon and heated in a nitrogen atmosphere will also yield nitrides where a finely divided metal powder can be seen as an intermediate.

The reaction of binary nitrides with thorium halides leads to the halide nitrides ThNX (X = F, Cl, Br, I). They have been shown to adopt the BiOCl-type of structure (Juza and Sievers, 1968; Blunck and Juza, 1974). Complex metal nitrides such as Th_2NOP can be prepared by heating binary nitrides with thoria and thorium phosphides (Benz and Zachariasen, 1969; Barker and Alexander, 1974). Heating the nitrides in oxygen generally yields thoria as the product and the nitrides are moisture-sensitive. Several complex mixtures of double salts have been prepared recently, namely $Ca_xTh_{3-x}N_{4-2x}O_{2x}$, $Sr_xTh_{3-x}N_{4-2x}O_{2x}$, and $Sr_xTh_{1-x}N_xO_{1-x}$ (Brese and DiSalvo, 1995a). Ternary nitrides are the lithium compound Li_2ThN_2 (Palisaar and Juza, 1971) as well as the very unique nitride perovskite phase, $TaThN_3$ (Brese and DiSalvo, 1995b).

This latter cubic perovskite was prepared by the action of Ta_3N_5 and Th_3N_4 at 1400°C as well as by the reaction of $Ta_2Th_2O_9$ and Ca_3N_2 at 1500°C.

The heavier pnictide analogs all form similar binary phases to the nitride that have been characterized by single crystal XRD analysis except for ThBi that is conspicuously absent (Ferro, 1957). Analogously to ThN, ThP, ThAs, and ThSb adopt the fcc NaCl structure (Ferro, 1955, 1956; Gingerich and Wilson, 1965; Javorsky and Benz, 1967; Baskin, 1969). The same structure has been reported for all of the actinide and lanthanide mononitrides and pnictides, respectively. Interestingly, the lattice constant has been shown to decrease when going from Th to U, then to increase through Cm, and finally to decrease again (Lam *et al.*, 1974; Damien and de Novion, 1981) (Fig. 3.14).

Adachi and Imoto reported that the cubic ThP could be made as ThP_{1-x} where x varied from 0 to 0.6. This behavior dramatically affected the hardness of the phase as well as its conductivity (Adachi and Imoto, 1968). Indeed, at 1200°C, the phase ranges from $ThP_{0.4}$ to $ThP_{0.6}$. The non-stoichiometric phases show a weak paramagnetism and the room temperature resistivity of the metallic ThP decreased with an increasing P/Th ratio for the ThP_{1-x} phases. ThP forms a solid solution with UP and displays an antiferromagnetic phase transition at 23 K with up to 40% ThP (Adachi *et al.*, 1973). ThP undergoes a

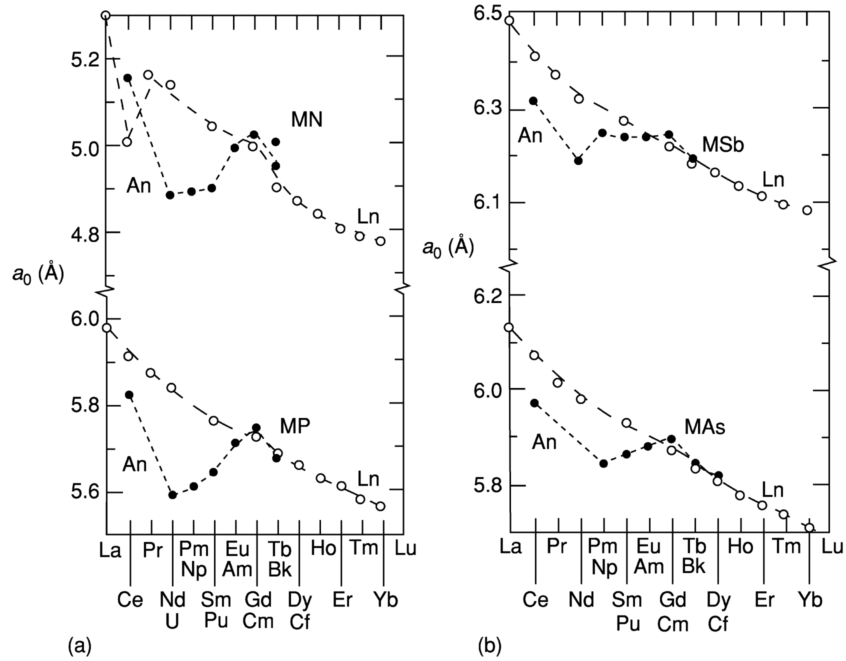

Fig. 3.14 *Lattice constants of actinide and lanthanide monopnicnitides: mononitrides and monophosphides (a); monoantimonides and monoarsenides (b) (Damien and de Novion,* 1981).

structural phase transition from the NaCl-type to the CsCl-type at 30 GPa (Staun Olsen *et al.*, 1988). The reaction between Th and Th_3P_4 at 1100°C will yield ThP (Gingerich and Wilson, 1965; Gingerich and Aronson, 1966; Javorsky and Benz, 1967). Th_3P_4 can be made by the direct combination of the elements (Gingerich and Wilson, 1965; Price and Warren, 1965), by heating $ThCl_4$ with phosphorus vapors (Moissan and Martinsen, 1905), and by the reaction of the hydride with phosphine gas (Lipkind and Newton, 1952). This phase of phosphide is a dark gray material, unlike the black ThP, and is unreactive in water. It releases phosphine upon action by acids and can be ignited to thorium phosphate by heating in air (Strotzer *et al.*, 1938; Meisel, 1939). Th_3P_4 is an n-type semiconductor with a band gap of 0.4 eV (Henkie *et al.*, 1976; Suzuki *et al.*, 1982). A very unique, phosphorus-rich Zintl phase was prepared by the action of phosphorus on thorium metal at 1040°C, yielding Th_2P_{11} (von Schnering *et al.*, 1980). This phase comprises chains of phosphorus atoms linked into two-dimensional nets comprising open and closed P_6 rings. This black, semiconducting phase (band gap of 0.3 eV) decomposes to Th_3P_4 upon heating to 1040°C in vacuum. Other complex ternary phosphides are known including $Th_5Fe_{19}P_{12}$, $ThFe_4P_2$, and $Th_2Mn_{12}P_7$ (Albering and Jeitschko, 1992; Jeitschko *et al.*, 1993). Finally, a dense, magnetoresistive skutterudite phase can be prepared from the elements to yield $ThFe_4P_{12}$ (Dordevic *et al.*, 1999).

In the thorium–arsenic system, ThAs and Th_3As_4 are black-gray compounds that are isomorphous with the associated phosphides and nitrides (Benz, 1968). Th_3As_4 is an n-type semiconductor with a band gap of 0.43 eV (Ferro, 1955; Warren and Price, 1964; Henkie and Markowski, 1978). In contrast to the Th–P system, a diarsenide, $ThAs_2$, is formed, which displays two modifications: a low-temperature phase (α), with the PbCl structure and a high-temperature phase (β) with the Fe_2As structure (Ferro, 1955; Hulliger, 1966). More complex mixtures of ThAs and ThS or ThSe have yielded compounds such as ThAsSe that display unique anomalous Kondo-like behavior (Henkie and Wawryk, 2002). Thorium antimony compounds form in the same structures as the arsenides, with ThSb, Th_3Sb_4, and $ThSb_2$ (Ferro, 1956; Hulliger, 1966, Chiotti *et al.*, 1981). Like the arsenide, ThSb undergoes a high-pressure phase transition from NaCl to the CsCl-type (Palanivel *et al.*, 1995). Kondo-like resistivity behavior was observed for solid solutions of USb and ThSb. The dilution of USb by ThSb lead to large modifications of the electrical transport properties, reflecting the change from antiferromagnetism to ferromagnetism with a concomitant decrease of the ordered magnetic moment per U atom (Frick *et al.*, 1982). In the thorium–bismuth system, three binary compounds with familiar structures are found: ThBi, $ThBi_2$, and Th_3Bi_4 (Ferro, 1957; Dahlke *et al.*, 1969). ThBi was reported as part of an alloy structure although a single crystal structure has not been determined (Borzone *et al.*, 1982). Another phase with the Mn_5Si_3-type was observed as well but was not confirmed by elemental analysis (Borzone *et al.*, 1982). Bismuth can be distilled from ThBi, yielding the thorium-rich Th_5Bi_3 hexagonal structure. During the U.S. breeder reactor program of the mid–1950s, breeder-blanket liquid Bi with a slurry of $ThBi_2$ suspended in the liquid bismuth showed promise but there was significant difficulty in suspending the inhomogeneous particles of $ThBi_2$ (Bryner and Brodsky, 1959).

3.7.7 Complex anions

Thorium compounds with complex anions play an important role in various fields, for example in separation techniques (cf. Section 3.4) and nuclear waste disposal, to name only two of them. Thus, this chemistry has been widely investigated, although often not in very detail, what is especially true with respect to structural characterizations. In the following the most important and more recent findings are summarized. For each complex anion an extra subdivision has been created and reliable crystallograhic data are presented in Table 3.11.

(a) Perchlorates

Thorium perchlorate is highly soluble in water and crystallizes, generally from acidic solution, in the form of the tetrahydrate $Th(ClO_4)_4{\cdot}4H_2O$ (Murthy and Patel, 1965). The structure of the tetrahydrate is not known, but the compound has been shown to decompose at 280°C to form $ThO(ClO_4)_2$ that finally forms ThO_2 at 335°C (Murthy and Patel, 1965). The oxide–perchlorate apparently will dissolve in water, and from XRD this is interpreted to be due to the formation of a tetrameric species (Bacon and Brown, 1969). An elegant (but somewhat dangerous) route to prepare anhydrous $Th(ClO_4)_4$ is the reaction of $ThCl_4$ with Cl_2O_6 (Koulkès-Pujo *et al.*, 1982). From X-ray powder diffraction, an orthorhombic lattice has been deduced with the space group probably being $P2_12_12$ (Ramamurthy and Patel, 1963). Due to the weak coordination tendency of the ClO_4^- ion, $Th(ClO_4)_4$ is frequently used to prepare coordination compounds of thorium in which the perchlorate anion in not included in the coordination sphere (Gmelin, 1985b, 1993a).

(b) Sulfates (VI, IV)

A detailed discussion of the older literature on thorium sulfates has been given by Mellor (1941). Thorium sulfates can be prepared by the reaction of various thorium salts, for example thorium nitrate, with concentrated sulfuric acid. Upon crystallization from aqueous solution, different hydrates can be obtained. At lower temperatures (0–45°C), $Th(SO_4)_2{\cdot}9H_2O$ has the lowest solubility (Clève, 1874; Roozeboom, 1890; Dawson and Williams, 1899). Nevertheless, the octahydrate is usually obtained even under these conditions (Clève, 1874; Krüss and Nilson, 1887b; Roozeboom, 1890; Koppel and Holtkamp, 1910). Furthermore, a hexahydrate has been mentioned and at higher temperature,

Table 3.11 *Crystallographic data of thorium compounds with oxo anions.*

		Lattice parameters				
Compound	*Space group*	*a* (Å)	*b* (Å)	*c* (Å)	*Angles* (°)	*References*
$Th(SO_4)_2{\cdot}8H_2O$	$P2_1/n$	8.51	11.86	13.46	$\beta = 92.65$	Habash and Smith (1983)
$Th(OH)_2SO_4$	Pnma	11.733	6.040	7.059		Lundgren (1950)
$K_4Th(SO_4)_4{\cdot}2H_2O$	$C\bar{1}$	10.096	16.75	9.762	$\alpha = 95.15$ $\beta = 95.22$ $\gamma = 91.00$	Arutyunyan *et al.* (1963)
$Na_2Th(SO_4)_3{\cdot}6H_2O$	$P2_1/c$	5.567	16.81	15.76	$\beta = 91.925$	Habash and Smith (1990)
$Cs_2Th(SO_4)_3{\cdot}2H_2O$	$P2_1/c$	6.415	15.95	13.078	$\beta = 90.88$	Habash and Smith (1992)
$Th(NO_3)_4{\cdot}5H_2O$	Fdd2	11.191	22.89	10.579		Taylor *et al.* (1966)
$Th(NO_3)_4{\cdot}4H_2O$	$P2_1/n$	7.438	17.530	9.183	$\beta = 99.72$	Charpin *et al.* (1987)
$ThOH(NO_3)_3{\cdot}4H_2O$	$P2_1/c$	6.772	11.693	13.769	$\beta = 102.63$	Johansson (1968a)
$(NH_4)_2Th(NO_3)_6$	$P2_1/n$	8.321	6.890	13.097	$\beta = 91.55$	Spirlet *et al.* (1992)
$MgTh(NO_3)_6{\cdot}8H_2O$	$P2_1/c$	9.080	8.750	13.610	$\beta = 97.03$	Scavnicar and Prodic (1965)
$(C(NH_2)_3)_6Th(CO_3)_5{\cdot}4H_2O$	B11b	16.15	16.70	13.23	$\gamma = 108.42$	Voliotis and Rimsky (1988)
$Na_6Th(CO_3)_5(H_2O)_{12}$	$P\bar{1}$	9.60	9.92	13.64	$\alpha = 90.47$ $\beta = 104.38$ $\gamma = 95.52$	Voliotis and Rimsky (1975)
$(C(NH_2)_3)_5(Th(CO_3)_3F_3)$	$P2_12_12_1$	9.53	29.79	9.11		Voliotis (1979)
$Na_6BaTh(CO_3)_6(H_2O)_6$	$R\bar{3}$	14.175		8.605		Yamnova *et al.* (1990)
$Th(P_2O_7)$	$Pa\bar{3}$	8.721				Burdese and Borlera (1963)
$KTh_2(PO_4)_3$	C2/c	17.57	6.863	8.138	$\beta = 101.77$	Matkovic *et al.* (1968)
$NaTh_2(PO_4)_3$	C2/c	17.37	6.81	8.13	$\beta = 101.13$	Matkovic *et al.* (1970)
$Pb_{0.5}Th_2(PO_4)_3$	C2/c	17.459	6.8451	8.1438	$\beta = 101.25$	El-Yacoubi *et al.* (1997)
$CuTh_2(PO_4)_3$	C2/c	22.029	6.7430	7.0191	$\beta = 108.58$	Louer *et al.* (1995)
$Na_2Th(PO_4)_2$	C2/c	7.01	21.50	9.12	$\beta = 111.02$	Galesic *et al.* (1984)

