CHAPTER TWENTY TWO

ACTINIDE STRUCTURAL CHEMISTRY

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22.1 INTRODUCTION

This chapter focuses on the solid state structural chemistry of actinide materials as determined by single-crystal X-ray diffraction, single-crystal neutron diffraction, powder X-ray diffraction, and powder neutron diffraction techniques. Since Burns' chapter, Structural Chemistry, was published in the 1986 edition of this work, significant improvements in crystallographic technology and instrumentation have advanced the field of solid state chemistry. Some of the most dramatic changes have been in computer technology and software, making the data collection, reduction, and refinement processes highly automated and simplified. As a consequence, X-ray diffractometers have become nearly ubiquitous in research departments globally and neutron-scattering resources have become more advanced and accessible, resulting in the elucidation and publication of a greater number of additional actinide structures since the last edition; these structures are the focus for this chapter.

In the past, the structural study of actinide compounds using diffraction techniques had often entailed complications, many of which were inherent difficulties attributable to the composition (very heavy and very light elements) and radioactivity of the samples themselves. However, modern advances and insights have made the study of actinide-containing compounds almost a routine process. For example, X-ray diffraction of actinide–organic complexes can be complicated by the scattering due to the heavy atoms, which often dominates that of light atoms; however, the complementary use of neutron diffraction techniques allows for the accurate placement of lighter atoms, particularly hydrogen, along with the heavy atoms (Suortti, 2002). In instances where the growth of sufficiently large single crystals for analysis has been an obstacle, powder diffraction, particularly when coupled with sophisticated refinement techniques, has allowed for the determination of positional and thermal parameters of samples containing randomly oriented crystallites with nearly the same degree of precision as single-crystal techniques (Rietveld, 1967). In addition, advances in the growth of single crystals from melts, solutions, and vapors have enabled many difficulties in this area to be overcome (Spirlet *et al.*, 1991). For many actinide isotopes, radioactive decay can cause defects and dislocations in single-crystal samples. However, substitution of less radioactive isotopes alleviates the rate at which lattice deterioration occurs, creating more stable samples for study. For short-lived isotopes available in larger quantities, self-heating or irradiation problems are encountered; for example, ^{242}Cm ($t_{1/2} = 162.8$ days) produces 122 W/g although substituting ^{244}Cm ($t_{1/2} = 8.1$ years) or ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ years) reduces that aspect of the problem (Haire and Eyring, 1994).

While our treatment is by no means exhaustive (in the sense that we do not include every actinide structure published in the literature), it is intended to represent a large number of important structures, to illustrate how advances in solid state techniques have led to the generation of larger numbers of structures, and to offer an appreciation for solid state actinide structures in general. In addition, this overview of actinide structural and coordination chemistry has the aim to establish an understanding of how the unique electronic properties of the actinide elements influence chemical bonding in their inorganic, coordination, and organometallic compounds.

22.2 SOLID STATE STRUCTURAL TECHNIQUES

Recent advances in crystallography and structure determination focus on improvements in instrumentation because the theory and preparatory steps (i.e., crystal growing, unit cell/orientation matrix determination) remain the same. Although many actinide inorganic structures were solved several decades ago, the use of state-of-the-art instrumentation for the determination of new structures or the refinement of old ones will be highlighted whenever possible throughout this chapter.

22.2.1 X-ray diffraction techniques

X-ray crystallography as a technique is based on the diffraction of X-rays by electron density that resides in defined planes within the crystalline lattice; the nature of the diffraction is governed by Bragg's law ($n\lambda = 2d\sin\theta$). Thus, X-ray diffraction yields information regarding the distribution of electrons in a crystalline solid. The application of X-ray crystallography to actinide science is met with a unique challenge; because X-rays are diffracted by electron density, the large, dense actinides can easily overshadow smaller atoms with less electron density. The study of heavy elements in this manner has become routine, however, through use of techniques to circumvent this problem (Deschamps and Flippen-Anderson, 2002).

In most small-scale X-ray diffractometers (i.e., non-synchrotron), X-ray tubes are used to accelerate electrons toward a target material (Mo or Cu), resulting in the generation of X-rays which are then filtered, collimated, and focused through an aligned single crystal that is subsequently rotated through space by a goniometer; the diffracted X-rays are then registered by an area detector, such as a charge coupled device (CCD), resulting in a diffraction pattern that is then interpreted. Current X-ray diffractometers are controlled by computers and software that assist in refining the data and aid in solving the crystal structure, making the method so attractive that it is regarded as an essential analytical instrument in many research departments. In fact, tasks that used to require several months of effort are now easily accomplished in minutes with modern day computational and graphical resources (Suortti, 2002).

The advent of the synchrotron has revolutionized the ways in which X-rays are generated and used for research purposes. Synchrotron radiation is emitted when light, charged particles (e.g., electrons or positrons) moving at relativistic speeds undergo radial acceleration. Unlike laboratory diffractometers, synchrotrons are large-scale facilities that are designated for the production of synchrotron radiation. Small synchrotrons of the past have paved the way for the development of third-generation synchrotron facilities; in the latter, electrons emitted by an electron gun are first accelerated in a linear accelerator (linac) and then transmitted to a circular accelerator (booster synchrotron) where they are accelerated to energy levels of several gigaelectron volts (GeV). These high-energy electrons are then injected into a large storage ring where they circulate in a vacuum environment, at a constant energy, for many hours. Magnets are used to deflect the particles, causing them to change direction and emit synchrotron radiation, which is then directed toward a beamline for use in experiments (Suortti, 2002).

The radiation produced is extremely bright over a broad spectral range; in fact, it is several orders of magnitude brighter than that produced by a conventional X-ray tube. The X-rays produced in this manner are collimated to a narrow beam, polarized, and pulsed (subnanosecond). Synchrotron radiation offers the advantage of being able to analyze very small crystals because 10^{10}–10^{11} photons sec^{-1} can be focused on a sample 10 μm in diameter (Suortti, 2002).

Powder X-ray diffraction refers to the use of a collimated monochromatic beam of X-rays to analyze a sample containing a large number of crystals with random orientations. Diffraction intensity is measured as a function of 2θ, thus allowing a simple application of Bragg's law to determine d-spacings within the lattice. The resulting set of d-spacings is a 'fingerprint' that can uniquely determine crystal symmetry and can identify a crystalline material or a mixture of crystalline materials, typically by comparisons with standards. Powder X-ray diffraction has become an important tool in the study of actinide compounds because it is often impossible to obtain sufficiently large single crystals for some classes of compounds (Suortti, 2002).

22.2.2 Neutron diffraction techniques

In X-ray diffraction, the scattering power of a given atom for a given reflection, or the ‘scattering factor’, is strongly dependent on the type of atom, the scattering angle, and thermal motion, thus drastically affecting the resolution and the determination of the position of lighter atoms in the presence of heavy ones. However, scattering in neutron diffraction occurs primarily from the nucleus; since the diameter of the nucleus is small relative to the wavelength of the neutrons, the ‘scattering factor’ is characteristic of the particular nucleus and independent of scattering angle. As a result, neutron diffraction offers the ability to distinguish among near neighbors in the periodic table, or determine the position of light atoms with the same degree of accuracy as the heavy elements. For example, the scattering amplitudes for ^{2}D and ^{238}U with X-rays are 0.28 and 25.92, respectively, while with neutrons, these values are 0.67 and 0.84, respectively. In this regard, X-ray diffraction and neutron diffraction are often thought of as complementary techniques (Deschamps and Flippen-Anderson, 2002).

Currently, monochromatic neutrons for scattering experiments are produced at large facilities because there is no laboratory-size instrument comparable to the X-ray diffractometer. Nuclear reactors offer a source of steady (i.e., not pulsed) neutrons; high-energy neutrons (1 MeV) from continuous self-sustained fission reactions in ^{235}U are moderated to thermal energies near 40 meV and extracted through holes that penetrate the moderator. Alternatively, pulsed (spallation) sources use short bursts of 1 GeV protons to generate a large number of neutrons by being spalled (‘chipped’) from target nuclei (e.g., 25 neutrons per incident photon for ^{238}U). The resulting neutrons are moderated (using hydrogenous materials) to a pulse of neutrons with energies less than 10 eV (Suortti, 2002).

Spallation-based neutron scattering has emerged as comparable and complementary to reactor-based neutron scattering, although there are fundamental differences between the experiments. Neutrons from a reactor are separated with a monochromator to provide a small energy band for use in diffraction experiments in a manner similar to the beam from an X-ray tube. Spallation neutrons have a wide energy distribution and diffraction patterns are analyzed as a function of the neutron wavelength by employing time-of-flight diffraction (Suortti, 2002).

Powder neutron diffraction, like its X-ray analog, is an important tool for analyzing samples containing randomly oriented crystallites. However, in recent years, powder X-ray and neutron diffraction have become more widely used due to the advantages offered by the Rietveld refinement technique, originally developed for analyzing neutron diffraction data; here, positional and thermal parameters can be determined from powder data. In fact, precision comparable to single-crystal X-ray diffraction data is achievable for positional parameters, but thermal parameters are less reliable (by a factor of 2 or 3) (Deschamps and Flippen-Anderson, 2002).

22.3 METALS AND INORGANIC COMPOUNDS

22.3.1 Actinide metals

The temperature-dependent phase diagrams of actinide metals are usually complicated by a variety of allotropic forms as illustrated in Fig. 22.1. As the temperature is increased, the metallic forms of the light actinides, in many cases, go through a series of allotropic changes, the most complicated of which is observed in plutonium metal (Smith and Kmetko, 1983). In general, as the metals approach melting, they take on the body-centered cubic (bcc) form, almost universally observed for high-temperature forms of lanthanide metals; however, this bcc form is predicted to be unstable for the later actinides (Sari *et al.*, 1972/73). This change in crystal structure is caused by intricate differences in the electronic nature of the early actinides, while these differences in the later actinides become less clear due to lack of research. In a paper by Wills and Eriksson (1992), predictions of the crystal structure properties of thorium, protactinium, and uranium metal were made based on electronic considerations which successfully reproduced the experimentally observed crystal structures.

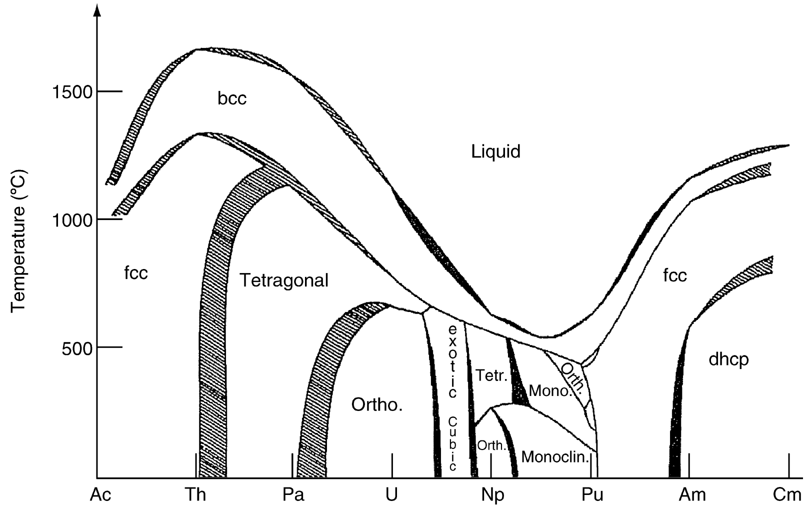

Fig. 22.1 *Binary phase diagram of the light actinides* (*bcc: body-centered cubic; fcc: face-centered cubic; ortho.: orthorhombic; mono.: monoclinic; dhcp: double hexagonal close packed*) (*Smith and Kmetko,* 1983. *Reproduced with permission from Elsevier*).

Described below are the different structural forms of the actinide metals from actinium through einsteinium. The transition temperatures listed reflect the widely agreed upon values from Chapters 2–12, 15, 19, and 21, although may not be reflective of the primary references listed, which have been included for completeness.

(a) Actinium

Actinium metal has a crystal structure identical to that of β-La, the high-temperature form of lanthanum. Actinium metal is a face-centered cubic (fcc) system with unit cell dimensions of 5.31(1) Å as determined by X-ray powder diffraction. Despite the existence of low-temperature α-La, a corresponding α-Ac has not been detected (Farr *et al.*, 1961).

(b) Thorium

Thorium metal exhibits two allotropic forms; at temperatures below 1360°C, the fcc form is present, after which it transforms into a bcc form. The bcc phase is present until the melting point of thorium is reached at 1750°C (Chiotti, 1954).

(c) Protactinium

Low-temperature protactinium metal (less then 1170°C) is a body-centered tetragonal crystal system. Upon heating, the axial ratio (*c*/*a*) increases exponentially from 0.8260(7) to 1.00, causing the structure to tend toward bcc at high temperature (up to 1572°C) (Marples, 1965).

(d) Uranium

Uranium metal has three temperature-induced allotropic forms. The room temperature allotropic form, α-phase (below 668°C), was the first to be discovered. This phase was originally reported by Wilson as having a monoclinic structure (Wilson, 1933). Within 4 years, it had been reindexed as an orthorhombic structure (Jacob and Warren, 1937). The last phase to be discovered was the β-phase which belongs to the tetragonal crystal system (Thewlis, 1951). This phase is present over the smallest temperature range, 668–776°C. X-ray single-crystal results are found in an article by Tucker (1951). The high-temperature γ-phase has a bcc crystal structure and is present until the melting point of uranium is reached (1135°C). Tucker (1950) also summarizes structural aspects of the allotropic forms of uranium in detail.

(e) Neptunium

Room-temperature neptunium metal belongs to the orthorhombic crystal system, known as the α-phase, and is different from that of uranium. In the α-phase, two different neptunium environments are present, only one of which resembles the environment of the atoms observed in α-uranium (Zachariasen, 1952a). The α-phase is stable up to about 280°C, after which it transforms into the β-phase, a tetragonal crystal system. The final phase, present above 576°C, is known as the γ-phase (bcc crystal system) and exists until the metal melts at 639°C (Zachariasen, 1952b).

(f) Plutonium

Plutonium metal, by far the most complex of the actinide metals, has six different temperature-dependent allotropic forms with a wide range of physical properties and crystal structures. The α-phase, present at room temperature, is monoclinic and exists up to 124.4°C, after which it transforms into the β-phase (Zachariasen and Ellinger, 1963a). The α-phase is the densest and has the largest positive thermal expansion coefficient of all the plutonium allotropes (Zachariasen and Ellinger, 1957). A comprehensive list of densities and thermal expansion coefficients for plutonium metal is available from Choppin and Stout (1991). The β-phase is body-centered monoclinic and is stable up to about 214.8°C. The α–β phase transition has no simple geometry transformation, thus making the change sluggish (Zachariasen and Ellinger, 1959, 1963b). Between 214.8 and 320.0°C, the orthorhombic γ-phase is present and is unlike any other metal, having ten close plutonium neighbors at an average distance of 3.157 Å. The mean linear thermal expansion coefficients of the metal are positive along the [010] and [001] crystallographic direction and negative along the [100] direction (Zachariasen and Ellinger, 1955). The δ and the δ′ allotropic forms of plutonium are the only two that exhibit negative thermal expansion, thus introducing special concerns during casting of plutonium metal. The δ-phase is present between 320.0 and 462.9°C and belongs to the fcc crystal system. The δ′-phase is only present in the small range of 462.9–482.6°C and possesses, in magnitude, the largest thermal expansion coefficient of all the plutonium allotropic forms. At temperatures higher then 482.6°C (up to the melting point of plutonium metal at 640°C), the bcc ε-phase is present (Ellinger, 1956). The changes in the thermal expansion coefficients with respect to the allotropic forms of plutonium are shown graphically in Fig. 22.2. A summary of all the physical and crystallographic properties of plutonium metal is presented in greater detail elsewhere (Jette, 1955).

(g) Americium

At room temperature, americium metal, like α-La, belongs to the double hexagonal closed-packed (dhcp) crystal system (Graf *et al.*, 1956; McWhan *et al.*, 1962). At temperatures between 600 and 700°C, it was originally reported that a dhcp to fcc change occurs; however, a later report by Sari *et al.* refuted the existence of this change and suggested evidence for a solid-solid transition around 1075°C (before melting at 1173°C), although the exact nature of the

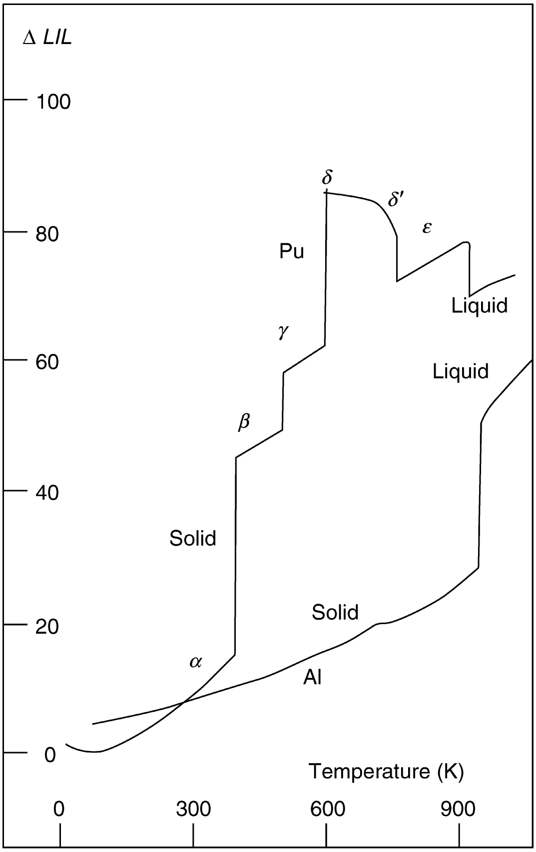

Fig. 22.2 *Dilation of aluminium and plutonium metals as a function of temperature. The allotropes are designated by their symbols* (*Choppin and Stout*, 1991. *Reproduced with permission from The Royal Society of Chemistry*).

modification could not be determined (Sari *et al.*, 1972/73). Further evidence supports the α to β-phase at 769°C, β to γ-phase 1077°C with melting occurring at 1176°C, (see chapter 8).