$KTh(P_3O_{10})$	$P2_12_12_1$	8.234	10.187	10.015		Ruzic Toros *et al.* (1974)
$Na_6(Th(PO_4)(P_2O_7))_2$	$P\bar{1}$	8.734	8.931	6.468	$\alpha = 93.33$ $\beta = 108.29$ $\gamma = 110.10$	Kojic-Prodic *et al.* (1982)
$Na_2Th(PO_4)_2$	$P2_1/c$	7.055	21.66	9.095	$\beta = 111.56$	Galesic *et al.* (1984)
$Th_4(PO_4)_4(P_2O_7)$	Pcam	12.865	10.437	7.0676		Bénard *et al.* (1996)
$KTh_2(VO_4)_3$	C2/c	18.564	7.157	8.077	$\beta = 101.05$	Quarton and Kahn (1979)
ThV_2O_7	Pnnm	7.216	6.964	22.80		Quarton *et al.* (1970)
$Pb_{0.5}Th_{0.5}(VO_4)$	$I4_1/a$	5.175		11.943		Andreetti *et al.* (1984)
$Pb_{0.5}Th_{0.5}(VO_4)$	$I4_1/amd$	7.428		6.590		Andreetti *et al.* (1984)
$Pb_{0.5}Th_{0.5}(VO_4)$	$P2_1/n$	7.046	7.3089	6.8066		Andreetti *et al.* (1984)
$Th(VO_3)_2O$	$Pn2_1a$	7.201	22.771	6.945		Launay *et al.* (1992)
$Th(MoO_4)_2$-I	Pbca	10.318	9.737	14.475		Cremers *et al.* (1983)
$Th(MoO_4)_2$-II	$P\bar{3}$	17.593		6.238		Larson *et al.* (1989)
$K_2Th(MoO_4)_3$	C2/c	17.649	12.143	5.3688	$\beta = 105.76$	Huyghe *et al.* (1991a)
$K_4Th(MoO_4)_4$	$I4_1/a$	11.586		13.069		Huyghe *et al.* (1991b)
$K_8Th(MoO_4)_6$	$P\bar{1}$	10.255	10.260	14.466	$\alpha = 75.87$ $\beta = 96.81$ $\gamma = 118.43$	Huyghe *et al.* (1993)
$Cu_2Th_4(MoO_4)_9$	$I\bar{4}3d$	14.477				Launay *et al.* (1998)
$CdTh(MoO_4)_3$	$P6_3/m$	9.803		6.350		Launay and Rimsky (1980)
$Th(OH)_2CrO_4 \cdot H_2O$	$P2_1/m$	7.67	6.11	6.94	$\beta = 113.91$	Lundgren and Sillen (1949)
$ThSiO_4$	$I4_1/amd$	7.133		6.319		Taylor and Ewing (1978)
$ThSiO_4$	$P2_1/n$	6.784	6.974	6.500	$\beta = 104.92$	Taylor and Ewing (1978)
$Ca_2ThSi_8O_{20}$	I422	7.483		14.893		Szymanski *et al.* (1982)
$Na_{12}Th_3(Si_8O_{19})_4 \cdot 18H_2O$	$R\bar{3}c$	29.124		17.260		Li *et al.* (2000)

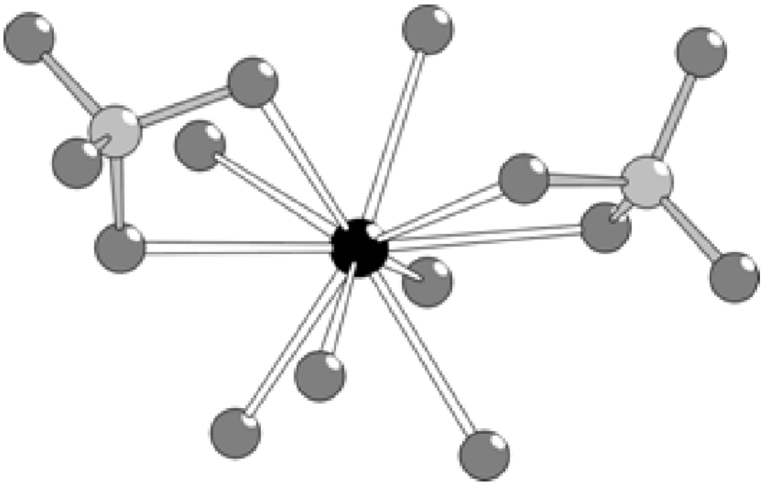

Fig. 3.15 *The* $[Th(SO_4)_2(H_2O)_6]$ *molecule in the crystal structure of* $Th(SO_4)_2{\cdot}8H_2O$.

a tetrahydrate is said to form (Roozeboom, 1890; Dawson and Williams, 1899; Wirth, 1912). A dihydrate was observed as an intermediate of the dehydration of higher hydrates (Rollefson, 1947) and $Th(SO_4)_2{\cdot}8H_2O$ has been structurally characterized (Fig. 3.15). It shows the Th^{4+} ions in a ten-fold coordination by oxygen atoms, which belong to six water molecules and two chelating sulfate ions. The coordination polyhedron is a distorted bicapped squared antiprism. The crystal structure is completed by two crystal water molecules (Habash and Smith, 1983).

The formation of basic thorium sulfates has also been frequently observed but these compounds are not well characterized (Krüss and Nilson, 1887b; Wyrouboff and Verneuil, 1898b, 1899; Meyer and Gumperz, 1905). $ThOSO_4$ has been reported to form upon dehydration of $ThOSO_4{\cdot}3H_2O$ but none of these compounds has been further investigated (Wyrouboff, 1901; Wöhler *et al.*, 1908; Hauser and Wirth, 1908; Barre, 1910, 1911; Halla, 1912). The structure is known only for $Th(OH)_2SO_4$, which has been thought to be $ThOSO_4{\cdot}H_2O$ (Lundgren, 1950). The thorium ions are connected as dimers by two OH^- ions. The coordination sphere of Th^{4+} is completed by four monodentate sulfate groups and the dimeric $[Th_2(OH)_2(SO_4)_8]$ units are linked into a three-dimensional network.

Various polynary sulfates containing alkali metals are thought to exist (Colani, 1909; Barre, 1912). The phase diagram of $Na_2SO_4/Th(SO_4)_2$ has been determined recently wherein the compound $Na_{12}Th(SO_4)_8$ is found (Fedorov and Fedorov, 2001). Solid state reactions of ThO_2 with $KHSO_4$, $K_2S_2O_8$, and $K_2S_2O_7$ afforded $K_4Th(SO_4)_4$ (Keskar *et al.*, 2000). Also the reactions of ThO_2 with $(NH_4)_2SO_4$, and mixtures of $(NH_4)_2SO_4$ with NH_4NO_3 or NH_4HF, have been studied (Singh Mudher *et al.*, 1995). Furthermore, the rubidium compound, $Rb_2Th(SO_4)_3$, has been synthesized. Despite these investigations no structural data of the anhydrous species have been reported until now. A little more information is available for the hydrated polynary sulfates (Cleve, 1874; Manuelli and Gasparinetti, 1902; Rosenheim *et al.*, 1903; Barre, 1910, 1911). According to very old data, they may contain alkali and thorium metal ions in a ratio of 1:1, 2:1, 3:1, and 4:1, but newer investigations determined the compositions as $A_2Th(SO_4)_3{\cdot}xH_2O$ and $A_4Th(SO_4)_4{\cdot}xH_2O$ (A = Na–Cs, NH_4) (Gmelin, 1986b), where the water content x varies from 2 to 6. Additionally, $M_6Th(SO_4)_5{\cdot}3H_2O$ (M = Cs, NH_4) and $(NH_4)_8Th(SO_4)_6{\cdot}2H_2O$ are known (Gmelin, 1986b). For several compounds, infrared spectroscopy (IR) data are available (Evstaf'eva *et al.*, 1966) and structure determinations have been done for $Na_2Th(SO_4)_3{\cdot}6H_2O$ (Habash and Smith, 1990), $Cs_2Th(SO_4)_3{\cdot}2H_2O$ (Habash and Smith, 1992), and $K_4Th(SO_4)_4{\cdot}2H_2O$ (Arutyunyan *et al.*, 1963). The sodium compound exhibits chains of $^{1}_{\infty}[Th(H_2O)_{3/1}(SO_4)_{6/2}]$ running along [100] in which the Th^{4+} ions are surrounded by six monodentate SO_4^{2-} ions and three H_2O molecules to form a tricapped trigonal prism. The chains are linked by the Na^+ ions and three non-coordinating water molecules are found in the unit cell. In $Cs_2Th(SO_4)_3{\cdot}2H_2O$ the $[Th(H_2O)_2(SO_4)_5]$ polyhedra are linked to layers according to $^{2}_{\infty}[Th(H_2O)_2(SO_4)_{4/2}(SO_4)_{1/1}]$ that are connected by the Cs^+ ions. For the Th^{4+} ions a coordination number of nine arises due to the chelating nature of two of the SO_4^{2-} groups. In $K_4Th(SO_4)_4{\cdot}2H_2O$ zigzag chains are found with the formula $^{1}_{\infty}[Th(H_2O)_{2/1}(SO_4)_{4/2}(SO_4)_{2/1}]$. One of the SO_4^{2-} ions acts as chelating ligand leading to a coordination number of 9 for Th^{4+}.

Thorium sulfates containing other counter-cations besides alkali metals are rarely described. They include the manganese compound $MnTh(SO_4)_3{\cdot}7H_2O$ that was obtained from an aqueous solution of the binary sulfates at 30°C, the tin compound, $Sn_2Th(SO_4)_4{\cdot}2H_2O$ (Weinland and Kühl, 1907), and the poorly characterized thallium sulfates (Fernandes, 1925). Finally, the organic guanidinium ion has been used for the precipitation of thorium sulfato complexes (Molodkin *et al.*, 1964).

With $Th(SO_3F)_4$, one fluorosulfate of thorium has been synthesized by the reaction of HSO_3F with thorium acetate. According to IR measurements the anions act as bidentate ligands. The thermal decomposition of the compound yields SO_2F_2 and $Th(SO_4)_2$ (Paul *et al.*, 1981).

Thorium sulfate (IV), $Th(SO_3)_2{\cdot}xH_2O$, is said to form as a white precipitate when SO_2 is passed through a solution containing Th^{4+} ions or when an alkali metal sulfite is added (Clève, 1874; Chavastelon, 1900; Baskerville, 1901; Grossmann, 1905). Based on differential thermal analysis (DTA) investigations, the water content x is believed to be four (Golovnya *et al.*, 1967a,b). Hydrolysis of the thorium sulfites or their thermal decomposition leads to basic compounds with different compositions (Golovnya *et al.*, 1964, 1967a). Furthermore, various ternary sulfites containing alkali metal ions or the ammonium ion have been mentioned, but a more precise characterization is needed for these compounds

(Chavastelon, 1900; Golovnya *et al.*, 1967b,c). A number of organic solvates of thorium sulfites are reported, but again, further characterization is still needed (Golovnya *et al.*, 1967b).

(c) Nitrates

Nitrates of thorium may be prepared by dissolving $Th(OH)_4$ in nitric acid. Depending on the concentration of the acid, three different hydrates form upon evaporation. If the acid concentration is in the range between 1 and 54%, a pentahydrate crystallizes while a tetrahydrate is obtained at concentrations up to 75% (Ferraro *et al.*, 1954). Both hydrates have molecular structures. The tetrahydrate contains $[Th(NO_3)_4(H_2O)_4]$ molecules with all of the nitrate groups being attached in a chelating manner to the Th^{4+} ions, leading to a coordination number of 12 (Charpin *et al.*, 1987). In the non-centrosymmetric pentahydrate, $Th(NO_3)_4 \cdot 5H_2O$, there are also four chelating nitrate groups around Th^{4+} but only three additional H_2O molecules, yielding a coordination number of 11. The remaining water molecules are held via hydrogen bonds in the structure so that the compound has to be formulated according to $[Th(NO_3)_4(H_2O)_3] \cdot 2H_2O$ (Ueki *et al.*, 1966). The structure of the pentahydrate has also been determined by neutron diffraction so that exact hydrogen positions are known (Taylor *et al.*, 1966). Furthermore, thermodynamic data have been provided for the pentahydrate (Ferraro *et al.*, 1956; Cheda *et al.*, 1976; Morss and McCue, 1976).

From nearly neutral solutions, a hexahydrate was said to crystallize (Fuhse, 1897; Misciatelli, 1930a,b). Unfortunately it has not been structurally characterized and due to the well-known tendency of Th^{4+} compounds to hydrolyze, it might be possible that the hexahydrate is in fact a basic species. With $ThOH(NO_3)_3 \cdot 4H_2O$, another basic nitrate is known (Johansson, 1968a,b). As seen in Fig. 3.16, it contains the dimers $[Th_2(OH)_2(NO_3)_6(H_2O)_6]$, with the Th^{4+} ions in an 11-fold coordination by three H_2O molecules, two hydroxide ions, and three chelating nitrate groups. The dimers are arranged in the lattice with additional crystal water molecules. The thermal decomposition of thorium nitrate hydrates leads to ThO_2. According to DTA and thermogravimetry (TG) measurements, various intermediates can be observed (Tiwari and Sinha, 1980). Acidic thorium nitrates have been reported, for example $H_2Th(NO_3)_6 \cdot 3H_2O$, but unfortunately they have not been characterized (Moseley *et al.*, 1971). Also $Th(NO_3)_4 \cdot 2N_2O_5$, which is said to form in highly concentrated HNO_3, has not been investigated further (Kolb, 1913; Misciatelli, 1930a,b; Ferraro *et al.*, 1954, 1955).

Thorium nitrate is well soluble in water and various oxygen-containing organic solvents such as alcohols, ketones, ethers, and esters (Imre, 1927; Misciatelli, 1929; Templeton and Hall, 1947; Rothschild *et al.*, 1948; Yaffe, 1949; Bock and Bock, 1950). The solid solvate $Th(NO_3)_4 \cdot 3H_2O \cdot 3C_2H_5OCH_2CH_2OC_2H_5$ has been crystallized from a solution of thorium

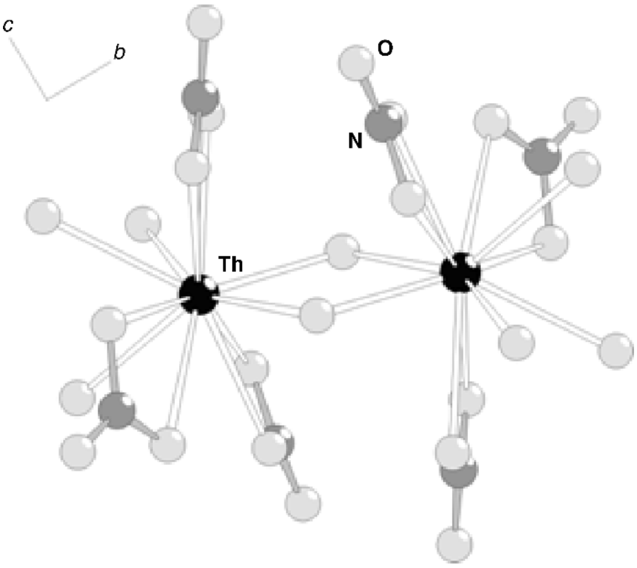

Fig. 3.16 *The dimeric unit* $[Th_2(OH)_2(NO_3)_6(H_2O)_6]$ *in the crystal structure of* $ThOH(NO_3)_3{\cdot}4H_2O$.

nitrate in the diethylether of ethyleneglycol (Katzin, 1948), and compounds with a variety of nitrogen bases in place of water are known (Kolb *et al.*, 1908; Kolb, 1913). It is possible to extract thorium nitrate from aqueous solution with an immiscible organic solvent if the aqueous phase is extremely concentrated, or if it contains high concentrations of ammonium nitrate (Templeton and Hall, 1947; Rothschild *et al.*, 1948; Hyde and Wolf, 1952; Newton *et al.*, 1952b). Since the rare earth metal ions do not extract well under the same conditions, being almost totally restricted to the aqueous phase, the procedure finds application in the preparation of pure thorium salts from ores containing rare earth elements.

A particularly useful liquid extractant is tri(*n*-butyl)phosphate (TBP) (Warf, 1949; Anderson, 1950), as well as other phosphate esters (Peppard, 1966, 1971; Shoun and McDowell, 1980). These compounds differ from ordinary nucleophilic solvents in that they interact specifically with the metal ion through the oxygen atom of the phosphoryl group to form a very strong solvation bond. In the case of thorium nitrate, this results in the formation of very stable complexes in the organic phase, with two and three molecules of phosphate per molecule of thorium nitrate (Katzin *et al.*, 1956). The TBP adduct is stable even against considerable dilution with 'inert' fluids such as benzene, CCl_4, or aliphatic hydrocarbons, which are themselves not solvents for thorium nitrate (Anderson, 1950; Katzin *et al.*, 1956). The coordination interaction of Th^{4+} in aqueous solution with phosphate esters is the basis of an important commercial process for the extraction and purification of thorium. Normally, addition of ammonia to the aqueous phase causes the formation of hydroxo complexes that reduce the efficiency of the thorium nitrate extraction. If this is coupled with addition of a neutral salting agent such as lithium nitrate, it is found that extraction is enhanced by formation of a hydroxynitrate of thorium. The polymeric complex has been formulated as $[Th_4(OH)_{10}(NO_3)_6(TBP)_4]$, thus contains one tri(*n*-butyl)phosphate molecule per thorium atom in contrast to the monomeric unhydrolyzed thorium nitrate complex (Klyuchnikov *et al.*, 1972). Thorium nitrate forms 1:1 or 1:2 complexes with crown ethers, depending on the size of the crown (Zhou *et al.*, 1981; Rozen *et al.*, 1982; Wang *et al.*, 1982). These can also be used as extractants (Wang *et al.*, 1983).

Organic donor molecules such as butylamine, dimethylamine, aromatic amine *N*-oxides, and others have been frequently used to prepare complexes with thorium nitrate (Rickard and Woolard, 1978). A compound with trimethylphosphine oxide, $Th(NO_3)_4 \cdot 3/8(Me_3PO)$, has been crystallographically characterized (Alcock *et al.*, 1978). It contains $[Th(NO_3)_3(Me_3PO)]^+$ cations and $[Th(NO_3)_6]^{2-}$ anions, a structural feature that is frequently displayed by transition metal–halide complexes (Katzin, 1966).

A number of ternary thorium nitrates with mono or divalent counter-cations are known (Jacoby, 1901; Meyer and Jacoby, 1901; Sachs, 1901). Those of the type $A_2Th(NO_3)_6$ contains the complex anion $[Th(NO_3)_6]^{2-}$ that shows the Th^{4+} ion in 12-fold coordination by oxygen atoms (Spirlet *et al.*, 1992). The latter contains six chelating nitrate groups, as it was shown from the structure determination of the ammonium compound. The same complex anion is found in the nitrates $BTh(NO_3)_6 \cdot 8H_2O$ with B = Mg, Mn, Co, Ni, Zn (Geipel, 1992). In this case, the counter-ions are octahedral $[B(H_2O)_6]^{2+}$ complexes according to the formulation $[B(H_2O)_6][Th(NO_3)_6] \cdot 2H_2O$ (Scavnicar and Prodic, 1965). Another series of ternary nitrates with monovalent cations includes members of the composition $ATh(NO_3)_5 \cdot xH_2O$, with A = NH_4, Na, K. They have not been fully characterized, so the amount of crystal water is not known (Meyer and Jacoby, 1901; Molodkin *et al.*, 1971; Volkov *et al.*, 1974). Furthermore, the nitrates $K_3Th(NO_3)_7$ and $K_3H_3Th(NO_3)_{10} \cdot 4H_2O$ have been reported, but again structural data are not known (Meyer and Jacoby, 1901; Molodkin *et al.*, 1971).

(d) Carbonates

Thorium hydroxide absorbs CO_2 readily (Berzelius, 1829; Chydenius, 1863; Clève, 1885; Chauvenet, 1911), where the end product is the hydrated $ThOCO_3$, and finally $Th(CO_3)_2 \cdot 0.5H_2O$ under high CO_2 pressures. The composition of this latter product has also been given as $Th(OH)_2CO_3 \cdot 2H_2O$ (Kharitonov *et al.*, 1969). Hydrates of the oxycarbonate are also produced by the action of sodium or ammonium carbonate on a solution of a thorium salt. The carbonate is somewhat soluble in excess alkali carbonate solution (Clève, 1885) because of the formation of complexes strong enough to prevent precipitation of thorium by ammonia, fluoride, or phosphate. Sodium hydroxide, however, will bring about precipitation (Sollman and Brown, 1907). The nature of the carbonato complexes (Dervin and Faucherre, 1973a,b; Shetty *et al.*, 1976) will be discussed in more detail in Section 3.8. Crystallization of these complexes is possible using various counter-cations, and compounds with Na^+, K^+, Tl^+, NH_4+, $(HGua)^+$ (guanidinium), Ca^{2+}, Ba^{2+}, and $[Co(NH_3)_6]^{3+}$ have been reported (Clève, 1874; Rosenheim *et al.*, 1903; Canneri, 1925; Rosenheim and Kelmy, 1932; Chernyaev *et al.*, 1958; Kharitonov *et al.*, 1969; Ueno and Hoshi, 1970; Dervin and Faucherre, 1973b; Dervin *et al.*, 1973; Voliotis and Rimsky, 1975, 1988). All of the salts are hydrated and the sodium compound, $Na_6Th(CO_3)_5 \cdot xH_2O$, has been reported to occur with a considerable range of hydration. In the crystal structures of $Na_6Th(CO_3)_5 \cdot 12H_2O$ and $[C(NH_2)_3]_6Th(CO_3)_5{\cdot}4H_2O$, the Th^{4+} ions are in ten-fold coordination by oxygen atoms (Voliotis *et al.*, 1977). In the mineral tuliokite, $Na_6BaTh(CO_3)_6 \cdot 6H_2O$, six chelating carbonate groups are attached to the Th^{4+} ion leading to a $[ThO_{12}]$ icosahedron (Yamnova *et al.*, 1990). Carbonates containing additional anions have been reported, for example $Na_5Th(CO_3)_4OH \cdot 9H_2O$, $Na_4Th(CO_3)_4 \cdot 7H_2O$, $(HGua)_4Th(CO_3)_4 \cdot 6H_2O$, $(HGua)_2Th(CO_3)_3 \cdot 5H_2O$, $K_3Th(CO_3)_3(OH) \cdot 5H_2O$, $(NH_4)_2Th(CO_3)_3 \cdot 6H_2O$, $Na_2Th(CO_3)_2(OH)_2 \cdot 10H_2O$, $K_2Th(CO_3)_2(OH)_2 \cdot 10H_2O$, and the fluoride carbonate $(HGua)_5Th(CO_3)_3F_3$ (Voliotis, 1979).

(e) Phosphates

Phosphates of thorium have been investigated for many years (Troost and Ouvrard, 1885; Johnson, 1889; Kauffmann, 1899; Hecht, 1928; King, 1945; Dupuis and Duval, 1949; Burdese and Borlera, 1963; Hubin, 1971; Laud, 1971). More recent studies were carried out in relation with the potential of phosphate matrices to be used as radioactive waste storage material, due to their resistance to radiation effects and their low solubilities (Baglan *et al.*, 1994; Merigou *et al.*, 1995; Genet *et al.*, 1996; Dacheux *et al.*, 1998; Volkov, 1999; Brandel *et al.*, 2001a,b). The system ThO_2/P_2O_5 has been studied in the 1960s and the phosphates $Th_3(PO_4)_4$, $(ThO_3)(PO_4)_2$, $(ThO)_2P_2O_7$, ThP_2O_7, and $ThO_2{\cdot}0.8P_2O_5$ have been reported. Recent investigations, however, show that $ThO_2{\cdot}0.8P_2O_5$ and the orthophosphate, $Th_3(PO_4)_4$, do not exist (Bénard *et al.*, 1996; Brandel *et al.*, 1998). Instead, the phosphate–diphosphate $Th_4(PO_4)_4P_2O_7$ has been obtained under similar conditions. Subsequently it has been shown that the compound can be synthesized applying dry or wet preparative routes and even single crystals have been grown. Besides ThP_2O_7 (Burdese and Borlera, 1963), the orthophosphate–disphosphate is the only structurally known binary thorium phosphate to date, although various other species, for example $ThOH(PO_4)$ and $Th_2(PO_4)_2HPO_4{\cdot}H_2O$, have been reported (d'Ans and Dawihl, 1929; Merkusheva, 1967; Molodkin *et al.*, 1968a; Brandel *et al.*, 2001a,b). In the crystal structure of the orthophosphate–diphosphate

(Bénard *et al.*, 1996), Th^{4+} is surrounded by four monodentate and one chelating PO_4^{3-} groups and one diphosphate ion. The latter suffers from a positional disorder. In ThP_2O_7, the Th^{4+} ions are octahedrally surrounded by six monodentate $P_2O_7^{4-}$ ions and the polyhedra are linked in a three-dimensional cubic network. The compound is thought to exhibit a second modification that has unfortunately not been structurally characterized.

Several ternary thorium phosphates are known, especially those with additional monovalent cations like alkali metals, silver, copper, and thallium (Wallroth, 1883; Palmer, 1895; Haber, 1897; Schmid and Mooney, 1964; Matkovic and Sljukic, 1965; Matkovic *et al.*, 1966, 1968, 1970; Molodkin *et al.*, 1970; Topic *et al.*, 1970; Popovic, 1971; Laügt, 1973; Ruzic Toros *et al.*, 1974; Kojic-Prodic *et al.*, 1982; Galesic *et al.*, 1984; Arsalane and Ziyad, 1996). Phosphates with the composition $MTh_2(PO_4)_3$ (M = Na, K) show ferroelectric properties and are thus of special interest. In the crystal structure, the Th^{4+} ions are nine-fold coordinated by oxygen atoms that belong to seven PO_4^{3-} ions. Two of the latter are chelating ligands. The linkage of the polyhedra leads to parallel layers (100) that are further linked into a three-dimensional network in [100] direction. The Na^+ or K^+ ions in $MTh_2(PO_4)_3$ can be replaced by Pb^{2+} ions, leading to the composition $Pb_{0.5}Th_2(PO_4)_3$ without structural changes (El-Yacoubi *et al.*, 1997). The structure of $CuTh_2(PO_4)_3$ is very similar, although the coordination number of Th^{4+} is lowered to eight. Another characteristic feature of the structure is the linear two-fold coordination of the Cu^+ ions (Louer *et al.*, 1995).

(f) Vanadates

The vanadates of thorium have been investigated to a much lesser extent than the respective phosphates. They seem to parallel the structural chemistry of the phosphates (Le Flem and Hagenmuller, 1964; Le Flem *et al.*, 1965; Quarton *et al.*, 1970; Baran *et al.*, 1974; Elfakir *et al.*, 1987), but high-quality structure determinations are rare. For example, such determinations have been performed for $MTh_2(VO_4)_3$ (M = K, Rb) and 'ThV_2O_7' (Quarton and Kahn, 1979; Elfakir *et al.*, 1987, 1989; Nabar and Mangaonkar, 1991; Launay *et al.*, 1992; Pai *et al.*, 2002). The latter compound is not a divanadate but a mixed *ortho*-vanadate–*catena*-vanadate with the formula $Th(VO_4)(VO_3)$ (Fig. 3.17). Other structurally characterized vanadates include $BaMTh(VO_4)_3$ (M = La, Pr) that adopt the monazite structure type (Nabar and Mhatre, 2001) and the silver compound, $AgTh_2(VO_4)_3$, in the zircon-type (Elfakir *et al.*, 1990). Monazite-, scheelite-, and zircon-type structures have also been frequently observed for other ternary or quaternary thorium *ortho*-vanadates, namely $Pb_{0.5}Th_{0.5}(VO_4)$ (Botto and Baran, 1981; Andreetti *et al.*, 1984; Calestani and Andreetti, 1984), $MLaTh(VO_4)_3$ (M = Sr, Pb) (Nabar and Mhatre, 1982), and $CdMTh(VO_4)_3$ (M = La, Yb) (Nabar *et al.*, 1981). Furthermore, a hydrogenvanadate, $Th(HVO_4)_2 \cdot 5H_2O$, is said to precipitate, when VO_4^{3-} is added to solution of a thorium salt (Clève, 1874; Volck, 1894; Neish, 1904).