(h) Curium

The crystal structure of curium metal as reported by Cunningham and Wallmann indicates a dhcp form at low temperatures (below 1295°C) that is isostructual with α-La and dhcp americium (1964). A later report by Smith *et al.* saw no evidence for the dhcp form, but rather a cubic close-packed structure. In their study, however, they reported broadened lines indicative of damaged curium structures, as well as weak curium lines compared to the tungsten lines. Also reported was a high-temperature phase (1295–1346°C) with fcc symmetry where the metallic radius of curium (1.54 Å) is consistent with the 4+ oxidation state (Smith *et al.*, 1969).

(i) Berkelium

X-ray powder diffraction of berkelium metal revealed the existence of two stable room-temperature crystallographic modifications: dhcp and fcc . In preparation of the metal, annealing at 800°C with slow cooling tended to favor the dhcp structure, while annealing at 900°C resulted primarily in the fcc structure (Peterson *et al.*, 1971). Current studies place the α-phase below 977°C while the β-phase exists until melting at 1050°C (see Chapter 10).

(j) Californium

Californium metal was also observed to exist in two allotropic forms at room temperature: fcc and hexagonal close-packed (hcp). Upon heating in a vacuum, the fcc structure usually changed to the hcp structure, but would not revert back to the fcc, even at liquid nitrogen temperatures (Haire and Baybarz, 1974). A subsequent study by Zachariasen (1975) called into question these results, and concluded that the hcp and fcc structures were attributable to Cf_2O_2S and CfS, respectively. Further studies by Haire and Asprey (1976) later showed the existence of two dhcp structures present as a mixture. Analysis of the data and comparisons with previous results suggest that californium metal is one of the most complex transplutonium metals, existing in both a divalent and higher valent form with dhcp, and fcc structures. Current evidence supports the dchp phase below 700°C and the fcc phase between 700 and 900°C (see Chapter 11).

(k) Einsteinium

Einsteinium metal has been investigated through the reduction of a thin film of Es_2O_3 by lanthanum. The metallic einsteinium has a fcc structure and at the present time is the only known allotropic form (Haire and Baybarz, 1979).

22.3.2 Oxides

Actinide oxides (An_xO_y) are refractory materials, indicating their collective resistance to decomposition at high temperatures. For example, ThO_2 has the highest melting point of any oxide (3378°C) (Ronchi and Hiernaut 1996). Research has focused on the use of appropriate actinide oxides as nuclear fuels, although the chemistry associated with the actinide elements tends to be complex and includes polymorphism, non-stoichiometric compounds, and intermediate phases. The oxides are basic in character (they are weak Lewis bases, able to donate electron pairs). Their chemical reactivity is usually influenced by their thermal history; actinide oxides are significantly more inert after they have been ignited (Greenwood and Earnshaw, 2001).

Several early studies of actinide monoxides reported structural data for Th through Am, although definitive evidence is lacking. A later study with plutonium oxides, however, contested their existence and presented data supporting the existence of plutonium oxycarbide rather than monoxide as a phase on plutonium metal surfaces (Larson and Haschke, 1981). Studies of lanthanides (La–Nd, Sm) under high-temperature and high-pressure conditions supported the formation of NaCl-type monoxides, but noted their instability in condensed form under standard conditions. This suggests that PuO may be attainable by similar high-pressure techniques (Leger *et al.*, 1981). Despite this evidence against plutonium monoxide under standard conditions, structural data for the remaining actinide monoxides will be presented herein for completeness.

Structural studies of other actinide oxides have largely been by means of powder diffraction techniques due to the refractory nature of the materials and the difficulty in obtaining single crystals. Actinide dioxides are known for the elements thorium through californium. All are isostructural and adopt the common face-centered cubic (fcc) fluorite structure (CaF_2). The unit cell constants for the dioxides from thorium to Californium are shown in Table 22.1. In the CaF_2 structure, the cations occupy the cubic closest packing sites and the anions fill the remaining tetrahedral holes, resulting in a coordination number (CN) of eight for each cation. Thus, the overall structure is three-dimensional with a strong covalent component due to the high formal charge on the cation, resulting in compounds with unusually high melting points. The dioxides, with the exception of PaO_2, tend to lose oxygen at high temperature and form substoichiometric compounds with oxygen vacancies in the anion part of the lattice; the protactinium and uranium dioxides can form superstoichiometric compounds at room temperature (Keller, 1973).

Actinide sesquioxides (An_2O_3) become increasingly stable progressing from the lighter to the heavier actinide elements. Their structures are analogous to those formed for rare earths and adopt three structures commonly classified according to the following types:

Table 22.1 *Unit cell constants for actinide dioxides.*

Compound	*Cell constant, a* (Å)	*Reference*
ThO_2	5.597	Sellers *et al.* (1954); Leigh and McCartney (1974)
PaO_2	5.505	Sellers *et al.* (1954)
UO_2	5.4704	Grønvold (1955); Hutchings (1987)
NpO_2	5.4334	Fahey *et al.* (1976)
PuO_2	5.396	Gardner *et al.* (1965)
AmO_2	5.373	Hurtgen and Fuger (1977)
CmO_2	5.359	Peterson and Fuger (1971)
BkO_2	5.3315	Fahey *et al.* (1974)
CfO_2	5.310	Baybarz *et al.* (1972a)

A-type: hexagonal structure, with AnO_7 units in capped octahedral arrangement (CN = 7);

B-type: monoclinic structure, with two AnO_7 units in capped trigonal prism arrangement and third in capped octahedral arrangement (CN = 7, possibly 6);

C-type: cubic structure (related to fluorite), where one-quarter of anions have been removed to reduce coordination number to 6, but not octahedral (CN = 6).

As with the lanthanides, the smaller actinides favor the C-type structure (Greenwood and Earnshaw, 2001). However, none of the actinide sesquioxides have been studied using single-crystal X-ray diffraction techniques, thus making precise structural characterization (i.e., atomic positions, bond lengths) impossible. The chemistry of this class of compounds may be further complicated by temperature or pressure dependence on the structures, as detailed by Haire and Eyring (1994).

More complex and less common actinide oxides, including AnO_3, An_3O_8, and An_2O_5, will be discussed on a case by case basis, where appropriate. For example, AnO_3 compounds are known, but typically exist in a hydrated state; the only known anhydrous trioxide is UO_3. Anhydrous uranium trioxide has been isolated in seven polymorphic forms, reflecting the ability of uranium(VI) to exist in a variety of low symmetry, high coordination environments with similar energies (Weller *et al.*, 1988).

(a) Actinium

Only one actinium oxide has been reported. Fried *et al.* (1950) reported that actinium sesquioxide, Ac_2O_3, can be obtained through decomposition of actinium oxalate at 1100°C. The compound has hexagonal symmetry and is isomorphous with certain lanthanide sesquioxides, including those of lanthanum, cerium, and praseodymium (A-type). It is interesting to note that the sample was prepared from less than 10 μg of actinium to minimize fogging of the X-ray film due to high gamma radiation encountered during structural data collection.

(b) Thorium

Two binary oxides have been reported for thorium. Metastable thorium monoxide has been reported to form on the surface of thorium metal exposed to air and subsequent crystallographic analysis revealed an fcc structure with a lattice parameter of 5.302 Å (Ackermann and Rauh, 1973). ThO_2, also with fcc symmetry (CaF_2 structure), is stable up to its melting point of 3390°C, although extensive heating to 1800–2000°C in a vacuum results in a blackened material due to loss of oxygen (Haire and Eyring, 1994).

(c) Protactinium

The oxides of protactinium are more complex than those of the two earlier actinide elements, ascribable to its more complex electronic structure. Three binary oxides are known: PaO, PaO_2, and Pa_2O_5. Several intermediate oxides of variable stoichiometry also exist between PaO_2 and Pa_2O_5, in addition to seven crystal modifications of Pa_2O_5 (Haire and Eyring, 1994).

Crystallographic analysis of the monoxide, PaO, showed the NaCl structure with a lattice cell length of 4.961 Å. This material, like ThO, has been reported to exist as a coating on metal. Its existence is further ascribed as PaO because the substance is slowly oxidized by air to form PaO_2 (Sellers *et al.*, 1954).

The white binary oxide Pa_2O_5 is formed by heating the hydrated oxide ($Pa_2O_5 \cdot nH_2O$), as well as several other protactinium compounds (hydroxide, nitrate, etc.), in air or oxygen above 650°C. The crystalline modification that is obtained (there are seven total, including fcc, tetragonal, hexagonal, orthorhombic, and rhombohedral forms) depends on the temperature to which the starting material is heated. The black dioxide, PaO_2, can be prepared by the reduction of Pa_2O_5 with H_2 at 1550°C and has a fluorite fcc structure (Sellers *et al.*, 1954).

Intermediate compounds with O/Pa ratios between 2.0 and 2.5 are obtained by selective oxidation of PaO_2 or reduction of Pa_2O_5. These compounds have been identified as $PaO_{2.18}$–$PaO_{2.21}$, $PaO_{2.33}$, $PaO_{2.40}$–$PaO_{2.42}$, and $PaO_{2.42}$–$PaO_{2.44}$, having fcc, tetragonal, tetragonal, and rhombohedral symmetries, respectively (Roberts and Walter, 1966).

(d) Uranium

The complexity of uranium oxides is due to the ability of uranium to exist in several valence states, both exclusively and simultaneously. Many uranium oxides are known, including UO_2, U_2O_5, U_3O_8, U_4O_9, and UO_3, each showing a range of content. Diffraction data for the monoxide have been reported and, like the analogous thorium compound, UO is unstable with respect to disproportionation (Ackermann and Rauh, 1973). The compound U_3O_8 is the most stable oxide of uranium under ambient conditions.

Uranium dioxide is the most widely studied of the dioxides due to its use in the nuclear industry. The room-temperature fcc fluorite crystal structure of stoichiometric UO_2 was first determined by Goldschmidt and Thomassen (1923) and they showed that the uranium atoms occupy the face-centered sites, while the oxygen atoms occupy the corners of a cube centered within the unit cell. Earlier, however, Hillebrand established the isomorphism of UO_2 with ThO_2 (Hillebrand, 1893). The fluorite structure possesses two types of lattice holes per unit cell: three positioned in the middle of the unit cell edges at (½, 0, 0), (0, ½, 0), and (0, 0, ½), and one large hole in the cube center at (½, ½, ½). The openness of the structure allows the anions to move toward the holes and causes anharmonic motion of the oxygen atoms (Rouse *et al.*, 1968).

In addition, the holes allow for the addition of oxygen atoms up to a composition of $UO_{2.25}$ without changing the cubic structure of the cell. Several studies have been performed to determine the exact positions of oxygen atoms in UO_{2+x} using X-ray (Belbeoch *et al.*, 1961; Willis, 1978) and neutron diffraction (Willis, 1964). Neutron diffraction on polycrystalline UO_2 has also been reported (Knowles *et al.*, 1981).

Hyperstoichiometric UO_{2+x}, resulting from the addition of oxygen to the dioxide lattice, has been thoroughly investigated using neutron diffraction (Willis, 1963, 1964). Willis showed that the additional oxygen atoms are not exactly on the (½, ½, ½) positions, but are slightly displaced around these holes. Vacancies are also still present in the oxygen sublattice. Electron diffraction of $UO_{2.19}$ revealed a superstructure composed of $4 \times 4 \times 1$ basic cells of UO_2 (fluorite); the oxygen atoms were displaced slightly from ideal locations with local accumulations of three oxygen atoms (Steeb and Mitsch, 1965). The structure of $UO_{2.25}$ (or U_4O_9) has also been thoroughly investigated using X-ray (Belbeoch *et al.*, 1961), neutron (Masaki and Doi, 1972), and electron diffraction (Blank and Ronchi, 1968). The superlattice is cubic with a cell dimension that is four times that of UO_2. The structures, dislocations, and defects in anion-excess uranium oxides are described in detail elsewhere (Vollath, 1984; Willis, 1987).

The three crystalline forms of U_2O_5 exist only at elevated temperature and pressure. The powder pattern of the α-form was not successfully indexed at first, but was observed as the predominant form below 800°C and between 10 and 60 kbar of pressure (Hoekstra *et al.*, 1970). It was later indexed as a monoclinic cell (Haire and Eyring, 1994). The β- and γ-forms exist mainly above 800°C and between 30 and 60 kbar of pressure; they are hexagonal and monoclinic, respectively. Samples prepared at the highest pressure (60 kbar) and above 800°C sometimes appeared as the β-form, and other times as the γ-form (Hoekstra *et al.*, 1970).

The most stable uranium oxide, U_3O_8, has two common polymorphs (α and β) that exist independently. Using neutron diffraction, Loopstra (1964) was able to model the two phases, both of which are orthorhombic. The most stable polymorph is α-U_3O_8 in which the oxygen atoms are all located at the corners of a pentagonal bipyramid around the central uranium. Generation of the β-U_3O_8 polymorph is accomplished by extended heating of α-U_3O_8 to 1350°C in air or oxygen, followed by slow cooling over about 2 weeks. The β-U_3O_8 polymorph exhibits two uranium coordination environments forming two distinct uranium polymeric chains along the *c*-axis. The first set of chains has uranium surrounded by oxygen atoms at the corners of a pentagonal bipyramid, while the remaining chains have the uranium surrounded by both pentagonal bipyramidal and octahedral oxygen atoms in an alternating fashion. Here, all neighbors of octahedrally coordinated uranium are pentagonal bipyramids (Loopstra, 1970). Other uncommon polymorphs include the γ-U_3O_8 which is formed from α-U_3O_8 at pressures and temperatures greater then 16,000 atm and

400°C (Herak and Jovanovic, 1969). If the α-U_3O_8 polymorph is exposed to an oxygen atmosphere for a prolonged time at 1350°C, the lattice converts to δ-U_3O_8 (Amirthalingam, 1966). Another form, p-U_3O_8, was discovered when α-U_3O_8 was held at room temperature and pressures greater than 50 kPa. This polymorph is not stable at temperatures greater then 1100°C in air or an argon atmosphere, and converts back to α-U_3O_8 (Steeb and Brucklacher, 1966).

Seven forms of UO_3, both crystalline and amorphous, have been characterized. Their methods of preparation are illustrated in Fig. 22.3. The amorphous form of the oxide is referred to as A-UO_3 (Hoekstra and Siegel, 1961). The structure of α-UO_3 has gone through many refinements, the latest of which corrects several discrepancies in previous studies. Here, Greaves and Fender (1972)

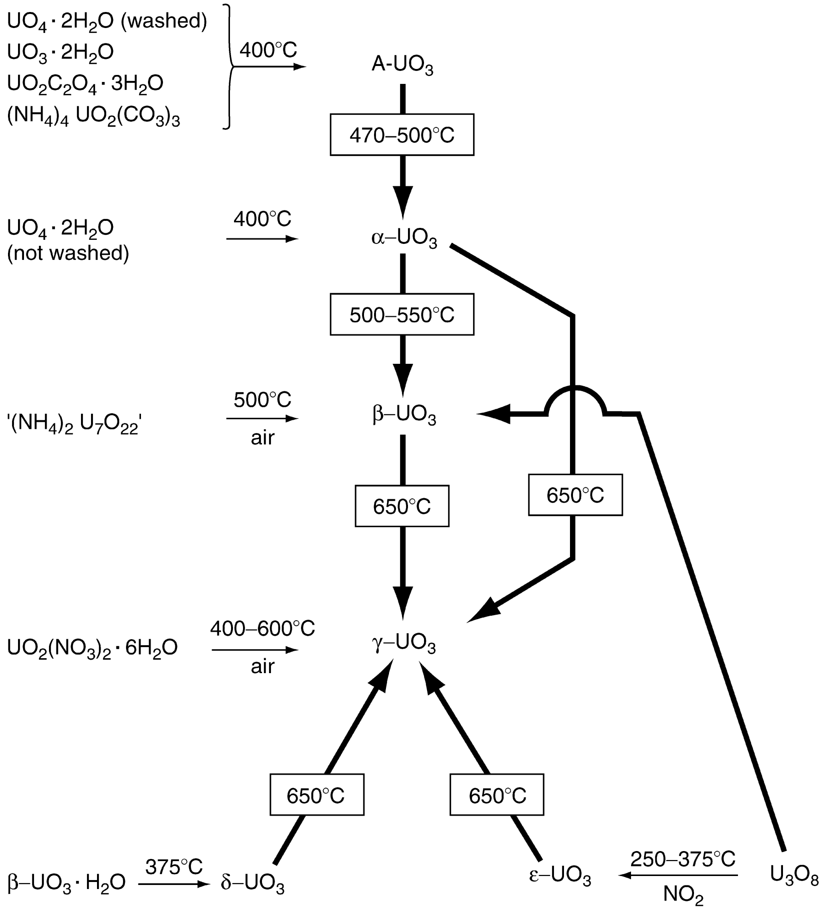

Fig. 22.3 *Uranium trioxide polymorphs and means of preparation (Weigel, 1986. Reproduced with permission from Chapman and Hall).*

based the structure on uranium-deficient α-U_3O_8; the loss of uranium atoms is countered by the shortening of some U–O distances from 2.1 to 1.6 Å, thus explaining the existence of some uranyl-like bonds. The diffraction pattern of β-UO_3 revealed three different environments for uranium with coordination numbers of 6, 6, and 7. The overall structure may be visualized as layers interconnected by distorted uranyl groups (Debets, 1966). The most recent neutron powder profile of γ-UO_3 shows the existence of three closely related phases between 373 and 77 K. At 373, 323, and 77 K, tetragonal, orthorhombic, and orthorhombic structures are observed, respectively. Of all the UO_3 crystalline phase, γ-UO_3 is the most thermodynamically stable (Loopstra *et al.*, 1977). Cubic δ-UO_3 has an unusual regular octahedral uranium environment and is isostructural with ReO_3. The structure has been confirmed with both powder X-ray diffraction (Wait, 1955), and powder neutron diffraction techniques (Weller *et al.*, 1988). Structural data for ε-UO_3 shows a triclinic cell (Hoekstra and Siegel, 1961). The last form isolated at high pressure, η-UO_3, is seven-coordinate with two *trans* oxygen atoms at 1.80 and 1.85 Å forming the uranyl group, and the remaining five oxygen atoms distributed equatorially in a puckered pentagon (Siegel *et al.*, 1966).

(e) Neptunium

Neptunium monoxide has been reported as having the NaCl structure type with a lattice parameter of 5.00(1) Å (Zachariasen, 1949a). However, like the other actinide monoxides, its existence is a point of debate except as a vapor phase species at high temperature and pressure.