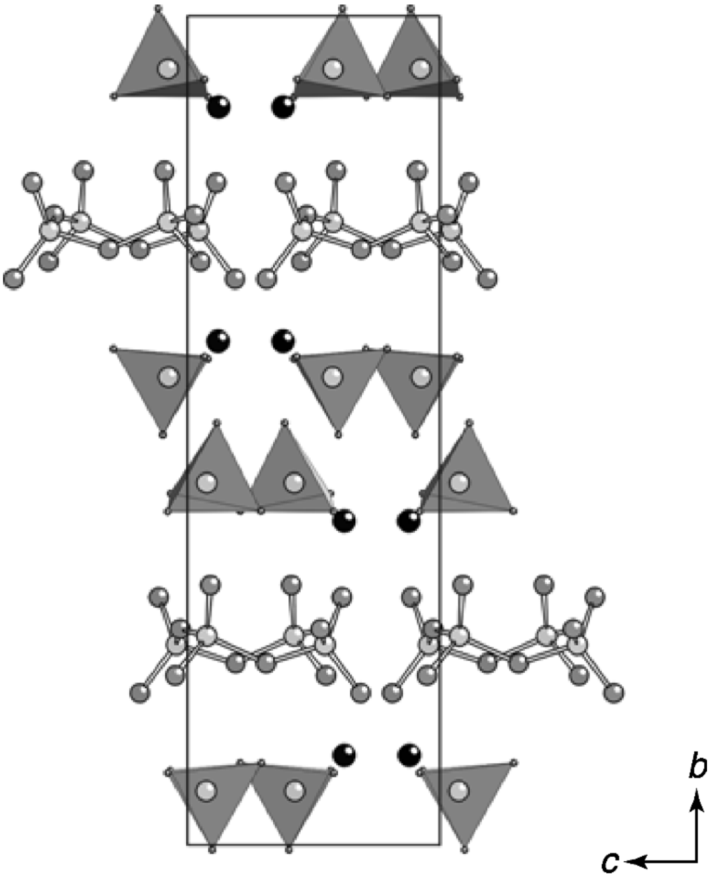

Fig. 3.17 *Crystal structure of Th(VO_4)(VO_3) (or ThV_2O_7). The structure contains isolated* ortho-*vanadate ions (drawn as tetrahedra) and* catena-*vanadate strands.*

(g) Molybdates

One compound, Th(MoO_4)$_2$, is found in the system ThO_2/MoO_3 (Zambonini, 1923; Thoret *et al.*, 1970; Pagès and Freundlich, 1971; Thoret, 1971, 1974). It can be obtained by fusion of the binary oxides or as a hydrate by adding ammonium or alkali metal molybdate to Th^{4+} solutions (Metzger and Zons, 1912; Banks and Diehl, 1947; Trunov and Kovba, 1963; Trunov *et al.*, 1966; Thoret *et al.*, 1968). Th(MoO_4)$_2$ is dimorphic. The orthorhombic low-temperature form shows the Th^{4+} ion in an eight-fold coordination by eight monodentate MoO_4^{2-} groups (Thoret *et al.*, 1970; Thoret, 1974). The molybdate tetrahedra are coordinated to four Th^{4+} ions, leading to a three-dimensional network. In the high-temperature trigonal modification, one set of thorium ions are coordinated by six oxygen atoms while the other set has tricapped trigonal-prismatic coordination polyhedra (Cremers *et al.*, 1983; Larson *et al.*, 1989).

With alkali metal molybdates, M_2MoO_4, $Th(MoO_4)_2$ forms a great variety of compounds (Barbieri, 1913; Thoret, 1971, 1974; Bushuev and Trunov, 1974). The compositions $M_2Th_4(MoO_4)_9$, $M_2Th_2(MoO_4)_5$, $M_2Th(MoO_4)_3$, $M_4Th(MoO_4)_4$, $M_6Th(MoO_4)_5$, and $M_8Th(MoO_4)_6$ have been reported, but only very few of them are properly characterized. In $K_2Th(MoO_4)_3$ the Th^{4+} ions are coordinated by eight oxygen atoms that belong to one chelating and six monodentate MoO_4^{2-} ions (Huyghe *et al.*, 1991a). The $[Th(MoO_4)_7]$ polyhedra are linked to chains along [001] that are held together by K^+ ions. $K_4Th(MoO_4)_4$ consists of a three-dimensional network with the formula $^3_\infty[Th(MoO_4)_{8/2}]$, where the potassium ions are found in holes in the structure (Huyghe *et al.*, 1991b). All of the MoO_4^{2-} groups are monodentate, leading to a coordination number of eight for Th^{4+}. The potassium-rich molybdate $K_8Th(MoO_4)_6$ contains isolated $[Th(MoO_4)_6]^{8-}$ ions in which Th^{4+} attains a coordination number of eight due to the chelating nature of two of the six molybdate groups (Huyghe *et al.*, 1993). The cadmium compound $CdTh(MoO_4)_3$ shows the Th^{4+} ions in tricapped trigonal-prismatic coordination of nine monodentate MoO_4^{2-} groups (Launay and Rimsky, 1980). The prisms are connected to columns along the *c*-axis that are stacked in a hexagonal fashion. In this way channels are formed in which the Cd^{2+} ions reside in an octahedral coordination. $Cu_2Th_4(MoO_4)_9$ has a complicated three-dimensional structure with nine-fold coordinated thorium ions (Launay *et al.*, 1998).

(h) Chromates

Upon addition of dichromate to a solution containing Th^{4+}, the thorium chromate $Th(CrO_4)_2 \cdot 3H_2O$ precipitates at room temperature (Palmer, 1895; Haber, 1897; Britton, 1923). At higher temperatures, a monohydrate precipitates (Palmer, 1895). Both hydrates have been investigated by optical microscopy and seem to be hexagonal or rhombic (Vasilega *et al.*, 1980). According to thermal investigations $Th(CrO_4)_2 \cdot 3H_2O$ dehydrates by a three-step mechanism (Vasilega *et al.*, 1980). Above 280°C, the anhydrous chromate is obtained that remains stable up to 620°C where it decomposes to ThO_2 and Cr_2O_3. Under acidic conditions, for example in concentrated chromic acid, $Th(CrO_4)_2 \cdot CrO_3 \cdot 3H_2O$ is found as the equilibrium solid in the system $ThO_2/CrO_3/H_2O$ (Palmer, 1895; Britton, 1923). None of these compounds is structurally characterized, but the basic chromate, $Th(OH)_2CrO_4 \cdot H_2O$ (Palmer, 1895; Britton, 1923), has been investigated by means of XRD (Lundgren and Sillen, 1949). Its crystal structure contains zigzag-chains of hydroxo-bridged Th^{4+} ions along [010]. Further linkage of the thorium ions is achieved through bonding to CrO_4^{2-} ions.

(i) Miscellaneous oxometallates

A limited number of thorium compounds with oxo-anions other than those discussed above have been mentioned in the literature. The arsenates of thorium are obviously related to the phosphates (Le Flem, 1967; Hubin, 1971; Chernorukov *et al.*, 1974a,b), while the tungstates resemble the molybdates (de Maayer *et al.*, 1972; Thoret, 1974). Thorium *ortho*-germanate, $ThGeO_4$, has been shown to be dimorphic (Bertaut and Durif, 1954; Perezy Jorba *et al.*, 1961; Harris and Finch, 1972) and adopts either the zircon or the scheelite structure type (Ennaciri *et al.*, 1986). This compound has been used as a host lattice for trivalent lanthanides (Gutowska *et al.*, 1981). Besides the most important silicate minerals thorite, huttonite, and thorogummite already mentioned in Section 3.3, a number of complex silicate minerals is known, which are, however, often not characterized completely. Structural data are, for example, available for ekanite, $Ca_2ThSi_8O_{20}$ (Szymanski *et al.*, 1982), and $Ca_6Th_4(SiO_4)_6O_2$, which has the apatite type of structure (Engel, 1978). Furthermore the structure of the mineral thornasite, $Na_{12}Th_3(Si_8O_{19})_4 \cdot 18H_2O$, has been reported recently (Li *et al.*, 2000). One borate, $Th(B_2O_5)$, has been structurally investigated. It contains $B_2O_5^{4-}$ ions and eight-fold coordinated Th^{4+} ions (Baskin *et al.*, 1961; Cousson and Gasperin, 1991).

Additional thorium compounds with transition metal oxo-anions such as the perrhenates should be mentioned. $Th(ReO_4)_4 \cdot 4H_2O$ was obtained from $Th(OH)_4$ and $HReO_4$ (Silvestre *et al.*, 1971; Zaitseva *et al.*, 1984). Its structure is not known but is has been shown to dehydrate in four steps yielding $Th(ReO_4)_4$, which finally decomposes to $Th_2O(ReO_4)_6$ (Zaitseva *et al.*, 1984). $Th(ReO_4)_4$ forms ternary compounds with alkali perrhenates and mixed anionic species with WO_4^{2-} and MoO_4^{2-} (Silvestre, 1978).

Other oxo-metallates reported are the titanate $ThTi_2O_6$ (brannerite structure) (Perezy Jorba *et al.*, 1961; Radzewitz, 1966; Ruh and Wadsley, 1966; Loye *et al.*, 1968; Kahn-Harari, 1971; Zunic *et al.*, 1984; Mitchell and Chakhmouradian, 1999), the niobate $ThNb_4O_{12}$ (Keller, 1965; Trunov and Kovba, 1966; Alario-Franco *et al.*, 1982), and the tantalates $ThTa_2O_7$, $Th_2Ta_2O_9$ (Keller, 1965; Schmidt and Gruehn, 1989, 1990), $Th_2Ta_6O_{19}$ (Busch *et al.*, 1996), and $Th_4Ta_{18}O_{53}$ (Busch and Gruehn, 1996) have been reported. Structurally, however, they are preferably described as double oxides rather than oxo-metallates. Values for the enthalpies of formation of thorite, huttonite (Mazeina *et al.*, 2005) and thorium brannerite (Helean *et al.*, 2003) are given in Chapter 19.

(j) Carboxylates and related organic salts

Carboxylate complexes of thorium have been frequently investigated with respect to the role they may play in solvent extraction processes. Carboxylates and related salts have also been employed in gravimetric analyses for thorium, either by direct weighing if the compound is stoichiometric, or after ignition to thorium dioxide. Thus, there are a large number of papers describing these compounds. Most of them have been mentioned in the *Gmelin Handbook* (Gmelin, 1988a), so only selected examples will be presented here.

The most investigated groups among the carboxylates are formates and acetates. Formates and formato complexes can be obtained by the reaction of formic acid with $ThCl_4$ or other salts of Th^{4+}. In acid solution, $Th(OOCH)_4$, is formed, which has been shown to be polymorphic (Mentzen, 1969, 1971a,b; Greis *et al.*, 1977) and may contain different amounts of crystal water (Claudel and Mentzen, 1966; Thakur *et al.*, 1980). If the pH of the solution increases above 6, basic formates start to form. They may have different compositions like $ThOH(OOCH)_3$, $Th(OH)_2(OOCH)_2$, and $Th(OH)_3(OOCH)$ (Gmelin, 1988a) but they have not been structurally characterized. Various metal ions have been used to crystallize formato complexes, such as $MTh(OOCH)_5$ ($M = K$, Rb, Cs, NH_4) and $MTh(OOCH)_6$ ($M = Sr$, Ba). All these complexes have been characterized by thermal analysis and vibrational spectroscopy (Molodkin *et al.*, 1968b; Gmelin, 1988a).

The structural knowlegde of thorium acetates and acetato complexes is also quite limited, although quite a number of compounds have been described. The tetraacetate, $Th(CH_3COO)_4$, is said to be isotypic with the respective uranium acetate (Eliseev *et al.*, 1967; Bressat *et al.*, 1968; Gmelin, 1988a), and similar to the formates, various hydrates and basic salts are known. Derivatives of acetic acid such as CF_3COOH, CCl_3COOH, $CHCl_2COOH$, $CH_2ClCOOH$, $C_6H_5CH_2COOH$, $C_6H_5CH(OH)COOH$, naphtyl acetic acid, and others, have been used to prepare the respective salts (Katzin and Gulyas, 1960; Gmelin, 1988a). Even bromo- and iodoacetates are known. Among the chloroacetates, one compound has been investigated crystallographically. It has the composition $[Th_6(CHCl_2\ COO)_{12}(OH)_{12}(H_2O)_2]$ and shows an octahedral $[Th_6]$ core surrounded by the ligands.

With increasing complexity of the carboxylic acids, less is known structurally about their thorium compounds. The compounds prepared include glycolates, propionates, butyrates, and their derivatives. Furthermore, compounds with unsaturated mono carboxylic acids have been reported, for example crotonates and cinnamates.

The largest group of thorium salts of dicarboxylic acids are the oxalates and oxalato complexes, for which some crystallographic data are available (Gmelin, 1988a). More complex dicarboxylic acids have been employed, and even the thorium salts of long-chain acids like sebacic acid, $HOOC(CH_2)_8COOH$, are known. The latter has been used, along with *m*-nitrobenzoic acid (Neish, 1904), picrolonic acid (Hecht and Ehrmann, 1935; Dupuis and Duval, 1949), or 'ferron' (7-iodo-8-hydroxyquinoline-5-sulfonic acid), for analytical purposes (Dupuis and Duval, 1949).

3.7.8 Coordination compounds

Coordination compounds of thorium are of special interest because the knowledge of their behavior and their properties is fundamental for the understanding of separation processes (for example, the thorium extraction [THOREX] process that involves tri(*n*-butyl)phosphate complexes) (Peppard and Mason, 1963), see Chapter 24, the development of decontamination methods, and the treatment of radioactive waste. Thus, the number of compounds reported in literature is very large. The *Gmelin Handbook* provides a comprehensive overview of the compounds investigated until 1983 (literature closing date) (Gmelin, 1985b). A more recent review (Agarwal *et al.*, 2000) covers thorium compounds with neutral oxygen donor ligands. These ligands can be divided with respect to the atom to which the oxygen donor is bonded: ligands containing a C–O group may, for example, be alcohols, phenols, ketones, esters, ethers, formamide, acetamide, those containing a N–O group are typically pyridine and quinoline *N*-oxides or even nitrosyl chloride and P=O, As=O, and S=O groups are known for the respective phosphine, arsine, and sulfoxides. The group of neutral oxygen donor ligands is probably the most investigated, but also a great number of complexes with neutral nitrogen donor ligands are known (Vigato *et al.*, 1977). Besides NH_3 (Matthews, 1898; von Bolton, 1908; Clark, 1924), the ligands are higher amines, hydrazine and its derivatives, and pyridine and its derivatives (Matthews, 1898;Adi and Murty, 1978; Al-Daher and Bagnall, 1984). Coordination compounds with charged ligands besides the above-mentioned carboxylates have been also frequently investigated. Among these ligands are the diketonates and related ligands, tropolone and its derivatives, and a great number of Schiff base ligands (Biradar and Kulkarni, 1972).

One of the most important thorium coordination compounds is thorium tetrakis(acetylacetonate), $Th(acac)_4$, which can be sublimed at temperatures below its melting point of 171°C (Urbain, 1896). This is also true for most of the substituted acetylacetonates, for example the trifluoromethylacetylacetonate, whose structure has been determined and that shows the thorium atoms in square antiprismatic coordination of oxygen atoms (Wessels *et al.*, 1972). These compounds are generally efficiently extracted into water-immiscible solvents, a property that has been used, for example, with thenoyltrifluoroacetone, to measure complexation of thorium with various anions (Calvin, 1944; Day and Stoughton, 1950). Another ligand that has been studied in more detail is 8-hydroxyquinoline ('oxine') and its derivatives (Frazer and Rimmer, 1968; Abraham and Corsini, 1970; Corsini and Abraham, 1970; Singer *et al.*, 1970; White and Ohnesorge, 1970). Also heteroleptic species involving oxine and another ligand, for example dimethylsulfoxide, are known (Singer *et al.*, 1970; Andruchow and Karraker, 1973). As a thorium complex with eight-fold thorium coordination with sulfur atoms, thorium(IV) tetrakis(*N*,*N*-diethyldithiocarbamate) should be mentioned (Brown *et al.*, 1970b). A path to related compounds is through intermediates such as $Th(NEt_2)_4$ (Bradley and Gitlitz, 1969; Watt and Gadd, 1973), which, when treated with CXY (X,Y = O, S, Se etc.), gives carbamates, thiocarbamates, mixed compounds like $Th[OSCN(CH_3)_2]_4$, and even $Th(Se_2CNEt_2)_4$ (Bagnall and Yanir, 1974). It is very surprising that despite the large number of complexes that have been prepared, the number of structure determinations is very limited.

3.7.9 Organothorium compounds

As Chapters 25 and 26 are devoted to the synthesis, the characterization and the properties of the organoactinide compounds, only selected examples shall be mentioned briefly here.

Thorocene, $Th(COT)_2$ (COT = cyclo-octatetraene), has been prepared by treating $ThCl_4$ in tetrahydrofuran (THF) with $K_2(COT)$ at dry-ice temperature (Streitwieser and Yoshida, 1969). The yellow crystals of $Th(COT)_2$ sublime at 0.01 mmHg pressure and 160°C. Thorocene, isomorphous with $U(COT)_2$ (uranocene) (Avdeef *et al.*, 1972), is unstable in air, decomposes in water, and undergoes thermal decomposition without melting above 190°C. Gas-phase photoelectron spectra have been used to elucidate the bonding in thoracene (Fragala *et al.*, 1976; Clark and Green, 1977). This compound has also been prepared by treating ThF_4 with Mg(COT) (Starks *et al.*, 1974). In addition, a number of half-sandwich Th(IV) complexes with COT have been reported (LeVanda *et al.*, 1980; Zalkin *et al.*, 1980).

Numerous complexes with the cyclopentadienyl (Cp^-) anion have been reported. $Th(Cp)_4$ was first prepared by the reaction of $ThCl_4$ with KCp (Fischer and Treiber, 1962). This compound sublimes between 250 and 290°C at 10^{-3} to 10^{-4} mmHg. Tris(cyclopentadienyl) halides and alkoxides of thorium have been synthesized (Ter Haar and Dubeck, 1964; Marks *et al.*, 1976), and, in general, these air-sensitive compounds sublime below 200°C and 10^{-3} to 10^{-4} mmHg pressure. Related tris(indenyl)thorium halides and alkoxides have been prepared (Laubereau *et al.*, 1971; Goffart *et al.*, 1975, 1977). The only bis (cyclopentadienyl)thorium dihalide reported is $ThI_2(Cp)_2$, prepared from ThI_4 and $Mg(Cp)_2$ (Reid and Wailes, 1966), whereas it is believed that the chloride analog would be unstable, similar to the uranium compound (Ernst *et al.*, 1979). In contrast, the permethylated Cp derivative $C_5(CH_3)_5^-$ (=Cp*) has been used to prepare stable dichlorides, $(Cp^*)_2ThCl_2$ (Manriquez *et al.*, 1978; Blake *et al.*, 1998). The CpTh trihalides have been described to exist as adducts with ethers, $CpThX_3 \cdot 2L$ (L = tetrahydrofurane or 1/2 dimethoxyethane [DME]) (Bagnall *et al.*, 1978). Analogous indenyl (Goffart *et al.*, 1980) and Cp* compounds have also been reported (Mintz *et al.*, 1982).

Tetrabenzylthorium, $Th(CH_2C_6H_5)_4$, is the best-characterized thorium homoalkyl compound reported to date (Köhler *et al.*, 1974). The light-yellow, air-sensitive, crystalline compound decomposes slowly at room temperature. A second tetrahydrocarbyl thorium complex has been reported, $Th(CH_3)_4(dmpe)_2$ (dmpe = bis(dimethylphosphino)ethane), prepared by the reaction of $ThCl_4(dmpe)_2$ with CH_3Li (Edwards *et al.*, 1981). It is stable up to –20°C in the absence of air and moisture. These two thorium phosphine complexes, along with $Th(OC_6H_5)_4(dmpe)_2$ and $Th(CH_2C_6H_5)_4(dmpe)_2$, were the first isolated and characterized species of their kind (Edwards *et al.*, 1984). Tetraallylthorium, $Th(C_3H_5)_4$, has been reported and decomposes slowly above 0°C (Wilke *et al.*, 1966).

The reaction of the Cp– (Marks and Wachter, 1976), indenyl– (Goffart *et al.*, 1977), and Cp*–thorium chlorides (Fagan *et al.*, 1981; Fendrick, 1984) with alkylating or arylating reagents has yielded the corresponding π-ligand thorium hydrocarbyls. In a thermodynamic study on the series $(Cp^*)_2ThR_2$, it was observed that the bond disruption enthalpies of the thorium–ligand σ-bonds were about 250–335 kJ mol^{-1}, significantly greater than similar transition metal bond enthalpies (Bruno *et al.*, 1983).

More recent investigations on organothorium chemistry were intended to introduce new ligands in that field and to synthesize low-valent thorium compounds. For example, the bicyclic pentalene dianion $C_8H_6^{2-}$ has been used to prepare a new type of thorium sandwich complex. The crystal structure, as well as the photoelectron spectra, of $[Th\{C_6H_4(Si^iPr_3–1,5)_2\}_2]$ was reported (Cloke and Hitchcock, 1997; Cloke *et al.*, 1999). Another very interesting ligand, the dicarbollide anion $C_2B_9H_{11}^{2-}$, should be mentioned: it is found in the complexes $[Li(THF)_4]_2[Th(\eta^5\text{-}C_2B_9H_{11})_2X_2]$ (X = Cl, Br, I) (Rabinovich *et al.*, 1997).

The number of potentially low-valent organothorium complexes is still very limited. Two forms of $Th(C_5H_5)_3$ have been reported. Purple $Th(C_5H_5)_3$ was prepared by sodium naphtalide reduction of $Th(C_5H_5)_3Cl$ in THF. The latter was removed under vacuum (Kanellakopulos *et al.*, 1974). According to X-ray powder diffraction measurements, the compound is isotypic with the analogs of heavier 5f elements and has an effective magnetic moment of $0.331\mu_B$. The green form of $Th(C_5H_5)_3$ was formed via photolysis of $Th(C_5H_5)_3[(CH(CH_3)_2]$ in benzene solution and has a magnetic moment of $0.404\mu_B$ (Kalina *et al.*, 1977). A recent example is $[Th\{COT(TBS)_2\}_2][K(DME)_2]$ – with $COT(TBS)_2$ = $\eta\text{-}C_8H_6(t\text{BuMe}_2\text{Si})_2\text{–}1,4$ – that has been prepared by the reaction of a suspension of $[Th\{COT(TBS)_2\}_2]$ in DME with elemental potassium (Parry *et al.*, 1999). Furthermore, the first organometallic compounds of divalent thorium have been reported recently. They contain the complex Et_8-calix[4]tetrapyrrole ligand and are potentially divalent synthons (Korobkov *et al.*, 2003).

3.8 SOLUTION CHEMISTRY

3.8.1 Redox properties

Thorium is known to have only one stable oxidation state in aqueous solution, the tetravalent state, Th^{4+}(aq) (Gmelin, 1988c).

Th(III) has been recently claimed by Klapötke and Schulz (1997) to be formed by reaction of $ThCl_4$ with HN_3 in slightly acidic solution and to be stable for at least 1 h. Reportedly, the reaction involved:

$$Th^{4+} + HN_3 \rightarrow Th^{3+} + 1.5N_2 + H^+$$

Yet, the reaction has been shown to be thermodynamically impossible by Ionova *et al.* (1998). First, the stabilization of d-electrons by the crystal field effect is not sufficient to assign, as suggested by Bratsch and Lagowski (1986), a value of –3.0 V to the redox potential of the couple M^{4+}/M^{3+}. Besides, a value between –3.35 and –3.82 V, in the same range as the previously published one, –3.7 V (Nugent *et al.*, 1973), is much more probable. Secondly, the reducing ability of HN_3 has been overestimated and the authors concluded that the spectra published by Klapötke and Schulz (1997), as a proof of the existence of Th^{3+}(aq) (broad absorption signal centered around 460 nm and intense peaks at 392, 190 and below 185 nm), correspond, in fact, to azido–chloro complexes of Th(IV).

3.8.2 Structure of the aqueous Th^{4+} ion

The LIII-edge extended X-ray fine structure (EXAFS) experiments on 0.03–0.05 M Th(IV) in 1.5 M $HClO_4$ solutions have clearly defined the structure of the Th(IV) aqua ion (Moll *et al.*, 1999). A least-squares refinement of the data leads to a Th–O distance of (2.45 ± 0.01) Å and a coordination number of (10.8 ± 0.5) which is larger than the older values estimated by Johansson *et al.* (1991) from low-angle X-ray scattering (LAXS) results (8.0 ± 0.5 water molecules at 2.485 Å) or by Fratiello *et al.* (1970) from ^{1}H NMR data at low temperatures and higher concentrations (nine water molecules in the first hydration sphere).

The results of Moll *et al.* are consistent with the structural parameters obtained in the same study for U^{4+}(aq) (CN = 10 ± 1; $R = 2.42 \pm 0.01$ Å) and previously by Allen *et al.* (1997) for Np^{4+}(aq) (CN = 11.2 ± 0.4; $R = 2.40 \pm 0.01$ Å). A correlation between the hydration number (higher than 6) of highly charged metal ions and the bond distance shows also that a M–O distance of 2.45 Å is in favor of a hydration number closer to 10 (Sandström *et al.*, 2001). More precise systematics and correlation between the space around the cation and its charge have been proposed by David and Vokhmin (2003). They give consistent coordination numbers of Th^{4+}, U^{4+}, Np^{4+}, and Pu^{4+}: 11.0, 10.65, 10.2, and 10.0, respectively. The same authors have evaluated the corresponding ionic radii, 1.178 Å for Th^{4+}, and a size of the coordinated water molecule of 1.335 Å, by assuming a pure electrostatic bond. It would result in a larger cation–oxygen distance of 2.51 Å. The observed difference with experimental data (0.06 Å) has been interpreted by a covalent effect and the effective charge of the Th^{4+} aquo ion has been evaluated to be 3.82 (David and Vokhmin, 2003). Finally, the same authors have determined the number of water molecules in a second hydration sphere as 13.4.

3.8.3 Thermodynamics of the Th^{4+}(aq) ion

The data on the standard enthalpy of formation, entropy, and corresponding Gibbs energy, adopted in this review and shown in Table 3.12, are those given in the compilation of Martinot and Fuger (1985), except for a small difference in the standard Gibbs energy of formation, due to the use of a more recent value for the entropy of Th(cr) (see Chapter 19).

Table 3.12 *Main thermodynamic properties of the thorium aqueous ion at* 25°C (*see text for references*).

$E°(Th^{4+}/Th)$	$\Delta_f H°$(kJ mol^{-1})	$\Delta_f G°$(kJ mol^{-1})	$S°$ (J K^{-1} mol^{-1})
−(1.828 ± 0.015) V/NHE	−(769.0 ± 2.5)	−(705.5 ± 5.6)	−(422.6 ± 16.7)

Thermodynamic models have been proposed recently by David and Vokhmin (2001) to evaluate the Gibbs hydration energy and the entropy of the aquo ions. Corresponding values are $\Delta_{hyd}G°(Th^{4+}) = -6100$ kJ mol^{-1} and $S°(Th^{4+},aq) = -438$ J mol^{-1} K^{-1} (David and Vokhmin, 2003). The entropy value is consistent with the experimental value, –(422.6 ± 16.7) J K^{-1} mol^{-1} (Martinot and Fuger, 1985).

The standard state partial molar heat capacities and volumes of Th^{4+}(aq) have been recently determined from 10 to 55°C under conditions minimizing complications due to hydrolysis and ion-pairing equilibria or ion–ligand complexation (measurements on aqueous solutions containing $Th(ClO_4)_4$ in dilute $HClO_4$ (Hovey, 1997)). The values obtained at 25°C, $C_p°(Th^{4+},aq) = -(224 \pm 3)$ J K^{-1}mol^{-1} and $V°(Th^{4+},aq) = -(60.6 \pm 0.5)$ cm^3 mol^{-1}, appear as more negative than those of any monoatomic aqueous ion. These results are also quite different from the previous estimations: $C_p°(Th^{4+},aq) = -(1 \pm 11)$ J K^{-1} mol^{-1} (Morss and McCue, 1976) recalculated as −(60 ± 11) J K^{-1} mol^{-1} using a newer $C_p°(NO_3^-,aq)$ value, –72 J K^{-1} mol^{-1} (Hovey, 1997) and $V°(Th^{4+},aq) =$ –53.5 and –54.6 cm^3 mol^{-1} from the values given in the International Critical Tables (1928) for the standard state partial molar volumes of $ThCl_4$(aq) and $Th(NO_3)_4$(aq), respectively.

3.8.4 Hydrolysis behavior

Being the largest actinide tetravalent ion, Th^{4+}(aq) is also the least hydrolyzable of them (Onosov, 1971). Because of its size, it is less hydrolyzable than many other multi-charged ions such as iron(III); tetravalent thorium may therefore be studied over a larger range of concentrations, at pH values up to 4. However, its tendency to undergo polynucleation reactions and colloid formation, as well as the low solubility of its hydroxide or hydrous oxide, limit the possibilities of investigation. For these reasons, the oxide/hydroxide solubility products and hydrolysis constants published in the literature show great discrepancies.

Very recently, Neck and Kim (2001) have proposed a critical review and a comprehensive set of thermodynamic constants at zero ionic strength and 25°C. In the first part of their work, they compared the frequently accepted constants of Baes *et al.* (1965), Baes and Mesmer (1976), Brown *et al.* (1983), Grenthe and Lagerman (1991), and Ekberg and Albisson (2000). All these data, which are reported in Table 3.13, are based on potentiometric titrations at 15, 25, or 35°C with relatively low thorium concentrations (2×10^{-4} to 10^{-5} M).