The first neptunium compound to be identified by X-ray powder diffraction was NpO_2 and is isostructural with other actinide dioxides (Zachariasen, 1949a). NpO_2 can be prepared by calcining nitrates, hydroxides, or oxalates of the metal in air or oxygen at 700–1000°C.

Neptunium(v) oxide, Np_2O_5, is prepared by bubbling ozone through a solution of Np(v) in molten $LiClO_4$ at 260°C and displays a very narrow compositional range with limited stability (Cohen, 1963). Anhydrous neptunium oxides above Np_2O_5 are not known. The pentoxide is monoclinic; however, the β angle is nearly 90°, allowing poor crystalline samples to be mistakenly indexed as orthorhombic (Cohen, 1963).

A hydrated oxide, $NpO_3 \cdot 2H_2O$, has been prepared by ozone oxidation of Np(v) in a $LiNO_3$–KNO_3 eutectic at 150°C (Cohen, 1963).

(f) Plutonium

The monoxide of plutonium, previously reported as belonging to the NaCl structure type, is actually a plutonium oxide carbide of the form PuO_xC_y. It is very similar to the samarium oxide carbide analog, thus aiding in its characterization. Due to these similarities, it is suggested that PuO likely exists in the vapor phase under high temperature and pressure (Larson and Haschke, 1981).

Two sesquioxides of plutonium have been identified. Interestingly, two forms of α-Pu_2O_3 have been observed, both of which are sub-stoichiometric compounds due to loss of oxygen from the dioxide. The first, α-form, is prepared by heating PuO_2 in a vacuum at 1650–1800°C in a tantalum crucible. This compound has a C-type bcc structure and exists at an O/Pu ratio of 1.515. An alternate form of α-Pu_2O_3, referred to as α'-Pu_2O_3, has also been observed at a O/Pu ratio of 1.61, although its classification as fcc is ambiguous. The only purely stoichiometric form, β-Pu_2O_3, is prepared by reducing PuO_2 with 20% excess of Pu metal at 1500°C and adopts an A-type, hexagonal structure. A more comprehensive analysis of plutonium oxide sub-stoichiometric behavior as a function of temperature is available (Gardner *et al.*, 1965).

Crystals of PuO_2, the most stable plutonium oxide, can be obtained by careful temperature control during decomposition in a molten salt (Schlechter, 1970), reaction of Pu with O_2 (Akimoto, 1960), or other methods, including the calcination of plutonium oxalate (or other salts) in air or oxygen to 800–1000°C for several hours. The dioxide is isostructural with other actinide dioxides and adopts the fluorite-type structure (Phipps and Sullenger, 1964).

(g) Americium

Although its existence is questionable, the monoxide of americium (NaCl type) has been reported by Zachariasen (1949b) and Akimoto (1967). Furthermore, the presence of certain X-ray powder diffraction lines from americium metal are possibly attributable to fcc AmO with a lattice parameter of 5.05 Å (McWhan *et al.*, 1960).

Two modifications of americium sesquioxide have been reported. The bcc (C-type) structure is the low-temperature form, prepared by heating the dioxide in H_2 at 600°C. The high-temperature hexagonal (A-type) structure was prepared by ignition of the metal oxalate at 850°C, followed by reduction in H_2 at 800°C (Templeton and Dauben, 1953). Chikalla and Eyring (1968) reported that samples with O/Am ratios between 1.54 and 1.51, when quenched from 800°C or above, gave several weak diffraction lines of neither C-type nor A-type origin. These lines compared reasonably well with those for monoclinic B-type Sm_2O_3 and were assigned as B-type Am_2O_3. The B-type sesquioxide was only found in quenched samples and it exists only at elevated temperatures; its upper temperature limit of stability lies between 950 and 1000°C. It is likely not stable as a dominant phase. The lattice constants for the americium sesquioxides are listed in Table 22.2.

Phase relations of americium oxides in the O/Am range of 1.5–2.0 have also been investigated. The cubic sesquioxide was observed to dissolve excess oxygen at room temperature up to a stoichiometry of $AmO_{1.67}$. In this range, there was either a single phase of continually variable composition or there were several

Table 22.2 *Lattice constants for Am_2O_3 (Templeton and Dauben,* 1953*; Chikalla and Eyring,* 1968).

Formula	*Symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
A – Am_2O_3	hexagonal	3.817	–	5.971	–
B – Am_2O_3	monoclinic	14.38	3.52	8.92	100.4
C – Am_2O_3	cubic	11.03	–	–	–

Table 22.3 *Lattice constants for Cm_2O_3 (Wallmann,* 1964*; Haug,* 1967*; Noé* et al., 1970*; Mosley,* 1972*; Morss* et al., 1983).

Formula	*Symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
A – Cm_2O_3	hexagonal	3.792	–	5.985	–
B – Cm_2O_3	monoclinic	14.282	3.641	8.883	100.29
C – Cm_2O_3	cubic	11.002	–	–	–

narrow regions separated by miscibility gaps. For stoichiometries between $AmO_{1.67}$ and AmO_2, an intermediate phase is thought to exist, likely from O/Am ratios between 1.67 and 1.80 (Chikalla and Eyring, 1968).

AmO_2 was the first reported americium compound (Zachariasen, 1948a, 1949b) and was shown to crystallize in the fluorite structure. It can be prepared in a variety of ways, including ignition of the nitrate or oxalate in air or oxygen up to 900°C (Templeton and Dauben, 1953). Self-irradiation effects in americium oxides are quite significant. Crystalline AmO_2 expands due to these effects, resulting in an enlargement of the lattice constant, an effect that was unaccounted for in early reports of the structure. Interestingly, lattice expansion varied between those samples stored under vacuum and those stored under O_2, with the latter occurring at a slightly slower rate. Likewise, self-irradiation of the low-temperature cubic form of the sesquioxide caused a transformation to the hexagonal form over the time span of about 3 years (Hurtgen and Fuger, 1977).

(h) Curium

The monoxide of curium has been reported during the study of curium metal, where three extra lines in the diffraction pattern were indexed as fcc CmO with a lattice constant of 5.09 Å (Cunningham and Wallmann, 1964).

Three crystalline forms of Cm_2O_3 have been characterized and the lattice constants are summarized in Table 22.3. The low-temperature bcc (C-type) structure is formed from the hydrogen reduction of a higher curium oxide (Wallmann, 1964). Heating the C-type structure between 800 and 1300°C irreversibly generates the monoclinic (B-type) structure (Mosley, 1972) and is remarkably stable with respect to self-irradiation (Haug, 1967). The reversible hexagonal (A-type) structure can be prepared in two ways: heating the B-type sesquioxide above 1600°C (Mosley, 1972) or from gradual self-irradiation of the C-type form at room temperature (Wallmann, 1964). In addition, it has been discovered that heating the A-type form to 500°C results in the B-type structure (Noé *et al.*, 1970).

The dioxide of curium can be prepared in several ways, including calcining of salts (i.e., oxalates, hydroxides) in oxygen followed by slow cooling (Asprey *et al.*, 1955) or by oxidation of the cubic sesquioxide at 400°C in air or oxygen for several days (Haug, 1967). Alternatively, CmO_2 can be prepared by thermally decomposing a resin loaded with Cm^{3+} (Hale and Mosley, 1973). The dioxide has the fluorite structure with a lattice parameter of 5.357(1) Å at room temperature, but in the case of ^{244}Cm, can undergo significant lattice damage due to self-irradiation, resulting in a swelling of the lattice parameter to 5.373 Å within 3 days (Mosley, 1972). A powder neutron diffraction study of the dioxide with Rietveld refinement yielded a stoichiometry of $CmO_{1.970\,\pm\,0.034}$; thus the material is probably hypostoichiometric. In fact, magnetic susceptibility measurements gave an effective moment of 3.36 μ_B, indicative of substantial Cm^{3+} impurity, thus favoring a nominal composition of $CmO_{1.91}$. The discrepancy between neutron diffraction data and thermogravimetric analysis (TGA) data (indicating CmO_2), and magnetic susceptibility data that favor the non-stoichiometric material, is yet to be resolved (Morss *et al.*, 1989).

Thermal decomposition of the dioxide has revealed two intermediate systems, $CmO_{1.81}$, with fluorite symmetry, and Cm_7O_{12}, with rhombohedral symmetry, finally ending with the C-type sesquioxide (Mosley, 1972). The complex nature of the curium–oxygen system bears some resemblance to the analogous plutonium system, and its intricacies are outlined elsewhere (Chikalla and Eyring, 1969).

(i) Transcurium elements

The monoxide of berkelium has been reported as having the NaCl structure type, although its existence is debatable (Fahey *et al.*, 1972).

Three berkelium sesquioxides have been identified as having A-, B-, and C-type structures and their lattice parameters are listed in Table 22.4. The low-temperature cubic C-form is produced by hydrogen reduction of the higher oxide, BkO_2 (Peterson and Cunningham, 1967a; Baybarz, 1968). Irreversible conversion of the C-type sesquioxide to the monoclinic, B-type structure occurs upon heating in the range 1200–1700°C. Further heating of the B-type sesquioxide to temperatures above 1750°C results in the hexagonal, A-type sesquioxide. The melting point occurs at 1920°C (Baybarz, 1973a).

The oxygen dissociation pressure of non-stoichiometric oxides of the form BkO_x, where $1.5 < x < 2.0$, have been investigated, resulting in the identification of three phases, $BkO_{1.5-1.77}$, $BkO_{1.81-1.91}$, and $BkO_{1.93-2.00}$

Table 22.4 *Lattice constants for Bk_2O_3 (Peterson and Cunningham,* 1967a*; Baybarz,* 1968, 1973*a*).

Formula	*Symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
A – Bk_2O_3	hexagonal	3.754	–	5.958	–
B – Bk_2O_3	monoclinic	14.197	3.606	8.846	100.23
C – Bk_2O_3	cubic	10.887	–	–	–

Table 22.5 *Lattice constants for Cf_2O_3 (Copeland and Cunningham,* 1969*; Baybarz,* 1973*a*).

Formula	*Symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
A – Cf_2O_3	hexagonal	3.72	–	5.96	–
B – Cf_2O_3	monoclinic	14.124	3.591	8.809	100.31
C – Cf_2O_3	cubic	10.839	–	–	–

(Turcotte *et al.*, 1971). A follow-up investigation of the phase behavior was consistent with previous studies, resulting in a phase diagram of the non-stoichiometric area at high temperatures. Two regions were indexed for BkO_x compounds in the non-stoichiometric range: a bcc region for $1.5 < x \leq 1.70$ and a fcc region for $1.78 < x < 2.0$ (Turcotte *et al.*, 1980). A more comprehensive investigation of the phase diagram in the temperature range from 200 to 900°C and from 59 to 67 atomic % oxygen is available from Okamoto (1999).

The stoichiometric dioxide of berkelium is obtained by calcination of berkelium salts (nitrate, oxalate, hydroxide, etc.) in air or oxygen, resulting in a fcc structure. The first structural determination of the dioxide was performed in 1962 using only 4 ng of sample; the diffraction pattern showed four lines that were indexed on the basis of a fcc cell (Peterson and Cunningham, 1967a). Subsequent studies used larger samples (μg) of ^{249}Bk that had been loaded onto an ion exchange resin, calcined, and indexed (Peterson and Cunningham, 1967a; Baybarz, 1968). BkO_2 also undergoes thermal expansion in 1 atm of oxygen, although the phenomenon is reversible with a decrease in temperature (Fahey *et al.*, 1974).

The three known sesquioxides of californium are the A-, B-, and C-type structures and their lattice constants are provided in Table 22.5. The first discovered was the monoclinic, B-type sesquioxide (Green and Cunningham, 1967) followed by the discovery of the cubic, C-type sesquioxide (Copeland and Cunningham, 1969). The hexagonal, A-type sesquioxide was the most difficult to obtain due to its small range of existence between the monoclinic form and the melting point. The low-temperature B-type sesquioxide is transformed to the C-type upon heating between 1200 and 1700°C, followed by a transformation to the A-type sesquioxide above 1700°C and melting at 1750°C (Baybarz, 1973a).

Table 22.6 *Lattice constants for Es_2O_3 (Haire and Baybarz,* 1973*; Haire and Eyring,* 1994).

Formula	*Symmetry*	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)
A – Es_2O_3	hexagonal	3.7	–	–	–
B – Es_2O_3	monoclinic	14.1	3.59	8.80	100
C – Es_2O_3	cubic	10.766	–	–	–

An intermediate between the sesquioxide and the dioxide was identified as Cf_7O_{12}. This rhombohedral structure can be prepared by heating the cubic sesquioxide in air or oxygen, at which time the sesquioxide takes up oxygen to an O/Cf ratio of 1.7; its existence is limited to a very narrow range of O/Cf values. It can also be prepared by heating the nitrate, oxalate, or nitrate salts in air or oxygen to 750°C, after which oxygen is lost to form the sesquioxide (Baybarz *et al.*, 1972a).

Californium dioxide has been prepared by the oxidation of the cubic sesquioxide with high-pressure molecular oxygen and by atomic oxygen. The dioxide has the fluorite structure with a lattice parameter of 5.310(2) Å, which has been corrected for expansion due to swelling. Preparation of CfO_2 can also be achieved through self-irradiation of lower californium oxides via the generation of active oxygen species from alpha decay (Baybarz *et al.*, 1972a).

The only characterized oxides of einsteinium have been the sesquioxides, the lattice parameters for which are provided in Table 22.6. The cubic C-type sesquioxide was prepared from the calcination of submicrogram amounts of the metal nitrate and analyzed by electron diffraction (Haire and Baybarz, 1973). The monoclinic B-type sesquioxide was produced from the oxidation of einsteinium metal under oxygen at elevated temperatures (800–1000°C). The hexagonal A-type sesquioxide is produced as a result of the self-irradiation of the monoclinic form. Both the B- and A-types were characterized by electron diffraction (Haire and Eyring, 1994). The rapid appearance of the highly radioactive daughter ^{249}Bk from the parent ^{253}Es (3% per day) has made the study of these compounds quite challenging.

Crystal structures for the oxides of transeinsteinium elements are not available due to limitations in abundance and their short half-lives.

22.3.3 Actinyl compounds

Actinide elements in the hexavalent oxidation state commonly exist as the actinyl (AnO_2^{2+}) ion in both aqueous solutions and solid state. The linear geometry of the uranyl ion with its *trans* oxo ligands (O=U=O) was first elucidated by Fankuchen (1935) from the space group symmetry of sodium uranyl acetate. The stability of the uranyl ion is evident in the hundreds of structural characterizations that have since been published, many of which were included by Burns in Chapter 20 of the previous edition (pre-1986) as well as Chapter 5 of the current edition. The ubiquity of the hexavalent uranyl moiety in both solution and the solid state has led to numerous studies in a variety of environments, including inclusion into the cavity of macrocyclic ligands (see Section 22.4.2) for separations applications, the interaction with ligands such as carbonate (Morse *et al.*, 1984), and citrate (Pasilis and Pemberton, 2003) to understand environmental mobility and/or immobilization, elucidation of the Lewis base properties of the oxo ligands with respect to ligand exchange, substitution, and cation–cation interactions (Sarsfield and Helliwell, 2004), and computational studies of the role of 5f electrons in bonding, electronic, and structural properties to understand the origin of its linearity (Zhang and Pitzer, 1999).

Hexavalent actinyl ions are also known for transuranic actinides Np (neptunyl), Pu (plutonyl), and Am (americyl). The entire series is isostructural although structural details are limited compared to uranyl. The An–O bond strength, as well as the resistance to reduction, decreases in the order U > Np > Pu > Am. Whereas uranyl salts are highly common, formation of AmO_2^{2+} requires the use of strong oxidizing agents such as peroxodisulfate. The An=O bond length in hexavalent actinyl compounds generally ranges between 1.7 and 2.0 Å. In all cases, the bond is very strong, while in uranyl, it appears that the bond order may be even greater than two as evidenced by the short bond length (Greenwood and Earnshaw, 2001).

The linearity of the uranyl and other hexavalent actinyl ions (Np, Pu, Am) has been the subject of many theoretical inquiries that sought to elucidate the relative contributions of orbitals from the actinide and oxygen atoms. Wadt (1981) noted that the difference in the gas-phase geometries of isoelectronic UO_2^{2+} and ThO_2 is due to the relative ordering of the 5f and 6d levels. In uranium, the 5f orbitals are lower in energy, thus favoring a linear geometry upon interaction with oxygen 2p orbitals. In thorium, however, the 6d orbitals are lower, resulting in a bent geometry. Furthermore, Tatsumi and Hoffmann (1980) and Pyykkö *et al.* (1989) have added that 6p interactions with oxygen are significant in uranium; this repulsive interaction activates the 5f orbitals of uranium in a coorperative manner through a 'pushing from below' mechanism, leading to short, linear oxo bonds. A review of the electronic structure of several actinide-containing molecules is available from Pepper and Bursten (1991).

It is estimated that 98% of all crystal structures have O=U=O angles in the range 174–180° (Sarsfield *et al.*, 2004). Despite the prevalence of the linear dioxo cation, nonlinear uranyl species have been observed. For example, the structure of $UO_2[(SiMe_3N)CPh(NSiMe_3)]_2THF$ contains a uranyl unit with a O=U=O angle of 169.7(2)° (Sarsfield and Helliwell, 2004). While this bend is a dramatic example of nonlinearity, more common deviations are observed in the structures of $UO_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2(pyr)_2$ (Barnhart *et al.*, 1995a) and $[UO_2(OCH({}^iPr)_2)_2]_4$ (Wilkerson *et al.*, 2000); the O=U=O angles in these examples are 173.4(2)° and 172.6(2)°, respectively.

Accurate determination of the uranium–oxygen bond length of uranyl in its compounds by X-ray diffraction have traditionally been difficult due to the large difference in scattering power (proportional to the number of electrons) between the two atoms. However, advances in neutron diffraction techniques and their wider availability have eliminated this problem. The nuclear cross sections of uranium and oxygen are comparable, thus allowing accurate atomic placement using neutrons.

In general for hexavalent actinyl ions, several factors have been identified that can lead to variations in the U=O bond length. The most significant is the bonding of ligands in the equatorial plane, perpendicular to the O=An=O axis. Actinyls readily form complexes with halides, such as F^- and Cl^-, oxygen donors such as OH^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, and carboxylates, as well as neutral donors, such as H_2O or pyridine. Coordination numbers between four and six from monodentate and bidentate ligands are common in the equatorial plane and generate octahedral, pentagonal bipyramidal, and hexagonal bipyramidal geometries. In uranyl, the formal charge on uranium is 2+, although other evidence suggests that it may be closer to 3+ (the formal charge is different from oxidation state); thus, depending on the extent of orbital overlap from equatorial ligands, the electron density withdrawn from the axial oxygen atoms greatly affects the M=O bond lengths (Sarsfield and Helliwell, 2004). Another factor is the local environment provided by the rest of structure, sometimes resulting in U=O bond lengths that vary within the same compound. For example, in the compound $UO\{OB(C_6F_5)_3\}[(SiMe_3N)CPh(NSiMe_3)]$, the interaction of one oxo ligand (Lewis base) with the borane (Lewis acid) results in an elongated U=O bond (1.898(3) Å) compared to the uncoordinated one (1.770(3) Å) (Sarsfield and Helliwell, 2004). Finally, reduction of the actinide oxidation state from 6+ to 5+ results in a lengthening, and hence weakening, of the oxo bond. Additional information on actinyl structures and structural changes with correlations to vibrational spectra has been compiled by Hoeskstra (1982).

Actinide elements in the pentavalent oxidation state form a less common type of actinyl represented by the formula AnO_2^+. This species is known for U, Np, Pu, and Am. Like AnO_2^{2+}, the AnO_2^+ ion is linear and symmetric, although the low charge on AnO_2^+ prevents the formation of very stable complexes. These compounds are very susceptible to disproportionation into An(IV) and An(VI). The most notable pentavalent actinyl is NpO_2^+; it has recently been observed to form an inclusion complex with the porphyrin, hexaphyrin(1.0.1.0.0.0). Here, the environment around the linear cation results in two different Np=O bond lengths: 1.762(1) and 1.826(1) Å. These distances are unusually short for the neptunyl ion where 1.85 Å is common in simple inorganic salts (Sessler *et al.*, 2001b).

Differences in the An=O bond length are also significantly influenced by the oxidation state of the metal; changing from a hexavalent to a pentavalent actinyl results in a bond length increase of about 0.14 Å (Burns and Musikas, 1977). This change in the bond length implies a weakening of the bond and is attributed to the additional non-bonding electrons in each AnO_2^+ ion compared to the corresponding AnO_2^{2+} ion. Both AnO_2^+ and AnO_2^{2+} exhibit the actinide contraction where incremental increases in the atomic number result in a lengthening of the An=O bond by about 0.01 Å (Zachariasen, 1954; Musikas and Burns, 1976). Self-assembled uranyl peroxide nanosphere clusters of 24, 28, and 32 polyhedra (some containing neptunyl) that crystallize from alkaline solution have been characterized (Burns *et al.*, 2005).

22.3.4 Hydrides, borohydrides, borides, carbides, and silicides

(a) Hydrides

A majority of the actinide hydrides attain either the $AnH_{2\pm x}$ or AnH_3 composition through direct reaction of the metal in a H_2 atmosphere. Structural information is available for hydrides of thorium through californium. The resulting actinide hydrides react readily with oxygen and all are pyrophoric.

(*i*) *Thorium*

Thorium dihydride was originally studied by Rundle *et al.* (1952) using neutron diffraction and was indexed as a body-centered tetragonal (bct) lattice; it is also isomorphous with ZnH_2. However, several weak maxima were observed in the X-ray diffraction pattern that were presumably due to unidentified impurities. An X-ray diffraction study by Korst (1962) examined sub-stoichiometric samples of thorium hydride in the overall composition range $ThH_{1.93}$ to $ThH_{1.73}$. Samples richest in hydrogen ($ThH_{1.93}$ and $ThH_{1.88}$) gave diffraction patterns corresponding to the bct lattice of Rundle *et al.*, while the other samples ($ThH_{1.84}$, $ThH_{1.79}$, and $ThH_{1.73}$) contained bct lines as well as face-centered cubic lines in their diffraction patterns. As a result, Korst reindexed all samples as face-centered tetragonal, for which the preferred setting is body-centered tetragonal.

The higher thorium hydride, Th_4H_{15}, was studied by X-ray diffraction and assigned a bcc lattice based on a H/Th ratio of 3.62 (representing the lower limit due to impurities) (Zachariasen, 1953). The structure of Th_4H_{15} was also confirmed by Korst (1962) with a H/Th ratio as high as 3.73.

(*ii*) *Protactinium*

X-ray diffraction studies of the complicated Pa–H system revealed the existence of four protactinium hydride phases during the hydriding process as a function of temperature and pressure. Phase I is present in mixtures with Phase II (>500 K) or Phase IV (<500 K) at H/Pa ratios less than 1.3 and has a body-centered tetragonal structure. Phase II exists solely at temperatures above 500 K in the range corresponding to Pa_3H_4–Pa_3H_5 and has a fcc structure. After a narrow two-phase region above 500 K, Phase III becomes dominant with a wide composition range corresponding to $2.0 \leq H/Pa \leq 3.0$. This phase has a cubic structure that is isostructural with β-UH_3, which will be described later. Phase IV forms rapidly below 500 K and exhibits an extremely wide composition range corresponding to $1.3 \leq H/Pa \leq 3.0$. This phase also has a cubic structure and is isostructural with α-UH_3 (Ward *et al.*, 1984).

(*iii*) *Uranium*

Two crystalline modifications of uranium trihydride have been characterized and are denoted α-UH_3 and β-UH_3. The first to be discovered was the β-form of the trihydride and was studied using both X-ray (Rundle, 1947) and neutron diffraction (Rundle, 1951). Neutron diffraction of UD_3 shows that each hydrogen atom lies in a distorted tetrahedron, surrounded by four uranium atoms at a distance of 2.32 Å. There are two types of uranium atoms in the lattice; each is surrounded by 12 hydrogens at this distance. Uranium atoms of the first type are surrounded by hydrogen atoms at the corners of an icosahedron (of T_d symmetry), while the uranium atoms of the second type are surrounded by sets of three hydrogen atoms, each forming the face of a different icosahedron. The absence of metallic U–U bonds indicates that the structure is held together solely by U–H interactions.

The less stable α-UH_3 was structurally characterized in 1954 and was found to be a metastable form of UH_3.The crystal structure of α-UH_3 is simple cubic with a lattice parameter of 4.160(5) Å and has U–H distances identical to the β-form. Interestingly, the reaction of hydrogen with uranium powder at the lowest temperatures (–80°C) produced mixtures of the α- and β-forms with the greatest percentage of α-UH_3. Heating of mixtures of known composition at 250°C resulted in total conversion to the β-form, but heating of the same mixture at 100°C resulted in no change in the diffraction pattern. Thus, the appearance of the α-form is only by virtue of it being formed more rapidly than it decomposes at low reaction temperatures (Mulford *et al.*, 1954).

(*iv*) *Transuranium*

The Np–H and Pu–H systems are the most thoroughly studied of the transuranium hydride systems. Two studies of the Np–H system have been performed, the latter of which used ultra-pure metal to confirm the existence of two structural forms, a cubic form and a hexagonal form as well as a two-phase region. An unusually sharp phase boundary is observed at a H/Np ratio of 2.13 marking the disappearance of neptunium metal. At temperatures below 400°C and a H/Np ratio above about 2.3, a cubic region is observed where the dihydride lattice expands upon addition of hydrogen, a phenomenon which has not been observed in any other systems. The transition to a hexagonal/cubic two-phase system occurs at a H/Np ratio of about 2.6, followed by a very narrow hexagonal NpH_{3-x} region, both of which were only observed upon dehydriding. Increasing the H/Np ratio to 3.0 resulted in a hexagonal trihydride structure with very weak indications of cubic artifacts due to decomposition (Mulford and Wiewandt, 1965; Ward *et al.*, 1987).

The Pu–H system is very complex. A recent study by Haschke *et al.* (1987) indicated the existence of five phases in the range $1.9 \leq \mathrm{H/Pu} \leq 3.0$ during the dehydriding process as a function of temperature. At lower temperatures (75–100°C), only the cubic (fcc) dihydride exists for H/Pu values less than 2.7. In the range of $2.7 < \mathrm{H/Pu} < 2.9$, a two-phase region exists that has both cubic and hexagonal (hcp) structural features. In the small region of H/Pu values between 2.9 and 2.95, only the hexagonal trihydride is present, but the region from 2.95 to 3.0 has not been structurally characterized. A neutron diffraction study describing the occupancy of hydrogen atoms in tetrahedral versus octahedral sites is also described. See Chapter 7, especially section 7.8.1 of this work, for further discussion of Pu hydrides.

X-ray diffraction studies of the americium–hydrogen system revealed both fcc AmH_{2+x} and a hexagonal AmH_3 phases, thus resembling the Np–H and Pu–H systems. The cubic dihydride was observed until a composition of $\mathrm{AmH}_{2.7}$ was reached, after which a transition to the hexagonal AmH_3 occurred. As in the Pu–H system, the lattice constant decreases in the cubic region as hydrogen content increases (Olson and Mulford, 1966; Roddy, 1973).

Curium and berkelium hydrides, like their transuranium predecessors, also exhibit both fcc MH_{2+x} (dihydride) and hexagonal MH_3 phases (Gibson and Haire, 1985a,b). Structural data on the cubic californium dihydride has also been collected, but a trihydride has not yet been observed (Gibson and Haire, 1987).

(b) Borohydrides

The limitations of single-crystal X-ray diffraction techniques were evident in the study of $\mathrm{U(BH_4)_4}$ as evidenced by an inherent inability to locate hydrogen atoms against the extreme electron density of the actinide (Bernstein *et al.*, 1972a). This problem was easily overcome with neutron diffraction (Bernstein *et al.*, 1972b). Whereas X-ray diffraction only revealed the interaction of uranium with boron atoms of the four bridging and two terminal groups, neutron diffraction data showed that, in actuality, the four bridging BH_4^- groups each donate two hydrogen atoms to the uranium polyhedron (resulting in a helical polymer), and the terminal groups donate three hydrogen atoms, resulting in a uranium coordination number of 14.

Similar borohydride compounds with dimethyl ether, $\mathrm{U(BH_4)_4 \cdot O(CH_3)_2}$, and diethyl ether $\mathrm{U(BH_4)_4 \cdot O(C_2H_5)_2}$ (Fig. 22.4), show slight variations in the structural trends due to metal–ether bonding. In both cases, the coordination number of 14 is maintained due to 13 hydrogen atoms (4 bridging, 9 terminal) and one ether oxygen atom contributing to the coordination polyhedron (Rietz *et al.*, 1978a). A coordination number of 14 was also observed in the borohydride/tetrahydofuran (THF) compound, $\mathrm{U(BH_4)_4 \cdot (OC_4H_8)_2}$ due to 12 hydrogen atoms from borohydride and two oxygen atoms from THF. This is a unique

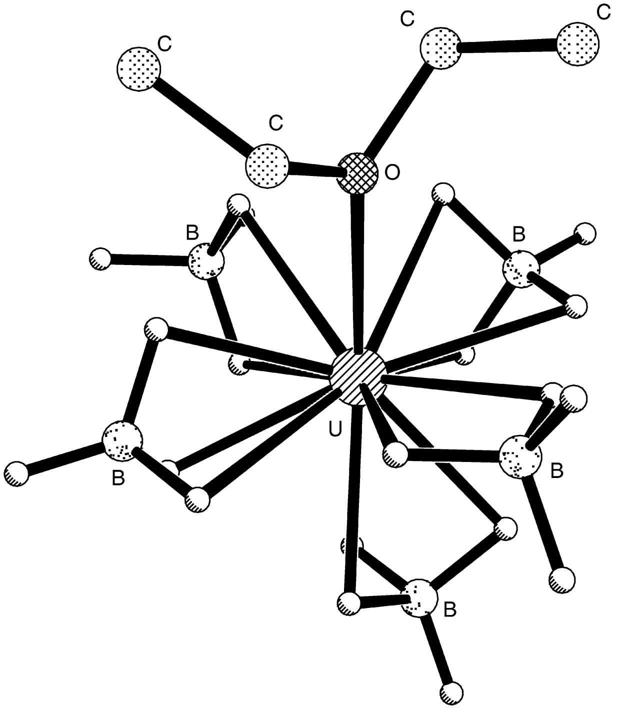

Fig. 22.4 *Crystal structure of* $U(BH_4)_4 \cdot O(C_2H_5)_2$ *with ether hydrogen atoms omitted* (*Rietz* et al., 1978*a*).

example in which all the borohydride groups are terminal, resulting in a monomeric solid state complex (Rietz *et al.*, 1978b). Interestingly, coordination numbers of 13 and 14 are observed for two different uranium atoms in the solid state structure of $U(BH_4)_4 \cdot (n\text{-}C_3H_7)_2$, resulting in an unsymmetrical dimer (Zalkin *et al.*, 1978a).

The stability of the $An(BH_4)_4$ (where An = Th, Pa, U, Np and Pu) compounds of the actinides decreases going from thorium to plutonium; the latter two decompose readily. Structural analyses using X-ray powder diffraction indicate that the Th, Pa, and U compounds are isomorphous tetragonal polymers. The Np and Pu compounds are also isomorphous, but have a different tetragonal structure and are monomeric in the solid state (Banks *et al.*, 1978).

(c) Borides, carbides, and silicides

The structures for actinide borides, carbides, and silicides are summarized in Table 22.7. In general, borides, carbides, and silicides are less chemically reactive relative to the hydrides and are refractory materials, enabling their consideration as nuclear fuels (Naito and Kamegashira, 1976). In general,

Table 22.7 *Actinide borides, carbides, and silicides and their crystal symmetries.*

Boride	*Symmetry*	*References*	*Carbide*	*Symmetry*	*References*	*Silicide*	*Symmetry*	*References*
ThB_4	tetragonal	a	ThC	fcc	g	Th_3Si_2	tetragonal	w
ThB_6	cubic	a	Th_2C_3	bcc	h	ThSi	orthorhombic	w
ThB_{12}	fcc	b	α-ThC_2	monoclinic	i, j	Th_3Si_5	hexagonal	x
–	–	–	β-ThC_2	tetragonal	j	α-$ThSi_2$	tetragonal	y
–	–	–	γ-ThC_2	fcc	j	β-$ThSi_2$	hexagonal	w, y
–	–	–	PaC	fcc	k	–	–	–
–	–	–	PaC_2	bcc	k	–	–	–
UB_2	hexagonal	c, d	UC	fcc	l	U_3Si	tetragonal	z
UB_4	tetragonal	c, d	U_2C_3	bcc	m	U_3Si_2	tetragonal	aa
UB_{12}	fcc	c, d	α-UC_2	tetragonal	n	USi	tetragonal	bb
–	–	–	β-UC_2	fcc	n	U_3Si_5	hexagonal	x
–	–	–	–	–	–	α-USi_2	tetragonal	aa
–	–	–	–	–	–	β-USi_2	hexagonal	aa
–	–	–	–	–	–	USi_3	cubic	cc
NpB_2	hexagonal	e	NpC	fcc	o	Np_3Si_2	tetragonal	dd
NpB_4	tetragonal	e	Np_2C_3	bcc	p	$NpSi_2$	tetragonal	q, aa
NpB_6	cubic	e	NpC_2	tetragonal	q	–	–	–
NpB_{12}	fcc	e	–	–	–	–	–	–
PuB_2	hexagonal	f	PuC	fcc	r	PuSi	orthorhombic	ee
PuB_4	tetragonal	f	Pu_2C_3	bcc	s	Pu_3Si_5	hexagonal	ff
PuB_6	cubic	f	α-PuC_2	tetragonal	t	α-$PuSi_2$	tetragonal	aa, ee
PuB_{12}	fcc	f	β-PuC_2	fcc	u	β-$PuSi_2$	hexagonal	gg, ee
–	–	–	–	–	–	Pu_5Si_3	tetragonal	hh, ee
–	–	–	–	–	–	Pu_3Si_2	tetragonal	ff, ee
AmB_4	tetragonal	e	Am_2C_3	bcc	v	Am_5Si_3	tetragonal	ii
AmB_6	cubic	e	–	–	–	AmSi	orthorhombic	ii, jj
–	–	–	–	–	–	α-$AmSi_2$	tetragonal	ii
–	–	–	–	–	–	"β"-$AmSi_2$	hexagonal	ii
–	–	–	–	–	–	CmSi	orthorhombic	kk
–	–	–	–	–	–	$CmSi_2$	tetragonal	kk
–	–	–	–	–	–	Cm_2Si_3	hexagonal	kk

their stoichiometries are highly varied. The monocarbides, AnC, are semi-metallic and primarily ionic, but with supernumerary electrons in a delocalized conduction band.

Actinide borides (in actuality, metal borides in general) are interstitial compounds through inclusion of the small boron atoms into the lattice holes of the metallic structure which becomes expanded, but maintain their simple structure. Metal borides are characterized by the fact that boron atoms can form direct B–B bonds in the lattice (Vegas *et al.*, 1995). This catenation increases with the concentration of boron atoms in the lattice, where the boron atoms rest at the centers of trigonal prisms of metal atoms (Greenwood and Earnshaw, 2001). Structural details of metal diborides, tetraborides, and hexaborides where the structure of the parent metal is retained are described elsewhere (Vegas *et al.*, 1995).

Actinide borides all contain either two- or three-dimensional lattices of covalent B–B bonds with lengths from 1.72 to 1.83 Å and these bond lengths are typically invariant with respect to changes in the metal atom type. The actinide–boron bonds show a range of distances depending on the crystal structure. They appear to adjust to the more rigid framework of the boron atoms and can be found in several compositions. The hexagonal UB_2 has been characterized by X-ray diffraction (Brewer *et al.*, 1951; Dancausse *et al.*, 1992). The structure contains triangular nets of boron atoms that alternate with similar layers of uranium to form a hexagonal stacking sequence. Alternatively, the structure can be described in terms of boron atoms at the center of trigonal prisms of uranium atoms. Thus, each uranium atom has 12 boron neighbors (Post *et al.*, 1954). The formation of AnB_4 is common and, as detailed for UB_4, the synthesis can be achieved through several methods, including floating zone melting, the tri-arc Czochralski method, and from a molten metal flux (Menovsky *et al.*, 1984). Like ThB_4, the structure of UB_4 consists of B_6 octahedra linked along the z-axis and joined in the xy plane by pairs of B_2 atoms. The resulting three-dimensional structure has tunnels along the z-axis that are filled by metal atoms; thus the B_6 and B_2 units are surrounded by metal cubes and metal trigonal prisms, respectively. Each metal has 18 nearest boron neighbors (Vegas *et al.*, 1995).