Ekberg and Albinsson have performed, in addition, solvent extraction experiments with a total concentration of Th(IV) in the range 10^{-5} to 10^{-7} M. It should be outlined that, under the conditions usually applied in potentiometric and solvent extraction studies ($[\mathrm{Th}]_{\mathrm{tot}} = 2 \times 10^{-4}$ to 2×10^{-2} M; pH = 2.5–4; Kraus and Holmberg, 1954; Hietanen and Sillen, 1964; Baes *et al.*, 1965; Nakashima and Zimmer, 1984), polynuclear species are of major importance and laser-induced breakdown detection (LIBD) has shown that a considerable amount of colloids were present at $\log[\mathrm{H}^+] \leq -(1.90 \pm 0.02)$ for $\log[\mathrm{Th}]_{\mathrm{tot}} = -(2.04 \pm 0.02)$ and at $\log [\mathrm{H}^+] \leq -(2.40 \pm 0.03)$ for $\log[\mathrm{Th}]_{\mathrm{tot}} = -(4.05 \pm 0.02)$ (Bundschuh *et al.*, 2000). We can also cite the work of Moulin *et al.* (2001) who recently applied electrospray ionization–mass spectrometry to determine the hydrolysis of Th(IV) in dilute solution, but the equilibrium constants so-determined $\log K^\circ_{11} = -(2.0 \pm 0.2), \log K^\circ_{12} = -(4.5 \pm 0.5),$ and $\log K^\circ_{13} = -(7.5 \pm 1.0)$ are so large, compared to those obtained from the above-cited well-established methods, that it is difficult to consider them as reliable.

As we can see from Table 3.13, the first mononuclear hydrolysis constants found by Brown *et al.* (1983) and Ekberg and Albinsson (2000) are about one order of magnitude higher than the constants derived by Baes and Mesmer (1976) and Grenthe and Lagerman (1991). Moreover, the hydrolysis constants reported for $\mathrm{Th(OH)_2^{2+}}$, $\mathrm{Th(OH)_3^+}$, and $\mathrm{Th(OH)_4(aq)}$ differ between authors by several orders of magnitude. In order to select the best available data, Neck and Kim (2000) estimated the 'unknown' formation constants of $\mathrm{Th(OH)}_n^{(4-n)+}$ by two methods.The first one, method A, is based on the empirical intercorrelation between hydrolysis constants of actinide ions at different oxidation states. The second method, B, developed by the authors consists of applying a semiempirical approach, in which the decrease of the stepwise complexation constants for a given metal–ligand system is related to the increasing electrostatic repulsion between the ligands. From their results collected in Table 3.13, Neck and Kim concluded that the higher $\log \beta^\circ_{11}$ values, in the range 11.7–11.9, and the lower $\log \beta^\circ_{13}$ and $\log \beta^\circ_{14}$ values (Ekberg and Albinsson, 2000) should be preferred. Consequently, their selected values are $\log \beta^\circ_{1n} = (11.8 \pm 0.2)$, (22.0 ± 0.6), (31.0 ± 1.0), and (39.0 ± 0.5) for $n = 1, 2, 3,$ and 4, respectively (Neck and Kim, 2000). These data have been used to plot the speciation diagrams given in Fig. 3.18.

Following a similar approach, Moriyama *et al.* (1999) analyzed the mononuclear hydrolysis constants of actinide ions by using a simple hard sphere model. Systematic trends were thus obtained, from which the values given in Table 3.13 have been deduced ($\log \beta^\circ_{1n} = 12.56, 23.84, 32.76,$ and 40.40 for $n = 1, 2, 3,$ and 4, respectively). These values are intermediate between the two series calculated by Neck and Kim (2000) and are in rather good agreement with the averages of literature data ($\log \beta^\circ_{1n} = 11.27, 22.43, 33.41,$ and 40.94 for $n = 1, 2, 3,$ and 4, respectively) given by Moriyama *et al.* (1999).

Table 3.13 *Experimental and estimated hydrolysis constants proposed for Th(IV) at 25°C and defined as follows ([i] and γ_i denoting the concentration and the activity coefficient of the species i):*

$$K_{1-n} = [Th(OH)_n^{(4-n)+}][H^+]^n/[Th^{4+}]$$

$$\beta^{\circ}_{1-n} = [Th(OH)_n^{(4-n)+}](\gamma_{Th(OH)n})/[Th^{4+}](\gamma_{Th})[OH^-]^n(\gamma_{OH})^n$$

The values at $I = 0$ (log β°_{1n}) have been calculated by Neck and Kim (2001) by applying the specific interaction theory (SIT) following the NEA Thermochemical Data Base project (Grenthe et al., *1992).*

References	*Method*	*Medium*	log β^{o}_{1-1} (*log* K_{1-1})	log β^{o}_{1-2} (*log* K_{1-2})	log β^{o}_{1-3} (*log* K_{1-3})	log β^{o}_{1-4} (*log* K_{1-4})
Hietanen and Sillen (1964)	potentiometry and coulometry	3 M NaCl	(–2.65/ <–2.33)			
Baes *et al*. (1965); Baes and Mesmer (1976)	potentiometry	1 M $NaClO_4$	11.0 ± 0.2 (–4.12 ± 0.03)[a]	22.2 ± 0.2 (–7.81 ± 0.03)[a]	<30.3[b]	40.1 ± 0.3[b]
Brown *et al*. (1983)	potentiometry	0.1 M KNO_3	11.7 ± 0.1 (–2.98 ± 0.07)			
Nakashima and Zimmer (1984)	solvent extraction	0.5 M KNO_3	11.8 ± 0.2 (–3.28)			
Bruno *et al*. (1987)	potentiometry	3 M $NaClO_4$	(–4.13 ± 0.06)			(–15.07 ± 0.2)
Moon (1989)	ThO_2 solubility	0.1 M $NaClO_4$	12.42 ± 0.02[c]	22.46 ± 0.15[c]	34.36 ± 0.07[c]	42.58 ± 0.08[c]
	$Th(OH)_4$ solubility	0.5 M $NaClO_4$	12.58 ± 0.02[c]	22.35 ± 0.15[c]	34.42 ± 0.07[c]	42.76 ± 0.08[c]
Grenthe and Lagerman (1991)	potentiometry	3 M $NaClO_4$	10.9 ± 0.3 (–4.35 ± 0.09)		32.7 ± 0.4 (–12.3 ± 0.2)	42.4 ± 0.4 (–16.65 ± 0.04)
Ekberg and Albinsson (2000)	potentiometry and solvent extraction	1 M $NaClO_4$	11.9 ± 0.2 (–3.3 ± 0.1)	21.4 ± 0.2 (–8.6 ± 0.1)	30.6[d] (–13.8)[d]	39.0 ± 0.5 (–19.4 ± 0.5)
Moriyama *et al*. (1999)	hard sphere model		12.56	23.84	32.76	40.40
Neck and Kim (2001)	estimation A		13.4	26.5	36.7	43.9
	estimation B		11.9	22.9	31.4	37.0
	selection		11.8 ± 0.2	22.0 ± 0.6	31.0 ± 1.0	38.5 ± 1.0

[a] Values based on the data of Kraus and Holmberg (1954).

[b] Values based on the data of Nabivanets and Kudritskaya (1964).

[c] Not extrapolated to zero ionic strength.

[d] Interpolated values (15–35°C).

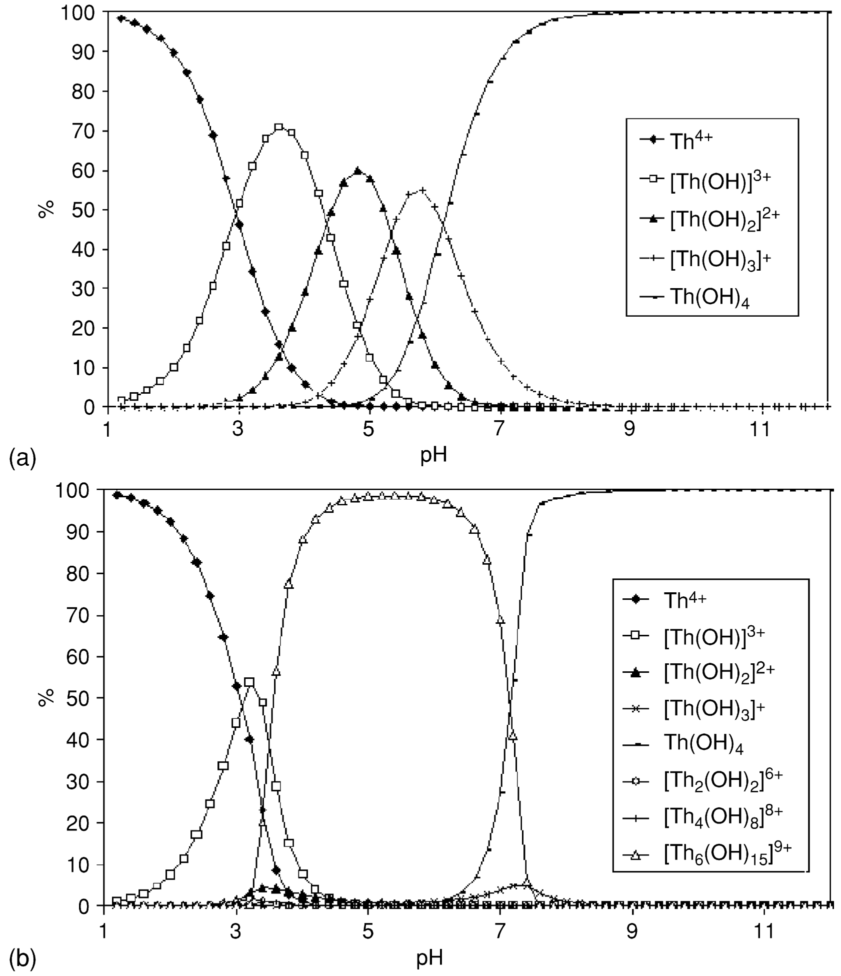

Fig. 3.18 *Thorium speciation diagrams in non-complexing aqueous solution* (*calculated for* 0.1 M *NaCl by using the hydrolysis constants given in Tables* 3.13 *and* 3.14 (*Neck and Kim,* 2001; *Ekberg and Albinsson,* 2000) *and the PHREEQUE program, version* 2.2). (*a*) *Species distribution for low concentrations of Th*(*IV*) (= 10^{-8}M *in the present case*). (*b*) *Species distribution for* $[Th]_{tot}$ = 0.1 M, *considering the possible formation of only three polynuclear species:* $Th_2(OH)_2^{6+}$, $Th_4(OH)_8^{8+}$, *and* $Th_6(OH)_{15}^{9+}$.

3.8.5 Solubility

(a) In non-complexing media

In perchlorate media, an average hydroxyl number, *n* (OH^- groups bound per thorium), of about 2.5 can be reached without delayed precipitation. All hydrolyzed solutions contain polymeric species and the weight-average degree of polymerization increases with the degree of hydrolysis (Danesi *et al.*, 1968; Hietanen and Sillen, 1964). The presence of the $Th_2(OH)_2^{6+}$ polymer is well recognized in most of the studies (Hietanen and Sillen, 1964; Baes *et al.*, 1965; Milic, 1971, 1981; Milic and Suranji, 1982; Moon, 1989), but other polymers such as $Th_2(OH)_3^{5+}$ (Milic, 1981, Moon, 1989), $Th_2(OH)_4^{5+}$ (Moon, 1989), $Th_4(OH)_8^{8+}$ (Baes *et al.*, 1965; Ekberg and Albinsson, 2000), $Th_4(OH)_{12}^{4+}$ (Brown *et al.*, 1983), $Th_5(OH)_{12}^{8+}$ (Lefèbvre, 1957), $Th_6(OH)_{14}^{10+}$ (Milic, 1981), $Th_6(OH)_{15}^{9+}$ (Baes *et al.*, 1965; Brown *et al.*, 1983; Ekberg and Albinsson, 2000) have been found as well. The corresponding conditional constants collected in Table 3.14 show a rather reasonable agreement between the different studies for the species commonly detected. The experimental conditions, especially the total thorium concentration involved in the measurements, may explain why different sets of polynuclear species are discussed in the different studies (some species can have a too low concentration to be detected and/or can precipitate). However, it is interesting to note that $Th_6(OH)_{15}^{9+}$ is the only polynuclear species expected to predominate in the simple Th(IV)/H_2O system, when the total Th(IV) concentration exceeds $\sim 10^{-3}$ M (and up to at least 1 M) and for a pH range centered around 4.5–5 (see Fig. 3.18(b)).

The structure of highly hydrolyzed thorium salt solutions has been studied by electronic microscopy (Dobry *et al.*, 1953; Dzimitrowickz *et al.*, 1985) and light or X-ray scattering techniques (Dobry *et al.*, 1953; Hentz and Johnson, 1966; Magini *et al.*, 1976). The details of this structure are dependent on sample history. At room temperature, the hydrolysis complexes contain a small number of Th(IV) atoms probably situated at the corners of slightly distorted face-sharing tetrahedral. At higher temperatures, small crystallites (~40 Å) are formed, which have the ThO_2 structure. These crystallites tend to join to other crystallites, in random orientation, to form particles of up to 170 Å in diameter (Magini *et al.*, 1976). Finally, the small fragments of fluorite can be connected (e.g. cross-linking by oxide bridges) in a random manner into larger, porous agglomerates irregular in shape and size up to 800–15000 Å (Dzimitrowickz *et al.*, 1985). In dilute colloidal solutions ($[Th]_{tot} < 10^{-2}$ mol L^{-1}), filamentous particles with a statistic average length of 700 Å are observed; they are wound into compact balls in more concentrated solutions (Dobry *et al.*, 1953).

The solubility products reported for the thorium oxide and hydroxide species show considerable discrepancies (Table 3.15). The reasons can be found in: (1) the characteristics of the solid phase (degree of crystallization, morphology, etc.), which depend on the history of its preparation (hydrolysis reaction, pretreatment, aging); (2) the composition of the solution (pH range, ionic strength); (3) the method of evaluating the total concentration of thorium in solution (cutting size for the phase separation); (4) the generally too simplified chemical model used to derive the solubility product; and (5) the set of hydrolysis constants used in the data treatment.

Concerning the first point, it is important to distinguish between the amorphous fresh hydroxide precipitate, just washed prior to experiments,

Table 3.14 *Conditional hydrolysis constants proposed for the polynuclear species of Th*(IV) *and defined as follows* ([*i*] *denoting the concentration of the species i*):

$$K_{x-y} = [Th_x(OH)_y^{(4x-y)+}]\,[H^+]^y/[Th^{4+}]^x.$$

Medium (*reference*)	$-logK_{2\text{–}2}$	$-logK_{2\text{–}3}$	$-logK_{2\text{–}4}$	$-logK_{4\text{–}8}$	$-logK_{4\text{–}12}$	$-logK_{6\text{–}14}$	$-logK_{6\text{–}15}$
3 M $NaClO_4$ (Hietanen and Sillen, 1964)	4.70 ± 0.05	8.83 ± 0.21				36.53 ± 0.19	40.37 ± 0.23
1 M $NaClO_4$ (Baes *et al*., 1965)	4.61 ± 0.02			19.01 ± 0.02			36.76 ± 0.02
3 M $NaClO_4$ (Brown *et al*., 1983)					30.55 ± 0.03		34.4 ± 0.03
3 M $NaClO_4$ (Bruno *et al*., 1987)	4.74 ± 0.04			19.15 ± 0.04		33.83 ± 0.03	
0.5 M $NaClO_4$	−2.05 ± 0.04	9.79 ± 0.11	−3.07 ± 0.04				
0.1 M $NaClO_4$ (Moon, 1989)	5.89 ± 0.10						
3 M $NaClO_4$ (Grenthe and Lagerman, 1991)	5.10 ± 0.17	7.87 ± 0.05		19.6 ± 0.2	34.86 ± 0.05	33.67 ± 0.05	
1 M $NaClO_4$ (Ekberg and Albinsson, 2000)				19.1[a]			39.5[a]

[a] Values used, after correction for the ionic strength, in the PHREEQUE program in order to calculate the speciation curves plotted in Fig. 3.18.