The structure of ThB_6 is a three-dimensional array of interconnected B_6 octahedra with An atoms in the lattice holes, forming a primitive cubic structure

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[a] Konrad *et al.* (1996); [b] Cannon and Farnsworth (1983); [c] Brewer *et al.* (1951); [d] Dancausse *et al.* (1992); [e] Eick and Mulford (1969); [f] Eick (1965); [g] Kempter and Krikorian (1962); [h] Krupka (1970); [i] Gantzeland Baldwin (1964); [j] Bowman *et al.* (1968); [k] Lorenz *et al.* (1969); [l] Olsen *et al.* (1986); [m] Mallett *et al.* (1951); [n] Bowman *et al.* (1966); [o] Lander *et al.* (1969); [p] Lorenzelli (1968); [q] Sheft and Fried (1953); [r] Zachariasen (1949c); [s] Zachariasen (1952c); [t] Chackraburtty and Jayadevan (1965); [u] Harper *et al.* (1968); [v] Mitchell and Lam (1970a); [w] Jacobson *et al.* (1956); [x] Brown and Norreys (1959); [y] Brown (1961); [z] Kimmel (1978); [aa] Zachariasen (1949d); [bb] Le Bihan *et al.* (1996); [cc] Brixner (1963); [dd] Mitchell and Lam (1974); [ee] Boulet *et al.* (2003); [ff] Land *et al.* (1965); [gg] Runnalls and Boucher (1955); [hh] Cromer *et al.* (1964); [ii] Weigel *et al.* (1984); [jj] Weigel *et al.* (1977); [kk] Weigel and Marquart (1983).

expanded by the B_6 clusters; this gives Th a coordination number of 24. The An–An distances in AnB_6 usually are similar to the An–An bond distances in the parent metal. Dodecaborides, AnB_{12}, can be described as a cubic closest packed structure of B_{12} units with actinide cations located in the octahedral lattice holes. The metal is coordinated with 24 boron atoms (Vegas *et al.*, 1995).

Heating AnO_2 with excess carbon usually leads to the formation of AnC_2, which may also be prepared by direct reaction of the metal with carbon (Troost, 1893). Three polymorphs of ThC_2 have been detected using both X-ray and neutron diffraction: monoclinic α-ThC_2 at room temperature (Hunt and Rundle, 1951; Bowman *et al.*, 1968), tetragonal β-ThC_2 at temperatures between 1430 and 1480°C, and cubic γ-ThC_2 at temperatures above 1480°C (Bowman *et al.*, 1968). The dicarbide of uranium has two polymorphs. The α-form is tetragonal (CaC_2-type) at 1700°C and differs from the tetragonal β-form of thorium dicarbide. The β-form of uranium dicarbide is cubic at 1900°C and is analogous to γ-ThC_2 (Bowman *et al.*, 1966). The α- and β-forms of PuC_2 are tetragonal (Chakraburtty and Jayadevan, 1965) and fcc (Harper *et al.*, 1968), respectively. The tetragonal form adopts the CaC_2 structure type. PaC_2 (Lorenz *et al.*, 1969) and NpC_2 (Sheft and Fried, 1953) have been observed with cubic and tetragonal structures, respectively. Careful control of the conditions for preparing AnC_2 can also be used to produce AnC. Structural information on AnC and An_2C_3 structures can be located in Table 22.7.

Of the actinide silicides, the uranium and thorium compounds are the most thoroughly characterized. The α-form of $ThSi_2$ was first identified in 1942 (Brauer and Mitius, 1942); the β-form readily transforms to α-$ThSi_2$ above 1350°C, and is reversible below 1250°C. A defect structure of the non-stoichiometric composition $ThSi_{1.67}$ is also known (Brown, 1961). The structure of USi was the most recent to be determined. Le Bihan *et al.* (1996) describe the synthesis of USi and assign a tetragonal symmetry to this compound despite previous reports of an orthorhombic cell. The unit cell has 68 uranium atoms. The plutonium–silicon binary system contains at least five different compounds, with Pu_5Si_3 being one of the few actinide silicide structures determined from single crystal X-ray diffraction (Cromer *et al.*, 1964). The structural determination of AmSi and $AmSi_2$ was first reported by Weigel *et al.* (1984) using X-ray powder diffraction. Further work produced a range of americium silicides between room temperatures and 900°C. Curium silicides were first prepared by Weigel and Marquart (1983) through the reduction of CmF_3 with stoichiometric amounts of elemental Si at 1260°C. The X-ray diffraction data was compared to X-ray data from known analogous compounds of uranium, neptunium, plutonium, and americium. However, the authors caution that, because of the use of ^{244}Cm in the structures, the large amount of self-irradiation that occurs can destroy the lattice and cause inaccuracies due to broadening of and intensity changes in the X-ray lines, although the destruction could be reduced by a factor of 20000 if ^{248}Cm were used in its place (Weigel and Marquart, 1983).

22.3.5 Pnictides and chalcogenides

Actinide pnictides (compounds with N, P, As, Sb, and Bi) and chalcogenides (compounds with S, Se, and Te) are of interest to solid state chemists because these compounds display interesting electronic properties based upon the degree of localization or delocalization of the 5f electrons, resulting in compounds that are not purely ionic. In most cases, the delocalized nature of the 5f electrons in thorium through plutonium (although the transuranium elements become weakly delocalized) allows them to participate in bonding, while the localized nature of these electrons in americium and beyond makes them non-bonding (Damien *et al.*, 1986). In general, the nature of the bonding in these compounds is considered to be semimetallic.

For example, the monopnictides are face-centered cubic (fcc) compounds with lattice parameters decreasing from Th to U, increasing through Cm, and then decreasing again (Damien and de Novion, 1981). This behavior reflects metallic character in ThN, delocalized 5f electrons in UN, less delocalization in NpN, PuN, and AmN, and localized lanthanide-like behavior in CmN and BkN (due to the prevalence of the trivalent oxidation state in the later actinides). Similar behavior is observed in other pnictides; when there is a direct comparison with lanthanide compounds, transamericium compounds show slightly larger lattice parameters than do isoelectronic lanthanides. The delocalized nature of UN, NpN, and PuN 5f electrons is indicative of band formation and metallic conduction. The variation in lattice parameters of monochalcogenides follows a similar trend, but transcurium elements are unknown.

Several structural lattice types are common within these compounds. A list of known actinide–pnictide and actinide–chalcogenide compounds are provided in Tables 22.8 and 22.9, respectively.

The majority of the structures listed in these tables were determined by X-ray powder diffraction (lattice parameters and structural type) because the compounds are sensitive to oxidation in air, are unstable at high temperature due to the considerable partial pressures of the nonmetal elements over the crystalline phases, and have high chemical reactivity at elevated temperatures. Common methods used for growing single crystals of the monopnictides involve considerable difficulties, including selecting sufficiently inert materials for the high-temperature sample container. While some single crystals have been grown for certain compounds in both classes, little has been done in terms of structure determination. Efforts to facilitate the synthesis have been detailed by Horyn *et al.* (1983).

The structural types adopted by actinide pnictides and chalcogenides are quite diverse. All monopnictides and monochalcogenides are NaCl fcc structures except for ThTe which has a CsCl structure. A thorough summary of the structural types of higher pnictides and chalcogenides is available (Damien *et al.*, 1986). Some interesting examples include the body-centered cubic (bcc) form of Th_3P_4

Table 22.8 *Actinide pnictides and their crystal symmetries.*

	N		*P*		*As*		*Sb*		*Bi*	
Composition	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
ThX	fcc	a	fcc	p	fcc	x	fcc	ee	–	–
Th_2X_3	hexagonal	b	–	–	–	–	–	–	–	–
Th_3X_4	hexagonal (α)	c	bcc	p, q	bcc	x	bcc	ee	bcc	kk
	rhombohedral (β)	d	–	–	–	–	–	–	–	–
ThX_2	–	–	–	–	orthorhombic (α)	q	tetragonal	ee	tetragonal	kk
	–	–	–	–	tetragonal (β)	x	–	–	–	–
PaX	fcc	e	–	–	fcc	y	–	–	–	–
Pa_3X_4	–	–	bcc	r	bcc	y	bcc	ff	–	–
PaX_2	–	–	tetragonal	r	tetragonal	y	tetragonal	ff	–	–
UX	fcc	a, f	fcc	s	fcc	s	fcc	s	fcc	ll
U_2X_3	cubic (α)	g	–	–	–	–	–	–	–	–
	hexagonal (β)	h	–	–	–	–	–	–	–	–

U_3X_4	–	–	bcc	t	bcc	z	bcc	gg	bcc	ll, mm
UX_2	fcc	a	tetragonal (α)	u	tetragonal	v	tetragonal	hh	tetragonal	nn
	–	–	tetragonal (β)	v	–	–	–	–	–	–
NpX	fcc	i	fcc	i	fcc	i	fcc	ii	fcc	i
Np_3X_4	–	–	bcc	w	bcc	aa	–	–	–	–
NpX_2	–	–	–	–	tetragonal	aa	orthorhombic	jj	–	–
PuX	fcc	j, k	fcc	s	fcc	s, bb	fcc	s	fcc	i
PuX_2	–	–	–	–	–	–	orthorhombic	jj	–	–
Pu_4X_3	–	–	–	–	–	–	bcc	i	–	–
AmX	fcc	l, m	fcc	m	fcc	m, bb, cc	fcc	m, cc	fcc	cc
AmX_2	–	–	–	–	–	–	orthorhombic	jj	–	–
Am_4X_3	–	–	–	–	–	–	bcc	m	–	–
CmX	fcc	n	fcc	m, n	fcc	m, n	fcc	m, n	–	–
BkX	fcc	o	fcc	o	fcc	o	fcc	o	–	–
CfX	–	–	–	–	fcc	dd	fcc	dd	–	–

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[a] Rundle (1948); [b] Zachariasen (1949b); [c] Benz and Zachariasen (1966); [d] Bowman and Arnold (1971); [e] Bohet and Müller (1978); [f] Marples (1970); [g] Serizawa *et al.* (1994); [h] Masaki and Tagawa (1975); [i] Charvillat (1978); [j] Zachariasen (1949c); [k] Olson and Mulford (1964); [l] Akimoto (1967); [m] Charvillat *et al.* (1975); [n] Damien *et al.* (1979a); [o] Damien *et al.* (1980a); [p] Gingerich and Wilson (1965); [q] Hulliger (1966); [r] Wojakowski *et al.* (1982); [s] Kruger and Moser (1967); [t] Zumbusch (1941); [u] Pietraszko and Lukaszewicz (1971); [v] Iandelli (1952a); [w] Sheft and Fried (1953); [x] Ferro (1955); [y] Calestani *et al.* (1979); [z] Iandelli (1952b); [aa] Wojakowski and Damien (1982); [bb] Charvillat and Damien (1973); [cc] Roddy (1974); [dd] Damien *et al.* (1980b); [ee] Ferro (1956); [ff] Hery *et al.* (1979); [gg] Smetana *et al.* (1975); [hh] Ferro (1952a); [ii] Mitchell and Lam (1971); [jj] Charvillat *et al.* (1977); [kk] Borzone *et al.* (1982); [ll] Ferro (1952b); [mm] Henkie *et al.* (1997); [nn] Ferro (1953).

Table 22.9 *Actinide chalcogenides and their crystal symmetries.*

	S		*Se*		*Te*	
Composition	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
Ac_2X_3	cubic	a	–	–	–	–
ThX	fcc	b	fcc	x	bcc	ll
Th_2X_3	orthorhombic	b	orthorhombic	x	hexagonal	d
Th_7X_{12}	hexagonal	c	hexagonal	x, y	hexagonal	mm
ThX_2	orthorhombic	b, d	orthorhombic	d, x, y	hexagonal	d
Th_2X_5	orthorhombic	e	orthorhombic	l, x	–	–
ThX_3	–	–	oonoclinic	l	monoclinic	d
PaX_2	orthorhombic	f	hexagonal	f	–	–
UX	fcc	b, g, h	fcc	h	fcc	h
U_3X_4	–	–	bcc	aa	bcc	nn
U_2X_3	orthorhombic	b, g	orthorhombic	bb	bcc	oo
	–	–	–	–	orthorhombic	pp
U_3X_5	orthorhombic	i, g	orthorhombic	cc	orthorhombic	qq
U_7X_{12}	–	–	hexagonal	dd	hexagonal	mm
UX_2	tetragonal (α)	g	tetragonal (α)	ee	orthorhombic	rr
	orthorhombic (β)	g, j	orthorhombic (β)	ff	–	–
	hexagonal (γ)	g, k	hexagonal (γ)	k	–	–
U_2X_5	orthorhombic	l	–	–	monoclinic	ss
UX_3	monoclinic	g	monoclinic	dd	monoclinic (α)	rr
	–	–	–	–	orthorhombic (β)	tt
NpX	fcc	m	fcc	gg	fcc	gg
Np_3X_4	–	–	bcc	hh	bcc	hh
Np_2X_3	orthorhombic (α)	m	cubic (γ)	ii	orthorhombic (η)	uu
	orthorhombic (β)	m	–	–	bcc (γ)	uu
	bcc (γ)	m	–	–	–	–
Np_3X_5	orthorhombic	m	orthorhombic	ii	–	–
NpX_2	orthorhombic	n	–	–	tetragonal	uu
Np_2X_5	orthorhombic	m	orthorhombic	jj	–	–

NpX_3	monoclinic	m	monoclinic	ii	orthorhombic	uu
PuX	fcc	b, h	fcc	h	fcc	u
Pu_2X_3	orthorhombic (α)	o	orthorhombic (η)	o	orthorhombic (η)	vv
	orthorhombic (β)	o	bcc (γ)	o	bcc (γ)	vv
	bcc (γ)	o	–	–	–	–
PuX_2	tetragonal	o	tetragonal	o	tetragonal	vv
PuX_3	–	–	–	–	orthorhombic	vv
AmX	fcc	p	fcc	gg	fcc	gg
Am_3X_4	–	–	bcc	kk	bcc	ww
Am_2X_3	orthorhombic (α)	p	bcc (γ)	w	orthorhombic (η)	ww
	tetragonal (β)	q	–	–	bcc (γ)	ww
	bcc (γ)	b	–	–	–	–
AmX_2	tetragonal	r	tetragonal	r	tetragonal	xx
AmX_3	–	–	–	–	orthorhombic	xx
CmX	fcc	s, t	fcc	s	fcc	s, t
Cm_2X_3	orthorhombic (α)	u	bcc (γ)	v	orthorhombic (η)	yy
	tetragonal (β)	u	–	–	bcc (γ)	t
	bcc (γ)	v	–	–	–	–
CmX_2	tetragonal	v	tetragonal	v	tetragonal	yy
CmX_3	–	–	–	–	orthorhombic	yy
Bk_2X_3	bcc (γ)	w	bcc (γ)	w	orthorhombic (ξ)	w
BkX_2	tetragonal	w	tetragonal	w	tetragonal	w
BkX_3	–	–	–	–	orthorhombic	w
Cf_2X_3	bcc (γ)	w	bcc (γ)	w	–	–
CfX_2	tetragonal	w	tetragonal	w	tetragonal	w

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[a] Fried *et al.* (1950); [b] Zachariasen (1949e); [c] Zachariasen (1949f); [d] Graham and McTaggart (1960); [e] Noël and Potel (1982); [f] Hery (1979); [g] Picon and Flahaut (1958); [h] Kruger and Moser (1967); [i] Potel *et al.* (1972); [j] Suski *et al.* (1972); [k] Kohlmann and Beck (1997); [l] Noël (1980); [m] Marcon (1969); [n] Thévenin *et al.* (1984); [o] Marcon and Pascard (1966); [p] Damien (1971); [q] Damien *et al.* (1972); [r] Damien and Jové (1971); [s] Damien *et al.* (1979a); [t] Damien *et al.* (1979b); [u] Damien *et al.* (1976a); [v] Damien *et al.* (1975); [w] Damien *et al.* (1986); [x] D'Eye *et al.* (1952); [y] D'Eye (1953); [z] Kohlmann and Beck (1999); [aa] Noël (1985); [bb] Khodadad (1959); [cc] Moseley *et al.* (1972); [dd] Breeze and Brett (1972); [ee] Noël and Le Marouille (1984); [ff] Noël *et al.* (1996); [gg] Damien and Wojakowski (1975); [hh] Mitchell and Lam (1970b); [ii] Damien *et al.* (1973); [jj] Thévenin *et al.* (1982); [kk] Roddy (1974); [ll] D'Eye and Sellman (1954); [mm] Tougait *et al.* (1998a); [nn] Ferro (1954); [oo] Matson *et al.* (1963); [pp] Tougait *et al.* (1998b); [qq] Tougait *et al.* (1998c); [rr] Stöwe (1997); [ss] Stöwe (1996); [tt] Noël and Levet (1989); [uu] Damien (1974); [vv] Damien (1973); [ww] Damien and Charvillat (1972); [xx] Damien (1972); [yy] Damien *et al.* (1976b).

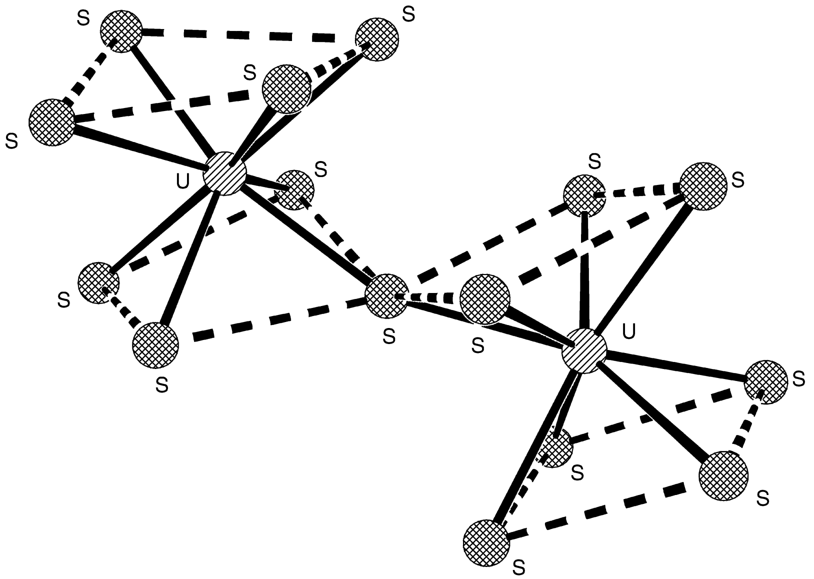

Fig. 22.5 *The two crystallographically independent uranium centers in the crystal structure of α-US_2. Dashed lines are used to delineate square antiprisms* (*Noël and Le Marouille,* 1984).

and the reverse structure, anti-Th_3P_4, adopted by pnictides such as Pu_4Sb_3 and Am_4Sb_3, which are different from hexagonal U_4Sb_3. The dichalcogenides are characterized by a variety of sub-stoichiometric phases that can either crystallize in different forms (i.e., tetragonal $PuS_{1.9}$ vs monoclinic PuS_2) or retain their structures (i.e., transuranium ditellurides). Fig. 22.5 shows the crystal structure of the α-form of the dichalcogenide, US_2. Finally, the sesquichalcogenides (An_2X_3) can take on up to five polymorphic forms, including α (orthorhombic), β (orthorhombic), γ (body-centered cubic), η (orthorhombic), and ξ (orthorhombic). Interestingly, berkelium is the first transuranic element to exhibit the ξ-type modification and an identical $\eta \rightarrow \xi$ transition occurs in the lanthanides at terbium, the homolog of berkelium (Damien *et al.*, 1979b). The existence of the β-modification in the actinides, although widely reported, may in fact be an oxychalcogenide (Damien *et al.*, 1986).

22.3.6 Halides and oxyhalides

The halides are the most widely examined of the actinide compounds from the point of view of structural determination. A review by Taylor (1976) noted that over 70 binary actinide halides, 60 actinide oxyhalides, and 70 binary transition metal fluorides were known as of 1976. Despite the large number of compounds, their structural study is simplified by the isostructural nature of the series due to common structural types. Thus, powder diffraction data are often sufficient for obtaining adequate structural information about these compounds.

The bonding in actinide halides is largely ionic in nature. In general, the structures of these compounds may be approximated as consisting of positive actinide cations surrounded by negative anions. The shape of the anionic polyhedron around the actinide cation is controlled by many factors, including significant size effects. For a given oxidation state of the metal, coordination number usually decreases in the order $F > Cl > Br > I$ due to increasing size of the anion. In addition, coordination number for a given ligand (i.e., F) typically increases as the oxidation state of the metal decreases due to size effects as in UF_6 (CN = 6) and UF_3 (CN = 11). This variability in size results in a large number of potential polyhedral types, significantly more diverse than those observed in transition metal halides. Further comprehensive structural reviews on actinide and lanthanide halides (Brown, 1968) as well as actinide fluorides (Penneman *et al.*, 1973) are available elsewhere. Important structural types and tables of known structures will be described herein.

In addition to size effects based on ligand type and metal oxidation state, clear trends are often also observed due to the actinide contraction. As one moves from left to right across the actinide series, the cation becomes smaller, resulting in an increasing occurrence of actinide halide polyhedra of lower coordination number. When polymorphism is observed for a given element, the high-temperature polymorph is typically the one of lower coordination number due to the generation of a more open lattice structure. Polymorphism is more common in the lower oxidation states due to larger size of the cation and enhanced ionic bonding (Taylor, 1976).

Dihalides are known for only a few of the actinides due to the instability of the An^{2+} oxidation state. Thorium diiodide was first prepared by the reaction of ThI_4 with Th metal at elevated temperatures and characterized in an X-ray powder pattern by Clark and Corbett (1963). A subsequent single-crystal X-ray diffraction study by Guggenberger and Jacobson (1968) confirmed the prediction by Clark and Corbett that the compound is not a true Th(II) salt, but rather contains Th(IV) with two supernumerary electrons. Thus, ThI_2 should be formulated as $Th^{4+}(I^-)_2(e^-)_2$. The structure contains four two-dimensionally infinite layers that alternate between trigonal prismatic and trigonal antiprismatic layers.

Americium dichloride, dibromide, and diiodide, each of which was prepared by reacting americium metal with the appropriate mercuric halide, have also been indexed using X-ray diffraction. The chloride and bromide belong to orthorhombic and tetragonal crystal systems, respectively (Baybarz, 1973b). The diiodide, AmI_2, has a monoclinic structure (Baybarz *et al.*, 1972b). Some dihalides of californium(II) have also been characterized; $CfBr_2$ (Peterson and Baybarz, 1972) and CfI_2 (Hulet *et al.*, 1976) are tetragonal and hexagonal, respectively.

The actinide trihalides are the most structurally complete series of all the actinide halides and they form a series of compounds showing strong similarities to the lanthanide trihalides. The trifluorides (through curium) exhibit a nine-coordinate LaF_3-type structure; however, berkelium trifluoride is dimorphic with its low-temperature modification being the eight-coordinate YF_3-type (Brown, 1973). The same type of change occurs in californium trifluoride above 600°C (Stevenson and Peterson, 1973). An analogous structural change occurs in the lanthanide trifluorides between promethium and samarium (Thoma and Brunton, 1966). These structural observations have been related to the actinide contraction in a paper by Brown *et al.* (1968a).

The actinide trichlorides follow a similar trend. At californium, there is a structural change as a consequence of the actinide contraction. The earlier actinides possess the nine-coordinate UCl_3 structure type. Californium trichloride is dimorphic and exhibits both a nine-coordinate UCl_3 modification, and an eight-coordinate $PuBr_3$-type modification. The structural change observed in the trichlorides occurs earlier in the tribromides; Ac through α-$NpBr_3$ are nine-coordinate UCl_3 types, while β-$NpBr_3$ through $BkBr_3$ are eight-coordinate $PuBr_3$ types. The triiodides are quite different altogether. The triiodides from protactinium through americium (α-modification) are $PuBr_3$-type structures, while the compounds from americium (β-modification) through californium are six-coordinate BiI_3-type structures (Brown, 1973). The trichlorides, tribromides, and triiodides are also moisture-sensitive materials and easily form hydrated compounds. The trihalides of the actinides are listed in Table 22.10.

The actinide tetrafluorides (Th–Cf) have been the most extensively characterized class of tetrahalides due to their isostructural nature (all are monoclinic); each eight-coordinate actinide is surrounded by a square antiprism of fluorine ligands (Keenan and Asprey, 1969). Structural details of the remaining tetrahalides are far less available (Table 22.11). The tetrachlorides (Th through Np) are also isostructural and have tetragonal crystal lattices. In $ThCl_4$, thorium is eight-coordinate and the ligands are arranged in a dodecahedron around the actinide. Both β-$ThBr_4$ and $PaBr_4$ are isostructural with the tetrachlorides. Few structural details are available for α-$ThBr_4$, UBr_4, and $NpBr_4$ other than them being orthorhombic, monoclinic, and monoclinic, respectively. Of the tetraiodides, structural data are only available for ThI_4 and UI_4. The former has an eight-coordinate distorted square antiprismatic geometry, while the latter is six-coordinate octahedral (Brown, 1973).

The pentahalides are quite uncommon; the only actinide for which all four pentahalides are known is protactinium, and none are known past neptunium (only NpF_5 is known). These compounds are extremely moisture sensitive and the hydrolysis of some is further complicated by disproportionation. PaF_5 and

Table 22.10 *Actinide trihalides (AnX_3) and their crystal symmetries.*

	Flouride		*Chloride*		*Bromide*		*Iodide*	
	Symmetry	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
Ac	hexagonal	a, b	hexagonal	b, g	hexagonal	b, g	–	–
Th	–	–	–	–	–	–	–	–
Pa	–	–	–	–	–	–	orthorhombic	p
U	hexagonal	a	hexagonal	g, h	hexagonal	g	orthorhombic	g, q
Np	hexagonal	a	hexagonal	g	hexagonal (α)	g	orthorhombic	g
	–	–	–	–	orthorhombic (β)	g	–	–
Pu	hexagonal	a	hexagonal	g, i	orthorhombic	g	orthorhombic	g
Am	hexagonal	c	hexagonal	d, g	orthorhombic	d, g	orthorhombic	g, r
	–	–	–	–	–	–	hexagonal	d
Cm	hexagonal	d	hexagonal	d, j	orthorhombic	d, i	hexagonal	d, r
Bk	orthorhombic	e	hexagonal	k	monoclinic	i	hexagonal	n
	trigonal	e	–	–	rhombohedral	i	–	–
	–	–	–	–	orthorhombic	i, n	–	–
Cf	orthorhombic	f	hexagonal	l	monoclinic	i	hexagonal	s
	trigonal	f	orthorhombic	l	rhombohedral	i	–	–
Es	–	–	tetragonal	m	monoclinic	o	–	–
	–	–	hexagonal	m	–	–	–	–

[a] Zachariasen (1949b); [b] Fried *et al.* (1950); [c] Templeton and Dauben (1953); [d] Asprey *et al.* (1965); [e] Peterson and Cunningham (1968a); [f] Stevenson and Peterson (1973); [g] Zachariasen (1948b); [h] Taylor and Wilson (1974a); [i] Burns *et al.* (1975); [j] Peterson and Burns (1973); [k] Peterson and Cunningham (1968b); [l] Burns *et al.* (1973); [m] Fujita *et al.* (1969); [n] Cohen *et al.* (1968); [o] Fellows *et al.* (1975); [p] Scherer *et al.* (1967); [q] Levy *et al.* (1975); [r] Haire *et al.* (1983); [s] Fried *et al.* (1968).

Table 22.11 *Actinide tetrahalides (AnX_4) and their crystal symmetries.*

	Fluoride		*Chloride*		*Bromide*		*Iodide*	
	Symmetry	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
Th	monoclinic	a, b	tetragonal	h	orthorhombic (α)	m	monoclinic	q
	–	–	–	–	tetragonal (β)	m	–	–
Pa	monoclinic	a, b, c	tetragonal	i, j	tetragonal	i, n	–	–
U	monoclinic	a, b, d, e	tetragonal	h, k	monoclinic	o	monoclinic	r
Np	monoclinic	a, b	tetragonal	l	monoclinic	p	–	–
Pu	monoclinic	a, b	–	–	–		–	–
Am	monoclinic	a, b	–	–	–	–	–	–
Cm	monoclinic	a, b, f	–	–	–	–	–	–
Bk	monoclinic	a, b, g	–	–	–	–	–	–
Cf	monoclinic	a, e	–	–	–	–	–	–

[a] Asprey and Haire (1973); [b] Keenan and Asprey (1969); [c] Stein (1964); [d] Kunitomi *et al.* (1964); [e] Haug and Baybarz (1975); [f] Asprey *et al.* (1957); [g] Haug and Baybarz (1975); [h] Mooney (1949); [i] Brown and Jones (1967); [j] Brown *et al.* (1973); [k] Taylor and Wilson (1973a); [l] Spirlet *et al.* (1994); [m] Scaife (1966); [n] Brown and Jones (1966); [o] Taylor and Wilson (1974b); [p] Brown *et al.* (1970); [q] Zalkin *et al.* (1964); [r] Levy *et al.* (1980).

β-UF_5 are isostructural (Brown, 1973), while the powder data from NpF_5 appears to be similar to that of α-UF_5 (Malm *et al.*, 1993); each has tetragonal crystal symmetry. PaF_5 and β-UF_5 are both seven-coordinate with pentagonal bipyramidal geometry. The structure of α-UF_5, however, is six-coordinate and octahedral. $PaCl_5$ is also seven-coordinate with infinite chains of edge-fused pentagonal bipyramids (Fig. 22.6). Of the remaining pentahalides, α-$PaBr_5$ and UBr_5 are isostructural, β-$PaBr_5$ and α-UCl_5 (cubic close-packed) both form edge-sharing dimers, β-UCl_5 dimers are based on hexagonal close-packing of anions, and PaI_5 is believed to be structurally similar to TaI_5 (Brown *et al.* 1976; Müller, 1979). The pentahalides are listed in Table 22.12.

Some intermediate compounds of the stoichiometries An_2X_9 and An_4X_{17} have also been discovered, including Pa_2F_9, U_2F_9, U_4F_{17}, and Pu_4F_{17}. The former two compounds are isostructural with bcc symmetry. In the nine-coordinate U_2F_9, it is believed that its black color results from resonance between oxidation states four and five. The latter two compounds are structurally uncharacterized (Brown, 1973).

Structural information for only four actinide hexahalides is available (Table 22.13). The hexafluorides of U, Np, and Pu are volatile solids obtained

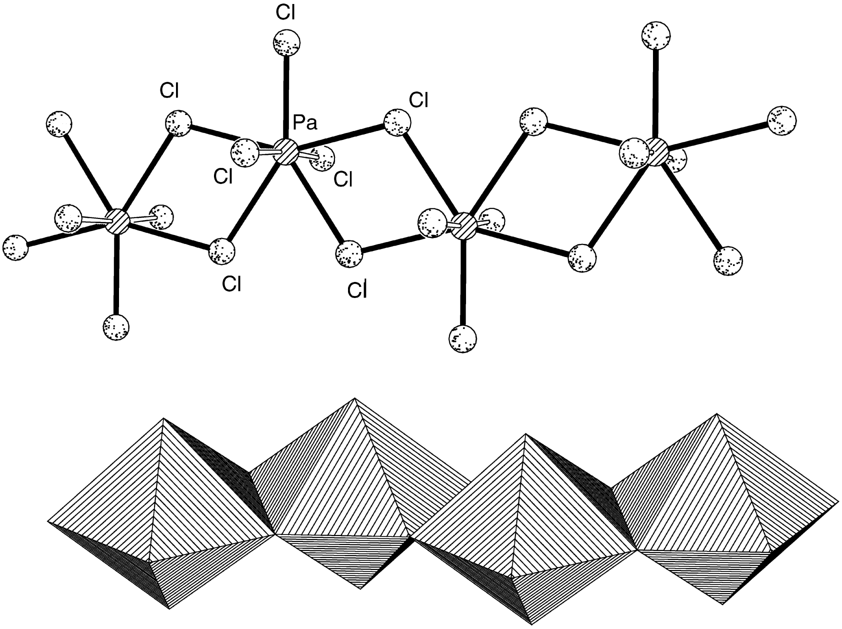

Fig. 22.6 *Crystal structure of $PaCl_5$ (top) with an illustration of the infinite chains of edge-sharing pentagonal bipyramids (bottom) (Dodge* et al., 1967).

Table 22.12 *Actinide pentahalides (AnX_5) and their crystal symmetries.*

	Fluoride		*Chloride*		*Bromide*		*Iodide*	
	Symmetry	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
Pa	tetragonal	a	monoclinic	h	monoclinic (α)	k	orthorhombic	o
	–	–	–	–	monoclinic (β)	k, l	–	–
	–	–	–	–	triclinic (γ)	k	–	–
U	tetragonal (α)	b, c, d	monoclinic (α)	i	triclinic	n	–	–
	tetragonal (β)	d, e	triclinic (β)	j	–	–	–	–
Np	tetragonal	f, g	–	–	–	–	–	–

[a] Stein (1964); [b] Zachariasen (1948b); [c] Eller *et al.* (1979); [d] Zachariasen (1949g); [e] Ryan *et al.* (1976); [f] Malm *et al.* (1993); [g] Baluka *et al.* (1980); [h] Dodge *et al.* (1967); [i] Smith *et al.* (1967); [j] Mueller and Kolitsch (1974); [k] Brown *et al.* (1969); [l] Brown *et al.* (1968b); [m] Brown (1979); [n] Levy *et al.* (1978); [o] Brown *et al.* (1976).

Table 22.13 *Actinide hexahalides* (*AnX_6*) *and their crystal symmetries.*

	Fluoride		*Chloride*	
	Symmetry	*References*	*Symmerty*	*References*
U	orthorhombic	[a, b]	hexagonal	[e, f, g]
Np	orthorhombic	[c]	–	–
Pu	orthorhombic	[d]	–	–

[a] Levy *et al.* (1976); [b] Hoard and Stroupe (1958); [c] Malm *et al.* (1958); [d] Florin *et al.* (1956); [e] Zachariasen (1948b); [f] Zachariasen (1948c); [g] Taylor and Wilson (1974c).

from AnF_4 fluorination, and UCl_6 is obtained from the reaction of $AlCl_3$ with UF_6. AmF_6 has been claimed as the result of oxidation of AmF_3 by KrF_2 in anhydrous HF at 40–60°C, although no structural data is available (Drobyshevskii *et al.*, 1980). All are powerful oxidizing agents and extremely sensitive to moisture; contact with water results in the formation of AnO_2X_2 and HX compounds. The hexafluoride of uranium is important in gaseous diffusion processes for the enrichment of uranium. The hexafluorides are isostructural compounds that form discrete octahedra, although in the case of UF_6, neutron diffraction data suggests that there are significant deviations from the ideal parameters of Hoard and Stroupe due to strong U–U repulsions (Taylor *et al.*, 1973). The hexachloride of uranium (the only other actinide hexahalide) contains a hexagonal crystal lattice with perfect octahedral geometry around uranium. It is isostructural with β-WCl_6 (Taylor, 1976).

Actinide oxyhalides of the type An(vi)O_2X_2, An(v)O_2X, An(iv)OX_2, and An(iii)OX are known although less thoroughly characterized than the halides themselves. In general, the higher oxidation state compounds are favored by the early actinides, while the lower oxidation states are favored by the later actinides. The trivalent actinide oxyfluorides are limited to AcOF, ThOF, PuOF, and CfOF. With the exception of PuOF, these oxyhalides have CaF_2 fluorite-type structures with the oxygen and fluorine atoms randomly distributed in the anion sites. The PuOF lattice is a tetragonal modification of the fluorite structure, probably stabilized by excess fluoride (Brown, 1973).

The remaining trivalent actinide oxychlorides, oxybromides, and oxyiodides (where structural data are available) are strictly of the tetragonal PbFCl structure type, thus making their characterization rather straightforward. In this arrangement, the metal atom has four oxygen neighbors and five halide neighbors. It is rather remarkable that compounds formed from both large and small cations ranging in size from Ac^{3+} to Es^{3+} and anions from Cl^- to I^- can all adopt this structure type. The known compounds are listed in Table 22.14.