Table 3.15 *Conditional solubility product,* K_{sp}, *and estimated value at infinite dilution,* K°_{sp}, *proposed for Th oxide and hydroxide species at* 17–25°C *and defined as follows* ([*i*] *and* γ_i *denoting the concentration and the activity coefficient of the species i*):

$$K_{sp} = [Th^{4+}][OH^-]^4$$

$$K^{\circ}_{sp} = K_{sp}(\gamma_{Th})(\gamma_{OH})^4(for Th(OH)_4, am)$$

$$K^{\circ}_{sp} = K_{sp}(\gamma_{Th})(\gamma_{OH})^4(a_w)^{(x=2)}(for ThO_2.xH_2O, s).$$

References	*Solid*	*Solution*	*log*$[Th]_{tot}$ *at pH* > 5	K_{sp}	K°_{sp}
Nabivanets and Kudritskaya (1964)	Th(IV) hydroxide or hydrous oxide	0.1 M $NaClO_4$ (17°C)	−6.3	−44.7	−46.8
Ryan and Rai (1987)	$ThO_2\cdot xH_2O$(am) (hydrous oxide)	0.1 M $NaClO_4$	−8.8 ± 0.2	−45.2	−45.5
Felmy *et al.* (1991)		0.6 M NaCl and KCl (room temp.)	−8.5 ± 0.6		−47.3[b]
Moon (1989)	$Th(OH)_4$(am)	0.5 M $NaClO_4$ (18°C)	−8.2 ± 0.3	−50.52 ± 0.08 −43.5[a]	−46.6 −52.9
Östhols *et al.* (1994)	ThO_2(cr) (700°C)	0.1 M $NaClO_4$(25°C)	−8.2 ± 0.3	−50.76 ± 0.08	−53.6[b]
	microcrystalline $ThO_2\cdot 2.5H_2O$	0.5 M $NaClO_4$ (25°C)		−45.1	−48.7 −48.2[b]
Bundschuh *et al.* (2000)	colloidal ThO_2(cr)	0.5 M NaCl (25°C)		−49.54 ± 0.22	−52.8 ± 0.3
Neck and Kim (2001)	$Th(OH)_4$(am)		−8.5 ± 0.6		−47.0 ± 0.8
	ThO_2(cr)		−8.5 ± 0.6		−53.5 ± 0.7

[a] Value calculated by Neck and Kim (2001) with the use of an other set of hydrolysis constants.

[b] Values calculated by Neck and Kim (2001) by applying the specific interaction theory (SIT) following the NEA Thermochemical Data Base project (Grenthe *et al.*, 1992).

the hydrous oxide or microcrystalline $ThO_2 \cdot nH_2O$ showing very broad X-ray powder diffraction peaks, and the well-crystallized thorine, obtained after appropriate heating steps. The four other points have to be taken into account to select and interpret the various solubility curves published in the literature. This task has been recently accomplished by Neck and Kim (2001). First, they analyzed the solubility data obtained for amorphous Th(IV) precipitates (not treated at higher temperature but only washed with water) at $I \leq 1$ M by using a chemical model that includes all mononuclear species $Th(OH)_n^{(4-n)+}$ up to $n = 4$ and two polynuclear species, $Th_4(OH)_{12}^{4+}$ and $Th_6(OH)_{15}^{9+}$. For this purpose, they chose the hydrolysis constants, $\log K_{4\text{–}12}$ and $\log K_{6\text{–}15}$, given in Table 3.14 and derived by Brown *et al.* (1983) from potentiometric titrations at pH = 3–4, in combination with their selected data for the mononuclear hydrolysis species (see Table 3.13).

By monitoring the initial colloid generation (with size of 16–23 nm) as a function of pH and Th(IV) concentration with the use of LIBD, Bundschuh *et al.* (2000) determined a value of $\log K_{sp}^{\circ}$ equal to – (52.8 ± 0.3) (also calculated with the specific interaction theory (SIT) coefficients of Nuclear Energy Agency Thermochemical Database Project [NEA-TDB] data), which corresponds both to the solubility products of crystalline ThO_2 (values of Moon (1989) revisited by Neck and Kim (2001) [see Table 3.15]) and to the value calculated from thermochemical data for ThO_2, $\log K_{sp}^{\circ} = -(54.2 \pm 1.3)$ (Rai *et al.*, 1987). The difference is ascribed to a particle size effect and it is concluded that the colloids formed in the coulometric pH titration experiments consist of crystalline thorium dioxide. This conclusion is also supported by the work of Dzimitrowickz *et al.* (1985).

Moreover, it is evident from Fig. 3.19 that the degree of crystallization of ThO_2 influences its solubility behavior essentially in acidic media. At pH < 2.5, the experimental solubility curve of ThO_2(cr) seems to indicate an equilibrium between the solid phase and Th^{4+}(aq) (slope of −4 for the microcrystalline precipitates only). However, such an equilibrium has never been observed when the dissolution process is studied from under-saturation (Hubert *et al.*, 2001; Neck, 2002). With increasing pH, the solubility data deviate more and more from the expected curve. The hydrolysis of the Th^{4+} ions leads to increased Th(IV) concentrations, which are not in equilibrium with ThO_2(cr), but with an amorphous surface layer of $Th(OH)_4$ covering the crystalline solid, as judiciously explained by Neck and Kim (2001). In fact, kinetic effects play an important role in the overall process, as outlined by Hubert *et al.* (2001).

(b) In complexing media

The precipitation of thorium by various inorganic and organic ligands and the characterization of the resulting solids were treated at some length in Section 3.7.7. Therefore the discussion here will be limited to the role of the carbonate

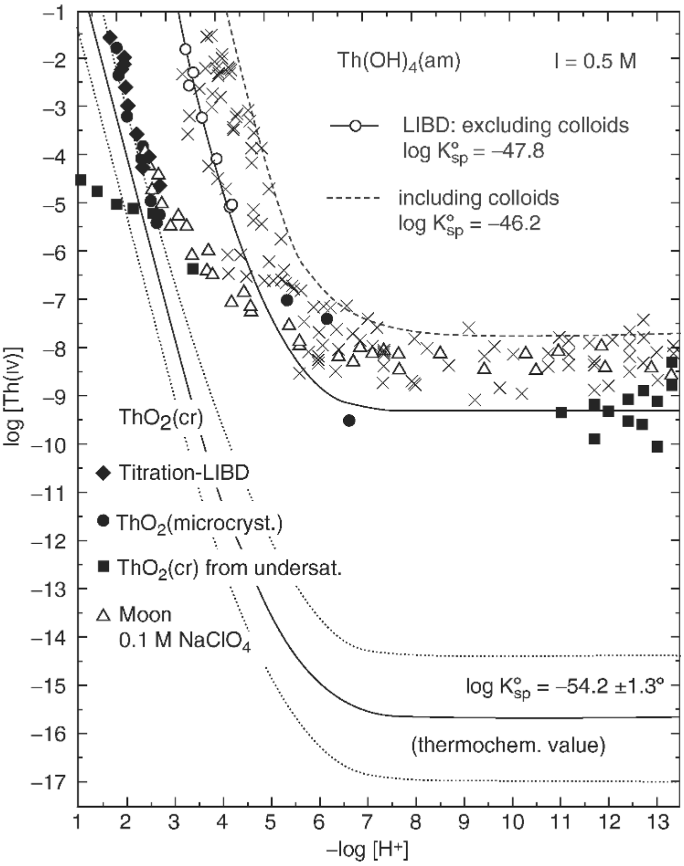

Fig. 3.19 *Experimental and calculated solubility of* $ThO_2(cr)$ *in comparison with that of Th(IV) hydroxide or hydrous oxide at* $I = 0.5$ M *and* 25°C (*Neck,* 2002). *The experimental data for* $ThO_2(cr)$ *are those determined by Neck* (2002) *by titration–LIBD and from under- and oversaturation* (*filled symbols*) *and by Moon* (1989) *in* 0.1 M $NaClO_4$ *at* 18°C (*open triangles*). *The solubility data for amorphous precipitates* (*crosses*) *are taken from Moon* (1989), *Felmy et al.* (1997), *Östhols et al.* (1994), *Rai et al.* (1997), *Neck and Kim* (2000), *all data being at* $I = 0.5$–0.6 M *and* 18–25°C. *The curves calculated for the two kinds of solids and for* $I = 0.5$ M *are based on the hydrolysis constants selected by Neck and Kim* (2001) *and on the solubility products* $\log K^{\circ}_{sp}(ThO_2, cr) = -(54.2 \pm 1.3)$ (*Rai et al.,* 1987) *and* $\log K^{\circ}_{sp}(Th(OH)_4, am) = -(47.0 \pm 0.8)$ (*Neck and Kim,* 2001).

and the phosphate ions on the solubility of thorium and, consequently, on its behavior in natural waters.

The presence of carbonates in solution greatly increases the solubility of thorium dioxide. An increase by one order of magnitude of the carbonate concentration (in the range 0.1–2.0 M Na_2CO_3) leads to an increase by about five orders of magnitude of the solubility of hydrous ThO_2(am) (Rai *et al.*, 1995). Moreover, for a fixed carbonate concentration [1 M Na_2CO_3 (Rai *et al.*, 1995) or pCO_2 = 0.1 atm (Östhols *et al.*, 1994)], a large pH dependency is observed. The fitting of their solubility data has lead Östhols *et al.* (1994) to propose the following equilibrium constants:

$$ThO_2 + H^+ + H_2O + CO_3^{2-} \leftrightarrow Th(OH)_3CO_3^-;\ \log K_{131} = 6.11 \pm 0.19,\ \log K^\circ_{131} = 6.78 \pm 0.30$$

$$ThO_2 + 4H^+ + 5CO_3^{2-} \leftrightarrow Th(CO_3)_5^{6-};\ \log K_{105} = 42.12 \pm 0.32,\ \log K^\circ_{105} = 39.64 \pm 0.40$$

that were calculated by using the hydrolysis constants determined in 3 M $NaClO_4$ by Grenthe and Lagerman (1991) and were corrected to 0.5 M $NaClO_4$ (Grenthe *et al.*, 1992) .

The ion interaction model of Pitzer has been developed, extending to high concentration, and applied satisfactorily by Felmy *et al.* (1997) to describe, on the basis of the above equilibria, the solubility data obtained by both Rai *et al.* (1995) and Östhols *et al.* (1994) in the aqueous Na^+–HCO_3^- – CO_3^{2-}–OH^-–ClO_4^- –H_2O system. They have estimated $\log K^\circ_{105}$ to be 37.6 and log K°_{131} to be 6.78; these values are identical or close to those previously determined by Östhols *et al.* (1994). However, a considerable uncertainty in the determination of the value for $\log K^\circ_{105}$, due to the introduction of large mixing terms with the bulk anionic species, has been outlined by the authors.

The effect of phosphate on the solubility of microcrystalline ThO_2 has been observed to be very limited (Östhols, 1995). The only data for which there is a significant deviation from the solubility of ThO_2(am) as predicted in the absence of phosphates, are those obtained in 0.1 M phosphate solutions in the pH range 10.5–13. Here, a small increase in solubility has been found. However, an analysis of the solid phase has shown a small but significant phosphate content. This suggests the formation of a sparingly soluble thorium phosphate in the experiments, meaning that there will eventually be a decrease of the thorium solubility in the presence of excess amounts of phosphate.

It has been concluded from other solubility measurements (Fourest *et al.*, 1999) carried out on a synthesized thorium phosphate–diphosphate, $Th_4(PO_4)_4P_2O_7$ (incorrectly named 'Th orthophosphate' in a previous study (Baglan *et al.*, 1994)) that the total concentration of Th(IV) in solution ($-3 < \log [Th] < -7$ for $0 < pH < 5$) is mainly controlled by the precipitation of two compounds: $Th(HPO_4)_2$ in acidic media (pH < 4.5) and $Th(OH)_4$ in basic and near-neutral media. However, more recently, Thomas *et al.* (2000) and Brandel *et al.* (2001b) have characterized by electron probe microanalysis (EPMA), XRD, IR, TGA, and DTA, the crystallized phase formed during the dissolution of $Th_4(PO_4)_4P_2O_7$, when the saturation of the leachate is reached. They have shown that the thorium concentration in phosphate-containing solutions is controlled by the precipitation of the thorium phosphate–hydrogenphosphate hydrate, $Th_2(PO_4)_2(HPO_4) \cdot H_2O$, which has a very low solubility product: $\log K^\circ_{sp} = -(66.6 \pm 1.2)$ (Thomas *et al.*, 2001).

3.8.6 Complexation

(a) Inorganic ligands

To our knowledge, the formation of Th(IV) complexes with most of the common inorganic ligands, such as F^-, Cl^-, SO_4^{2-}, andNO_3^{2-}, has not been re-investigated recently (Hogfeld, 1982). The stability constants of the corresponding equilibria, collected in Table 3.16, are those previously reported by Langmuir and Herman (1980) in their review paper. From these values, it can be concluded that weak 1:1 complexes are formed with chloride and nitrate anions and that higher order complexes, even if they have been pointed out in the literature (Langmuir and Herman, 1980; Fuger *et al.*, 1992), are unimportant. Colin-Blumenfeld (1987) has thus shown, through thermodynamic calculations, that $Th(NO_3)_2^{2+}$ can only exist in acidic solutions (pH $<$ 3.2) containing high concentrations of nitrates (>0.1 M). Similarly, $Th(Cl)_2^{2+}$ is expected to be found only at pH $<$ 4 and for $[Cl^-]_{tot} > 0.5$ M (Colin-Blumenfeld, 1987).