Tetravalent actinide oxyhalides are very limited in number; none are known beyond neptunium (Table 22.15). With the exception of $ThOF_2$, all adopt the $PaOCl_2$ structure type. This rather unusual structure consists of infinite

Table 22.14 *Trivalent actinide oxyhalides (AnOX) and their crystal symmetries.*

	Fluoride		*Chloride*		*Bromide*		*Iodide*	
	Symmetry	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
Ac	fcc	a	tetragonal	a	tetragonal	a	–	–
Th	fcc	b	–	–	–	–	–	–
Pa	–	–	–	–	–	–	–	–
U	–	–	tetragonal	e	tetragonal	e	tetragonal	e
Np	–	–	tetragonal	f	tetragonal	f	tetragonal	f
Pu	tetragonal	a,p	tetragonal	a	tetragonal	a	tetragonal	a
Am	–	–	tetragonal	g	tetragonal	l	tetragonal	o
Cm	fcc	c	tetragonal	h	tetragonal	c	–	–
Bk	–	–	tetragonal	i	tetragonal	m	tetragonal	m
Cf	fcc	d	tetragonal	j	tetragonal	n	tetragonal	n
Es	–	–	tetragonal	k	–	–	–	–

[a] Zachariasen (1949b); [b] Rannou and Lucas (1969); [c] Weigel and Kohl (1985); [d] Peterson and Burns (1968); [e] Levet and Noël (1981); [f] Brown and Edwards (1972); [g] Templeton and Dauben (1953); [h] Peterson (1972); [i] Peterson and Cunningham (1967b); [j] Copeland and Cunningham (1969); [k] Fujita *et al.* (1969); [l] Weigel *et al.* (1979); [m] Cohen *et al.* (1968); [n] Fried *et al.* (1968); [o] Haire *et al.* (1983); [p] Zachariasen (1951).

polymeric chains along the *c*-direction with cross-linking in the *ab* plane. The protactinium environments are diverse and can be either seven-, eight-, or nine-coordinate with three- or four-coordinate oxygen atoms. The LaF_3 structure type of $ThOF_2$ is orthorhombic but is largely structurally uncharacterized (Taylor, 1976).

The pentavalent actinide oxyhalides can be of An(v)OX_3, An(v)O_2X, or An(v)$_2OX_8$ composition. In general, structural data are few, if available at all (Table 22.16). The most thoroughly characterized of these oxyhalides are the isostructural $PaOBr_3$ and $UOBr_3$ systems. The structure of the former compound is composed of endless double chains (with random terminations) with pentagonal bipyramidal polyhedra around the Pa atoms. Four out of every five pentagonal edges of the polyhedra are shared (Brown *et al.*, 1975).

Hexavalent actinide oxyhalides are typically of the form An(vi)O_2X_2 (actinyl) or An(vi)OX_4. The actinyl fluorides, UO_2F_2, NpO_2F_2, PuO_2F_2, and AmO_2F_2, are isostructural and have the rhombohedral UO_2F_2 structure type. Here, the linear uranyl cation is surrounded equatorially by six fluorides, generating a coordination number of 8 for uranium. The U–O bond distance of 1.74(2) Å is common for the uranyl cation. Neutron diffraction of UO_2Cl_2 reveals a linear uranyl cation surrounded equatorially by five atoms, four of which are chlorides and the fifth is an oxygen atom from a neighboring uranyl group. Uranyl bromide, UO_2Br_2, is also known structurally, but the last in the series, UO_2I_2, is as of yet unknown. Known compounds are listed in Table 22.17 (Taylor, 1976).

Actinide halo-complexes containing alkali, ammonium, or other cations will not be discussed here. The reader is referred elsewhere for comprehensive reviews of structural characterizations (Brown, 1973).

22.3.6 Carbonates, nitrates, phosphates, arsenates, and sulfates

In general, a limited number of anhydrous binary compounds of actinides and these ligands are reported in the literature. This is due to the greater stability of the hydrated compounds and higher order complexes. In most examples, the common structural feature is that the anions all provide oxygen atoms that surround the actinide cation. Coordination numbers for the metal atom in these compounds can be as high as eight to 12 for tetravalent thorium, but typically decrease across the series to between six and nine due to the actinide contraction. A coordination number of six is observed in a few uranyl structures. The high coordination numbers are predominantly due to the ability of these ligands to act in both monodentate and bidentate (symmetric and asymmetric) coordination modes. Bidentate coordination is most common because of the small 'bite' distance ($O \cdots O$ distance) of the ligand.

Table 22.15 *Tetravalent actinide oxyhalides ($AnOX_2$) and their crystal symmetries.*

	Fluoride		*Chloride*		*Bromide*		*Iodide*	
	Symmetry	*References*	*Symmetry*	*References*	*Symmetry*	*References*	*Symmetry*	*References*
Th	orthorhombic	a	orthorhombic	b	–	–	orthorhombic	g
Pa	–	–	orthorhombic	b, c, d	orthorhombic	c	orthorhombic	c
U	–	–	orthorhombic	b, e, f	orthorhombic	f	orthorhombic	f
Np	–	–	orthorhombic	b	–	–	–	–

[a] D'Eye (1958); [b] Bagnall *et al*. (1968a); [c] Brown and Jones (1967); [d] Dodge *et al*. (1968); [e] Taylor and Wilson (1974d); [f] Levet and Noël (1979); [g] Scaife *et al*. (1965).

Table 22.16 *Pentavalent actinide oxyhalides and their crystal symmetries.*

Fluoride			*Bromide*			*Iodide*		
Compound	*Symmetry*	*References*	*Compound*	*Symmetry*	*References*	*Compound*	*Symmetry*	*References*
PaO_2F	orthorhombic	a	$PaOBr_3$	monoclinic	e	PaO_2I	hexagonal	h
Pa_2OF_8	bcc	b	–	–	–	–	–	–
Pa_3O_7F	orthorhombic	a	–	–	–	–	–	–
UO_2F	monoclinic	c	UO_2Br	orthorhombic	f	–	–	–
–	–	–	$UOBr_3$	monoclinic	g	–	–	–
NpO_2F	tetragonal	d	–	–	–	–	–	–
$NpOF_3$	rhombohedral	d	–	–	–	–	–	–

[a] Brown and Easey (1970); [b] Stein (1964); [c] Kemmler-Sack (1969); [d] Bagnall *et al.* (1968b); [e] Brown *et al.* (1975); [f] Levet *et al.* (1977); [g] Brown (1973); [h] Brown *et al.* (1967).

Table 22.17 *Hexavalent actinide oxyhalides and their crystal symmetries.*

Fluoride			*Chloride*		
Compound	*Symmetry*	*References*	*Compound*	*Symmetry*	*References*
UO_2F_2	rhombohedral	[a, b]	UO_2Cl_2	orthorhombic	[l, m]
UOF_4 (α)	trigonal	[c, d]	–	–	–
UOF_4 (β)	tetragonal	[e]	–	–	–
NpO_2F_2	rhombohedral	[a, f]	–	–	–
$NpOF_4$	trigonal	[g]	–	–	–
PuO_2F_2	rhombohedral	[h, i]	–	–	–
$PuOF_4$	trigonal	[j]	–	–	–
AmO_2F_2	rhombohedral	[k]	–	–	–

[a] Zachariasen (1949b); [b] Atoji and McDermott (1970); [c] Paine *et al.* (1975); [d] Levy *et al.* (1977); [e] Taylor and Wilson (1974e); [f] Bagnall *et al.* (1968b); [g] Peacock and Edelstein (1976); [h] Florin *et al.* (1956); [i] Alenchikova *et al.* (1958); [j] Burns and O'Donnell (1977); [k] Keenan (1968); [l] Debets (1968); [m] Taylor and Wilson (1973b).

(a) Carbonates

Structures of actinide carbonates number very few in the literature and mostly contain the actinyl cation, thus restricting ligand bonding to the equatorial region. Carbonates typically bond in a bidentate fashion, but instances of monodentate bridging carbonate are also known. Actinide carbonates are sometimes geologically occurring minerals such as rutherfordine. Rutherfordine is the naturally occurring form of the mineral UO_2CO_3 and its structure has been investigated both as the natural mineral (Christ *et al.*, 1955) and a synthetic compound (Cromer and Harper, 1955). The crystal structure of the natural mineral has reccently been refined (Finch *et al.*, 1999). In both cases, UO_2CO_3 crystallizes as an orthorhombic lattice and there are six oxygen atoms bound in the equatorial plane. Two carbonate groups act in a symmetrical bidentate fashion, while the remaining two oxygens are from monodentate carbonate groups, resulting in hexagonal bipyramidal geometry. Other instances of uranyl carbonate compounds are listed in Table 22.18. While the hexagonal bipyramidal geometry is common in several uranyl carbonates, slight differences in the U=O actinyl bond length are still observed; for example, 1.67(9), 1.79(1), and 1.80(1) Å distances are observed in UO_2CO_3, $(NH_4)_4UO_2(CO_3)_3$ (Graziani *et al.*, 1972), and $Tl_4UO_2(CO_3)_3$ (Mereiter, 1986b), respectively.

Simple carbonates of the transuranium actinyls (AnO_2^{2+}) are known for both neptunium and plutonium. NpO_2CO_3 (Thévenin *et al.*, 1986; Kato *et al.*, 1998) and PuO_2CO_3 (Navratil and Bramlet, 1973) are both isostructural with the uranium analog and have orthorhombic lattices. The tetraammonium tricarbonate compounds of neptunyl and plutonyl, $(NH_4)_4NpO_2(CO_3)_3$ and

Table 22.18 *Some actinide carbonates and their crystal symmetries.*

Carbonates	*Symmetry*	*References*
$[C(NH_2)_3]_6[Th(CO_3)_5] \cdot 4H_2O$	monoclinic	Voliotis and Rimsky (1975a)
$Na_6[Th(CO_3)_5] \cdot 12H_2O$	triclinic	Voliotis and Rimsky (1975b)
UO_2CO_3	orthorhombic	Cromer and Harper (1955)
$Sr_2UO_2(CO_3)_3 \cdot 8H_2O$	monoclinic	Mereiter (1986a)
$Na_4UO_2(CO_3)_3$	hexagonal	Císařová *et al.* (2001)
$K_4UO_2(CO_3)_3$	monoclinic	Malcic (1958a)
$Tl_4UO_2(CO_3)_3$	monoclinic	Mereiter (1986b)
$(NH_4)_4UO_2(CO_3)_3$	monoclinic	Graziani *et al.* (1972); Malcic (1958b)
NpO_2CO_3	orthorhombic	Thévenin *et al.* (1986)
$KNpO_2CO_3$	hexagonal	Keenan and Kruse (1964)
$Na_3NpO_2(CO_3)_2 \cdot nH_2O$	monoclinic	Volkov *et al.* (1981)
$Rb_3NpO_2(CO_3)_2 \cdot nH_2O$	orthorhombic	Volkov *et al.* (1981)
$K_4NpO_2(CO_3)_3$	monoclinic	Musikas and Burns (1976)
$(NH_4)_4NpO_2(CO_3)_3$	monoclinic	Marquart *et al.* (1983)
$[Na_6Pu(CO_3)_5]_2 \cdot Na_2CO_3 \cdot 33H_2O$	monoclinic	Clark *et al.* (1998a)
PuO_2CO_3	orthorhombic	Navratil and Bramlet (1973)
$(K,NH_4)PuO_2CO_3$	hexagonal	Ellinger and Zachariasen (1954)
$(NH_4)_4PuO_2(CO_3)_3$	monoclinic	Marquart *et al.* (1983)
$Am_2(CO_3)_3 \cdot 2H_2O$	cubic	Weigel and ter Meer (1967)
$KAmO_2CO_3$	hexagonal	Keenan and Kruse (1964)
$CsAmO_2CO_3$	hexagonal	Keenan (1965)
$RbAmO_2CO_3$	hexagonal	Ellinger and Zachariasen (1954)
$NH_4AmO_2CO_3$	hexagonal	Nigon *et al.* (1954)
$(NH_4,Cs)_4AmO_2(CO_3)_3$	monoclinic	Fedoseev and Perminov (1983)

$(NH_4)_4PuO_2(CO_3)_3$, are also isostructural with the corresponding uranium compound and crystallize in monoclinic crystal systems. Only bidentate coordination of the carbonate ion is observed. Pentavalent actinyl (AnO_2^+) carbonate compounds containing americium have also been studied; the compounds $KNpO_2CO_3$, $KPuO_2CO_3$, and $KAmO_2CO_3$ (Ellinger and Zachariasen, 1954; Keenan and Kruse, 1964) are isostructural with hexagonal symmetry.

Tetravalent thorium and plutonium carbonate compounds include $Na_6Th(CO_3)_5 \cdot 12H_2O$ (Voliotis and Rimsky, 1975b) and $Na_6[Pu(CO_3)_5]_2 \cdot Na_2CO_3 \cdot 33H_2O$ (Clark *et al.*, 1998a); the crystal structure of the latter is shown in Fig. 22.7. In both structures, the actinides are ten coordinate and all the carbonate groups are bidentate. The geometry of each has been described as a modified hexagonal bipyramid; two *trans* carbonate ligands occupy axial positions analogous to the *trans* oxo ligands in an actinyl ion, while the remaining carbonates occupy the equatorial sites, thus forming the hexagon. An example of a trivalent actinide carbonate can be seen in the structure of $Am_2(CO_3)_3 \cdot 2H_2O$ (Weigel and ter Meer, 1967).

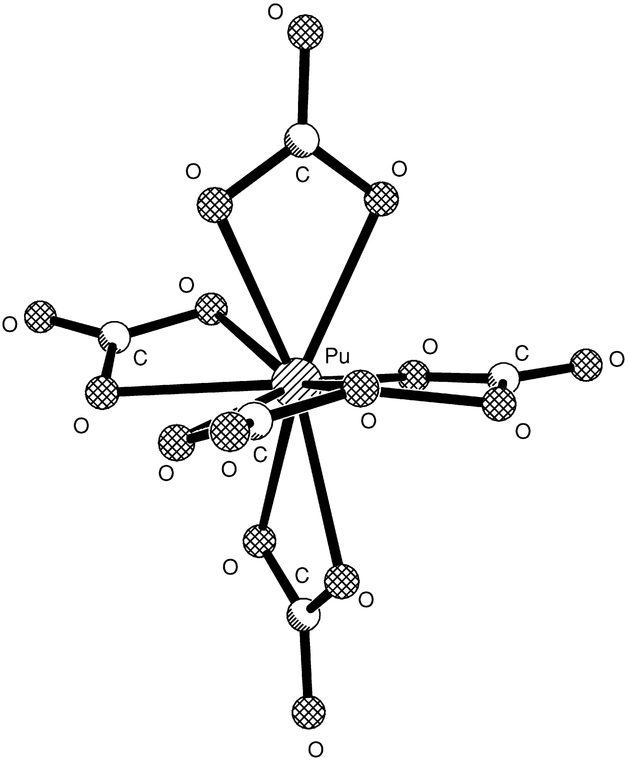

Fig. 22.7 *Coordination geometry of* $[Pu(CO_3)_5]^{6-}$ *anion (showing axial and equatorial carbonate ligands) in the crystal structure of* $[Na_6Pu(CO_3)_5]_2 \cdot Na_2CO_3 \cdot 33H_2O$ *(Clark* et al., 1998*a*).

(b) Nitrates

Structures of simple actinide nitrates containing only actinide/actinyl cations and nitrate anions are unknown. All known structures are hydrated, contain additional non-actinide monovalent or divalent cations, or contain various donor ligands. Actinide nitrate compounds are limited mainly to Th(VI) and uranyl cations, although a few neptunium and plutonium structures exist. In the tetravalent thorium and plutonium compounds, the nitrate anions are typically bidentate, thus allowing for extraordinarily high coordination numbers ranging from eight to as high as 12. In actinyl compounds, the *trans* oxo ligands enforce equatorial nitrate coordination, thus causing both bidentate as well as monodentate coordination in the case of four equatorial nitrate ligands. Hexagonal bipyramidal geometry is common in this case. Examples of actinide nitrate compounds are available from the previous edition of this work or Brown (1973).

Thorium(IV) nitrate pentahydrate has been investigated using both X-ray and neutron diffraction (Taylor *et al.*, 1966; Ueki *et al.*, 1966). The structure as determined by neutron diffraction is shown in Fig. 22.8. Four bidentate nitrate groups and three of the five water molecules are coordinated to the metal center, resulting in a coordination number of 11. Water–water and water–nitrate hydrogen bonds are significant in terms of stabilizing the overall structure, with the latter being slightly longer than the former by about 0.2 Å. The plutonium analog, $Pu(CO_3)_4 \cdot 5H_2O$, is isostructural with the thorium compound, both of which have orthorhombic symmetry (Staritzky, 1956).

The dihydrate (Dalley *et al.*, 1971), trihydrate (Hughes and Burns, 2003), and hexahydrate (Hall *et al.*, 1965) of uranyl nitrate each exhibit eight-coordinate uranium centers of hexagonal bipyramidal geometry. In each compound, both nitrates are bidentate and two waters are coordinated through oxygen. Once again, extensive hydrogen bonding is present between hydrogen atoms of water molecules and unbound oxygen atoms of the nitrate groups (Hall *et al.*, 1965; Dalley *et al.*, 1971). The U=O bond lengths are shorter in the dihydrate (1.754(4) and 1.763(5) Å) than in the hexahydrate (1.85 and 1.87 Å), presumably due to the greater effects of hydrogen bonding in the latter.