On the contrary, strong complexes of Th(IV) are formed with F^- and SO_4^{2-} and particularly with carbonate and phosphate ligands which are known to appreciably affect the speciation of Th(IV) in natural waters. A very strong complexation of Th(IV) by the HPO_4^{2-} species is indicated by the stability constants published by Moskvin *et al.* (1967) (see Table 3.16). These data are found in many databases used for geochemical modeling, but they were derived from solubility of an ill-defined solid thorium phosphate in acidic phosphate media (hydrogen concentration of 0.35 M). They cannot explain the ThO_2 solubility results obtained by Östhols (1995). Moreover, extraction experiments by acetylacetone in the two-phase system 1 M $Na(H)ClO_4$/toluene carried out by Engkvist and Albinsson (1994) at pH 8 and 9 (HPO_4^{2-} being thus the dominant species) give cumulative stability constants of Th^{4+}/HPO_4^{2-} much lower than the values published earlier; these new β values suffer, however, from large uncertainties.

The stability constants known for $Th^{4+}/H_2PO_4^-$ and Th^{4+}/H_3PO_4, and reported in Table 3.16, are those collected by Langmuir and Herman (1980). They have not been checked by subsequent studies, but their role is of minimal importance in the speciation of thorium in neutral and basic media. No data have been published on the complexation of Th^{4+} by the PO_4^{3-} ions, except the following equilibrium proposed by Östhols (1995):

$$Th^{4+} + 4H_2O + PO_4^{3-} \leftrightarrow Th(OH)_4PO_4^{3-} + 4H^+ \quad \log K = -(14.90 \pm 0.36)(0.35\ \mathrm{M})$$

Finally, mention can be made of the study of Fourest *et al.* (1994). The solubility curves obtained by equilibrating solid thorium phosphate-diphosphate and highly concentrated phosphate solutions have led to the determination of $ThO(HPO_4)_3(H_2PO_4)^{5-}$ and $ThO(HPO_4)_3(H_2PO_4)_2^{6-}$ as the presumed complex forms of Th(IV) at pH 6–7 and for $0.3 < [PO_4]_{tot} < 0.8$ and $0.8 < [PO_4]_{tot} < 1.5$ M, respectively.

Table 3.16 *Cumulative formation constants of the Th(IV) complexes formed with the main inorganic ligands at* 25°C.

Complex	*log* β_{1xn}	I (M)	*References*
ThF^{3+}	8.03	0	Langmuir and Herman (1980)
ThF_2^{2+}	14.25	0	Langmuir and Herman (1980)
ThF_3^{+}	18.93	0	Langmuir and Herman (1980)
ThF_4	22.31	0	Langmuir and Herman (1980)
$ThCl^{3+}$	1.09	0	Langmuir and Herman (1980)
$ThCl_2^{2+}$	0.80	0	Langmuir and Herman (1980)
$ThCl_3{}^{+}$	1.65	0	Langmuir and Herman (1980)
$ThCl_4$	1.26	0	Langmuir and Herman (1980)
$ThSO_4^{2+}$	5.45	0	Langmuir and Herman (1980)
$Th(SO_4)_2$	9.73	0	Langmuir and Herman (1980)
$Th(SO_4)_3^{2-}$	10.50	0	Langmuir and Herman (1980)
$Th(SO_4)^{4-}$	8.48	0	Langmuir and Herman (1980)
$ThNO_3^{3+}$	0.94	0	Langmuir and Herman (1980)
$Th(NO_3)_2^{2+}$	1.97	0	Langmuir and Herman (1980)
$Th(OH)_4PO_4^{3-}$	–14.9 ± 0.36	0.35	Östhols (1995)
$Th(HPO_4)^{2+}$	10.8	0.35	Langmuir and Herman (1980)
	(8.7 – 9.7)	1	Engkvist and Albinsson (1994)
$Th(HPO_4)_2$	22.8	0.35	Langmuir and Herman (1980)
	(15 – 17.3)	1	Engkvist and Albinsson (1994)
$Th(HPO_4)_3^{2-}$	31.3	0.35	Langmuir and Herman (1980)
	(21–23)	1	Engkvist and Albinsson (1994)
$ThH_2PO_4^{3+}$	4.52	0	Langmuir and Herman (1980)
$Th(H_2PO_4)_2^{2+}$	8.88	0	Langmuir and Herman (1980)
$ThH_3PO_4^{4+}$	1.9	2	Langmuir and Herman (1980)
$Th(OH)_3CO_3^{-}$	41.5	0	Östhols *et al.* (1994)
$Th(CO_3)_5^{6-}$	21.6[a]	0.05	Joao *et al.* (1995)
	32.3	0	Östhols *et al.* (1994)
	27.1[b]	0	Felmy *et al.* (1997)

[a] Recalculated by Östhols *et al.* (1994) (see text) to be 33.2 in 1 M carbonate media.
[b] Derived by using the K°_{sp} value of Ryan and Rai (1987) given in Table 3.15.

Despite the studies mentioned above, the thermodynamic database for tetravalent actinides remains rather poor for the complexation with inorganic anions, such as carbonate, phosphate, sulfate, fluoride, and chloride, which are dominant in natural aquatic systems. Consequently, a new semiempirical approach (based on an energy term describing the interligand electrostatic repulsion) has been developed by Neck and Kim (2000) with a first application for the mononuclear complexes with a high number of carbonate ligands. For such a ligand, this model predicts a slight decrease from $\log\beta_4^{\circ}$ to $\log\beta_5^{\circ}$ and a strong decrease from $\log\beta_5^{\circ}$ to $\log\beta_6^{\circ}$. Hence the pentacarbonate complex is expected to be the limiting Th(IV)–carbonate complex at high carbonate concentration. Moreover, the existence of $Th(CO_3)_5^{6-}$ has been confirmed by several experiments using various methods: cryoscopy, conductometry, and ionic exchange (Dervin and Faucherre, 1973a), solvent extraction followed by neutron activation (Joao *et al.*, 1987, 1995), solubility of amorphous or microcrystalline ThO_2 (Rai *et al.*, 1995; Felmy *et al.*, 1997; Östhols *et al.*, 1994) and X-ray absorption (Felmy *et al.*, 1997). The pentacarbonate complex structure is also well established in solid phase investigations (Voliotis and Rimsky, 1975). The stability constant values published in the frame of these works for the corresponding reaction:

$$Th^{4+} + 5CO_3^{2-} \leftrightarrow Th(CO_3)_5^{6-}$$

are collected in Table 3.16. The value obtained by Joao *et al.* (1987) recalculated by taking into account the complex really formed between Th(IV) and ethylenediaminetetraacetic acid (EDTA) at high pH (Th(OH)Y and not ThY) (Östhols *et al.*, 1994) is in general agreement with the value estimated by these authors. The estimation of Faucherre and Dervin (1962) from measurements of freezing point depressions is open to criticism, because only the dominant reaction is postulated and Th(IV) hydrolysis is neglected in the data treatment. The remaining values (Östhols *et al.*, 1994; Rai *et al.*, 1995; Felmy *et al.*, 1997) depend on the hydrolysis constants applied for their evaluation.

X-ray absorption spectroscopy (XAS) data (Felmy *et al.*, 1997) have clearly shown a change in speciation at low bicarbonate concentrations (0.01 M solution), but the total thorium concentration was too low to allow a definitive identification of the species. Solubility data of amorphous or microcrystalline ThO_2 have been most satisfactorily explained by the introduction of a mixed $Th(OH)_3CO_3$ (Östhols *et al.*, 1994; Felmy *et al.*, 1997) with $\log K^{\circ}_{131} = 41.5$ (see Table 3.16).

(b) Organic ligands

The organic species, such as oxalate ($C_2O_4^{2-}$), citrate ($C_6H_5O_7^{3-}$), and EDTA ($C_{10}H_{12}O_8N_2^{4-}$), form strong complexes with thorium and 'organic' complexation can predominate in natural waters over 'inorganic' by orders of magnitude, even when the concentrations of organic ligands are low as compared with inorganic ones (Langmuir and Herman, 1980).

The interaction of Th(IV) with citrate has been investigated both by potentiometry in 0.1 M chloride solution (Raymond *et al.*, 1987) and solvent extraction (thenoyltrifluoro-acetone [TTA] or dibenzoylmethane [DBM] in toluene) in perchlorate (0.1–14 M $NaClO_4$; pH: 1.8–4.0) and chloride (0.1–5.0 M NaCl; pH: 3) solutions (Choppin *et al.*, 1996). The former study covers a wider pH range (pH: 1–6) and a larger set of stability constants has been derived from the results than in the latter one. However, attention should be paid to the choice of hydrolysis constants used to fit the results. Moreover, the contribution of mixed hydroxy species, not yet identified, can be expected to be more important in basic media. Nevertheless, a relatively good agreement is observed for the two $Th(Cit)^+$ formation constants (see Table 3.17).

Table 3.17 *Cumulative formation constants of the Th(IV) complexes with some organic ligands at* 25°C.

Complex	$\log \beta^{o}_{1n}$	*References*
$Th(Cit)^+$	16.17	Nebel and Urban (1966)
	14.13	Raymond *et al.* (1987)
	13.7 ± 0.1	Choppin *et al.* (1996)
$Th(Cit)_2^{2-}$	24.94	Nebel and Urban (1966)
	24.29	Raymond *et al.* (1987)
$ThH(Cit)_2^-$	16.6 ± 0.1	Choppin *et al.* (1996)
$ThH_2(Cit)_2$	31.9 ± 0.1	Choppin *et al.* (1996)
$Th(Cit)_2(OH)_2^{4-}$	14.67	Raymond *et al.* (1987)
$Th(Cit)_3^{5-}$	28.0	Raymond *et al.* (1987)
$ThH(Cit)_3^{4-}$	33.31	Raymond *et al.* (1987)
$ThC_2O_4^{2+}$	10.6	Moskvin and Essen (1967)
	9.30	Langmuir and Herman (1980)
	9.8	Erten *et al.* (1994)
$Th(C_2O_4)_2$	20.2	Moskvin and Essen (1967)
	18.54	Langmuir and Herman (1980)
	17.5	Erten *et al.* (1994)
$Th(C_2O_4)_3^{2-}$	26.4	Moskvin and Essen (1967)
	25.73	Langmuir and Herman (1980)
$Th(C_2O_4)_4^{4-}$	29.6	Moskvin and Essen (1967)
$Th(HC_2O_4)^{3+}$	11.0	Erten *et al.* (1994)
$Th(HC_2O_4)_2^{2+}$	18.13	Erten *et al.* (1994)
ThEDTA	25.30	Langmuir and Herman (1980)
$ThHEDTA^+$	17.02	Langmuir and Herman (1980)

The Th(IV)/oxalate constants determined by using solvent extraction techniques (TTA and bis(2-ethylhexyl)phosphoric acid [HDEHP] in toluene; pH: 1.3–4.0; $I = 1, 3, 5, 7$, and 9 M) (Erten *et al.*, 1994) appear somewhat different from the values previously obtained from solubility measurements, but the approach of Moskvin and Essen (1967) has already been subjected to some criticism in the case of the phosphate ligands (Östhols, 1995).

Other anions of organic acids, such as formate, acetate, chloroacetate, tartrate, malate, salicylate, sulfosalicylate, and so on, form complexes with Th(IV). They are too numerous to be listed in Table 3.16, but the corresponding stability constants can be found in various compilations: Sillen and Martell (1964, 1971), Perrin (1982), or the most recent database issued by the National Institute of Standards and Technology (NIST, 2002).

Humic and fulvic acids have been identified as efficient complexing agents for ions such as Th^{4+}. Their influence on thorium mobilization in natural waters have been discussed in several publications (Choppin and Allard, 1985; Cacheris and Choppin, 1987; Miekeley and Küchler, 1987). The Th(IV)–humate complex has been recently analyzed by X-ray photoelectron spectroscopy (XPS)

(Schild and Marquardt, 2000). The XPS study corroborates EXAFS results (Denecke *et al.*, 1999) according to which Th(IV) is predominantly bound to carboxylic groups of humic acids.

3.8.7 Analytical chemistry

As Chapter 30 is devoted to trace analysis of actinides in geological, environmental, and biological matrices, only summarized considerations will be given here, centered on the determination of thorium in natural waters. Extensive information on the techniques used in analytical chemistry of thorium, including the 'classical' gravimetric, titrimetric, and photometric methods, is also given in the *Gmelin Handbook* (1990b).

Because of its low solubility and its ability to be sorbed as hydroxo complexes, the concentration of thorium in natural waters is, in general, below 0.1 μg L^{-1} and its quantitative determination is difficult. The most important analytical methods for the determination of Th(IV) in the range of low concentrations have been compiled and discussed by Hill and Lieser (1992). In most cases, a preconcentration step – coprecipitation, solvent extraction, and/or ion exchange separation – is performed prior to the measurement.

Inductively coupled plasma mass spectrometry (ICP-MS) is the most sensitive method with usual limits of detection around 0.01 μg kg^{-1} (Gray, 1985) and a reported limit value as low as 0.2 ng kg^{-1} (Chiappini *et al.*, 1996), but this method needs costly pieces of equipment. Two other methods exhibit low detection limits (0.1 μg kg^{-1}) and are well suited for routine analysis (Hill and Lieser, 1992):

- Spectrophotometry, with the procedure described by Keil (1981) coupling preliminary extraction and Th(IV) complexation with arsenazo;
- Voltammetry, with the procedure reported by Wang and Zadeii (1986) using a chelating reagent (with a concentration to be optimized).

However, in practical applications, drawbacks are encountered with both methods due to the presence of uranium and aluminium, respectively. To avoid these drawbacks, a selective preconcentration of Th(IV) is thus necessary (Hill and Lieser, 1992).

Gamma- and alpha-spectrometries, with sensitivity around 1 μg kg^{-1} (Singh *et al.*, 1979; Kovalchuk *et al.*, 1982; Jiang and Kuroda, 1987), are essentially used for isotopic determinations. However, these standard radiochemical techniques require preconcentration and long counting times. ^{228}Th can be determined from two successive gamma-measurements of the ^{224}Ra daughters, but a delay of 20 days is necessary to obtain reliable results for ^{228}Th (Surbeck, 1995). The chemical separation techniques for the classical alpha-spectrometry have been reviewed by De Regge and Boden (1984). These techniques often need optimization because around 50% of the initial activity can be lost at the chemical separation stage (Vera Tomé *et al.*, 1994). Liquid scintillation spectrometers, which allow discrimination between alpha and beta decays, and are commercially available, offer, in combination with selective extractive scintillators, a more advantageous solution to the problem of the isotopic determination of ^{232}Th, ^{230}Th, and ^{228}Th, in spite of a low-energy resolution compared to alpha-spectrometry (Dacheux and Aupiais, 1997). With the PERALS (name registered to Ordela, Inc.) system, a limit of detection as low as 0.2 μg kg^{-1} can be reached for ^{232}Th [value obtained for 250 mL and 3 days of counting (Dacheux and Aupiais, 1997)]. Moreover, PERALS spectrometry can be associated to six short liquid–liquid extraction steps to isolate Th from other actinides (U, Pu, Am, and Cm) prior to its detection at very low levels (the use of spikes during the chemical procedure is necessary for complex matrices).

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