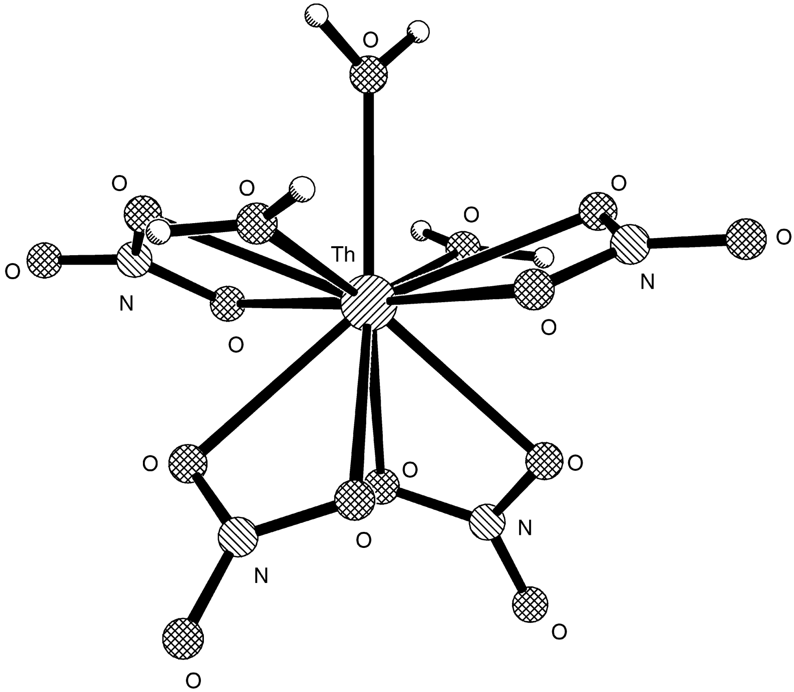

Fig. 22.8 *Coordination environment of thorium in the neutron diffraction crystal structure of* $Th(NO_3)_4 \cdot 5H_2O$ (*Taylor* et al., 1966).

Neptunyl nitrate hexahydrate, $NpO_2(NO_3)_2 \cdot 6H_2O$, has orthorhombic symmetry and appears to be isostructural with the uranium analog. X-ray powder data are also available for the compounds $NpO_2NO_3 \cdot H_2O$ and $Np(NO_3)_4 \cdot N_2O_5$, but structural details are inconclusive (Laidler, 1966).

The series of tetravalent thorium nitrates having the formula M(II)Th$(NO_3)_6 \cdot 8H_2O$ [M(II) = Mg, Mn, Co, Ni, Zn] are isomorphically related. Further studies of the Mg compound have shown that the coordination is best described by the formula $[Mg(H_2O)_6] \cdot [Th(NO_3)_6] \cdot 2H_2O$. All the nitrates bond in a bidentate fashion, leading to a coordination number of 12 for thorium (Šćavničar and Prodić, 1965). In some cases, anhydrous nitrate compounds can be obtained such as $RbUO_2(NO_3)_3$. All the nitrate groups are bidentate to the metal, thus resulting in hexagonal bipyramidal geometry around the uranium atom (Barclay *et al.*, 1965). Also included in the anhydrous uranyl compounds are $KUO_2(NO_3)_3$ (Krivovichev and Burns, 2004) and $CsUO_2(NO_3)_3$ (Zivadinovic, 1967), as well as the tetranitrate $Rb_2[UO_2(NO_3)_4]$ (Irish *et al.*, 1985).

(c) Phosphates and arsenates

Phosphate and arsenate compounds containing the following actinides have been the subject of a series of extensive articles: uranium(VI) (Weigel and Hoffmann, 1976a), neptunium(VI) (Weigel and Hoffmann, 1976b), ammonium–americyl(VI)–phosphate (Weigel and Hoffmann, 1976c), plutonium(VI) (Fischer *et al.*, 1981), americium(VI) (Lawaldt *et al.*, 1982), thorium(IV), uranium(IV), and neptunium(IV) (Bamberger *et al.*, 1984a), and plutonium(III) and plutonium(IV) (Bamberger *et al.*, 1984b). Representative examples of actinide phosphates will be presented herein (Table 22.19).

The structural chemistry of actinide phosphates and arsenates is important on a number of levels. Uranyl phosphates and arsenates in particular are found geologically in large numbers as naturally occurring minerals, which include autenite, tobernite, metazeunerite, and uranocircite. Additionally, the long-term stability of the rare-earth phosphate mineral monazite has led to studies involving the immobilization of actinides in synthetic monazites for long-term storage. Phosphate chemistry is also critically important for understanding the behavior of actinides in the environment as well as in separations schemes.

Actinide phosphate compounds typically contain the orthophosphate (PO_4^{3-}), metaphosphate (PO_3^-), or pyrophosphate ($P_2O_7^{4-}$) anions; arsenate structures are typically limited to the former type. The tetrahedral PO_4^{3-}ion lends itself to both monodentate and bidentate metal bonding, as illustrated in Fig. 22.9. The pyrophosphate anion contains two tetrahedral centers, each of which can be monodentate or bidentate. The various types of phosphate coordination modes in the solid state are exemplified in the structure of $Th_4(PO_4)_4P_2O_7$. Each heavy thorium atom is bound to eight oxygen atoms from five PO_4^{3-} groups and one $P_2O_7^{4-}$ group. One of the former groups is bidentate and the remaining four are monodentate; the pyrophosphate

Table 22.19 *Some actinide phosphates, by type, and their crystal symmetries.*

Phosphate	*Symmetry*	*References*
orthophosphates (*including double phosphates*)		
$AcPO_4 \cdot 0.5H_2O$	hexagonal	Fried *et al.* (1950)
$Th_3(PO_4)_4$	monoclinic	Shankar and Khubchandani (1957)
$U(UO_2)(PO_4)_2$	triclinic	Bénard *et al.* (1994)
$U_3(PO_4)_4$	monoclinic	Burdese and Borlera (1963)
$(U_2O)(PO_4)_2$	orthorhombic	Albering and Jeitschko (1995)
$(UO_2)_3(PO_4)_2(H_2O)_4$	orthorhombic	Locock and Burns (2002)
$PuPO_4$	monoclinic	Bjorklund (1957)
$PuPO_4 \cdot 0.5H_2O$	hexagonal	Bjorklund (1957)
$Pu(PO_4)_3$	orthorhombic	Bamberger *et al.* (1984b)
$AmPO_4$	monoclinic	Keller and Walter (1965)
$AmPO_4 \cdot 0.5\ H_2O$	hexagonal	Keller and Walter (1965)
$CmPO_4$	monoclinic	Weigel and Haug (1965)
$(Li,Na,K,Rb,Cs)Th_2(PO_4)_3$	monoclinic	Matković *et al.* (1968a)
$KTh_2(PO_4)_3$	monoclinic	Matković *et al.* (1968b)
$NaTh_2(PO_4)_3$	monoclinic	Matković and Šljukić (1965)
$Na_2Th(PO_4)_2$	monoclinic	Galešić *et al.* (1984)
$(Ca,Sr,Cd,Ba,Pb)_{0.5}Th_2(PO_4)_3$	monoclinic	Guesdon *et al.* (1999)
$CuTh_2(PO_4)_3$	monoclinic	Louër *et al.* (1995)
$TlTh_2(PO_4)_3$	monoclinic	Laugt (1973)
$PbTh(PO_4)_3$	monoclinic	Quarton *et al.* (1984)
$Pb_3Th_6(PO_4)_{10}$	monoclinic	Quarton *et al.* (1984)
$Pb_7Th(PO_4)_6$	cubic	Quarton *et al.* (1984)
$(H,Li,Na)UO_2PO_4 \cdot 4H_2O$	tetragonal	Weigel and Hoffmann (1976a)
$H_{11}(UO_2)_2(PO_4)_5$	monoclinic	Staritzky and Cromer (1956)
$(Li,Na)U_2(PO_4)_3$	monoclinic	Matković *et al.* (1968a)
$(Na,K,NH_4)UO_2PO_4 \cdot 3H_2O$	tetragonal	Weigel and Hoffmann (1976a)
$(Mg,Ca,Sr,Ba)(UO_2PO_4)_2 \cdot nH_2O$ ($n = 2$–6.5, 8–12)	tetragonal	Weigel and Hoffmann (1976a)
α-$KU_2(PO_4)_3$	monoclinic	Guesdon *et al.* (1999)
β-$(K,Rb)U_2(PO_4)_3$	rhombohedral	Volkov *et al.* (2003)
α-$CaU(PO_4)_2$	orthorhombic	Dusausoy *et al.* (1996)
β-$CaU(PO_4)_2$	monoclinic	La Ginestra *et al.* (1965)
$Ca(UO_2PO_4)_2 \cdot nH_2O$ ($n = 0$–2)	orthorhombic	Weigel and Hoffmann (1976a)
$Cu_2UO_2(PO_4)_2$	monoclinic	Guesdon *et al.* (2002)
$(H,Li)NpO_2PO_4 \cdot 4H_2O$	tetragonal	Weigel and Hoffmann (1976b)
α-$NaNp_2(PO_4)_3$	monoclinic	Nectoux and Tabuteau (1981)
β-$(Na,K,Rb)Np_2(PO_4)_3$	rhombohedral	Volkov *et al.* (2003)
$(Na,K,NH_4)NpO_2PO_4 \cdot 3H_2O$	tetragonal	Weigel and Hoffmann (1976b)
$Mg(NpO_2PO_4)_2 \cdot 9H_2O$	tetragonal	Weigel and Hoffmann (1976b)
$(Ca,Sr,Ba)(NpO_2PO_4)_2 \cdot 6H_2O$	tetragonal	Weigel and Hoffmann (1976b)
$(H,K,NH_4)PuO_2PO_4 \cdot nH_2O$	tetragonal	Fischer *et al.* (1981)
α-$NaPu_2(PO_4)_3$	monoclinic	Burnaeva *et al.* (1992)
β-$(Na,K,Rb)Pu_2(PO_4)_3$	rhombohedral	Burnaeva *et al.* (1992); Volkov *et al.* (2003)
$(K,Rb,Cs,NH_4,)AmO_2PO_4 \cdot nH_2O$	tetragonal	Lawaldt *et al.* (1982)
$NH_4AmO_2PO_4 \cdot 3H_2O$	tetragonal	Weigel and Hoffmann (1976c)

Table 22.19 (*Contd.*)

Phosphate	*Symmetry*	*References*
metaphosphates		
$Th(PO_3)_4$	orthorhombic	Douglass (1962)
$Pa(PO_3)_4$	orthorhombic	Le Cloarec and Cazaussus (1978)
α-$U(PO_3)_4$	monoclinic	Baskin (1967)
β-$U(PO_3)_4$	orthorhombic	Douglass (1962)
α-$Np(PO_3)_4$	tetragonal	Nectoux and Tabuteau (1981)
β-$Np(PO_3)_4$	triclinic	Nectoux and Tabuteau (1981)
γ-$Np(PO_3)_4$	orthorhombic	Nectoux and Tabuteau (1981)
$Pu(PO_3)_4$	orthorhombic	Douglass (1962)
pyrophosphates		
α-ThP_2O_7	cubic	Bamberger *et al.* (1984a); Burdese and Borlera (1963)
β-ThP_2O_7	orthorhombic	Bamberger *et al.* (1984a); Burdese and Borlera (1963)
PaP_2O_7	cubic	Le Cloarec and Cazaussus (1978)
$(PaO)_4(P_2O_7)_3$	monoclinic	Le Cloarec *et al.* (1976)
α-UP_2O_7	cubic	Kirchner *et al.* (1963)
β-UP_2O_7	orthorhombic	Douglass and Staritzky (1956)
NpP_2O_7	cubic	Keller and Walter (1965)
PuP_2O_7	cubic	Bjorklund (1957)
other		
$Th_4(PO_4)_4P_2O_7$	orthorhombic	Bénard *et al.* (1996)
$KThU(PO_4)_3$	monoclinic	Guesdon *et al.* (1999)
$Pa_2O_5 \cdot P_2O_5$	orthorhombic	Le Cloarec *et al.* (1976)
$UXPO_4 \cdot 2H_2O$ (X = Cl, Br)	tetragonal	Bénard-Rocherullé *et al.* (1997)
$U_2(PO_4)(P_3O_{10})$	orthorhombic	Podor *et al.* (2003)
$[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$	tetragonal	Burns *et al.* (2004)
$U(HPO_4)_2 \cdot 4H_2O$	N/A	Voinova (1998)

group donates two oxygen atoms, one from each tetrahedral center (Bénard *et al.*, 1996).

Actinide pyrophosphates can adopt two different structural modifications: the orthorhombic β-form and the cubic α-form. Structural details of the former type are scarce, but the latter modification is known for structures including the actinides Th, Pa, U, Np, and Pu. These pyrophosphates are all isostructural and lattice parameters decrease with increasing atomic number. Six oxygen atoms are coordinated to the metal center in each instance (Le Cloarec and Cazaussus, 1978). The β-UP_2O_7 modification has orthorhombic symmetry (Douglass and Staritzky, 1956). Simple metaphosphates of tetravalent Th, Pa, U, and Pu of the composition $An(PO_3)_4$ are all isostructural and have orthorhombic symmetry

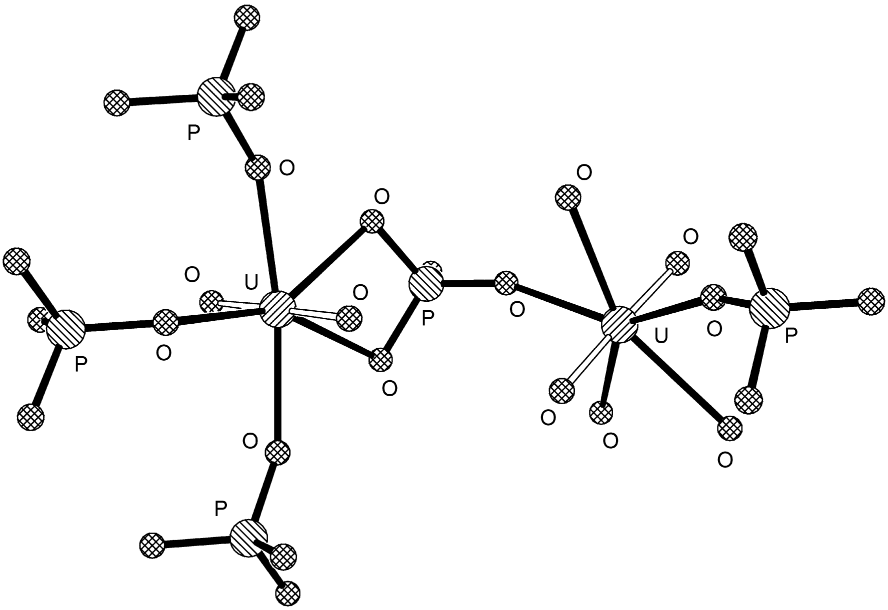

Fig. 22.9 *The two crystallographically independent uranyl centers in the crystal structure of* $(UO_2)_3(PO_4)_2(H_2O)_4$. *Hydrogen atoms have been omitted from the three water molecules bound to the uranium on the right* (*Locock and Burns,* 2002).

(Douglass, 1962; Le Cloarec and Cazaussus, 1978). Structural details for the simple arsenates of $AmAsO_4$ and $PuAsO_4$ (monoclinic symmetry) are available elsewhere (Keller and Walter, 1965).

(d) Sulfates

Actinide sulfates enjoy a unique place in the history of nuclear chemistry; it was A. H. Becquerel who, in 1896, discovered radioactivity in the uranyl double sulfate $K_2UO_2(SO_4)_2 \cdot 2H_2O$. He simply noticed that in the absence of sunlight (actually, in the total darkness of laboratory drawer), the salt will darken a photographic plate and so must spontaneously emit its own type of radiation (Becquerel, 1896).

Additionally, sulfates have traditionally played an important role in the mining of uranium ores. Uranium is leached from crushed ores using sulfuric acid, resulting in soluble ionic species such as $UO_2(SO_4)_3^{4-}$. Despite its prevalence in actinide chemistry, structural characterizations of actinide sulfates are relatively few (Table 22.20).

Actinide sulfate compounds are usually found in hydrated form where as few as one to as many as ten water molecules are present in the structural formula.

Table 22.20 *Some actinide sulfates and their crystal symmetries.*

Sulfate	*Symmetry*	*References*
$Th(SO_4)_2$	hexagonal	Mudher *et al.* (1999)
$Th(SO_4)_2 \cdot 8H_2O$	monoclinic	Habash and Smith (1983)
$Th(OH)_2SO_4$	orthorhombic	Lundgren (1950)
$(NH_4)_2Th(SO_4)_3$	monoclinic	Mudher *et al.* (1999)
$K_4Th(SO_4)_4 \cdot 2H_2O$	triclinic	Arutyunyan *et al.* (1966a)
$H_3PaO(SO_4)_3$	hexagonal	Bagnall *et al.* (1965)
$U(OH)_2SO_4$	orthorhombic	Lundgren (1952)
$U_6O_4(OH)_4(SO_4)_6$	tetragonal	Lundgren (1953)
α-UO_2SO_4	monoclinic	Kovba *et al.* (1965)
β-UO_2SO_4	monoclinic	Brandenburg and Loopstra (1978)
$Cs_2(UO_2)_2(SO_4)_3$	tetragonal	Ross and Evans (1960)
$K_2UO_2(SO_4)F_2 \cdot 2H_2O$	monoclinic	Alcock *et al.* (1980a)
$(NH_4)_2UO_2SO_4 \cdot 2H_2O$	monoclinic	Niinisto *et al.* (1978)
$(K,Rb)_4U(SO_4)_4 \cdot 2H_2O$	monoclinic	Mudher *et al.* (1988)
$(NH_4, K)_2UO_2(SO_4)_2 \cdot 2H_2O$	monoclinic	Weigel and Hellmann (1986)
$UO_2SO_4 \cdot 2.5H_2O$	monoclinic	Weigel and Hellmann (1986)
$UO_2SO_4 \cdot 3H_2O$	orthorhombic	Traill (1952)
$Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$	monoclinic	Burns and Hayden (2002)
$U(SO_4)_2 \cdot 4H_2O$	orthorhombic	Kierkegaard (1956)
$(NH_4, Rb)U(SO_4)_2 \cdot 4H_2O$	monoclinic	Chadha *et al.* (1980)
$H_2(UO_2)_2(SO_4)_2 \cdot 5H_2O$	orthorhombic	Traill (1952)
$(NH_4)_2(UO_2)_2(SO_4)_3 \cdot 5H_2O$	orthorhombic	Staritzky *et al.* (1956)
$CsU(SO_4)_2 \cdot 5.5H_2O$	orthorhombic	Chadha *et al.* (1980)
α-$2UO_2SO_4 \cdot 7H_2O$	orthorhombic	Zalkin *et al.* (1978b)
β-$2UO_2SO_4 \cdot 7H_2O$	monoclinic	Brandenburg and Loopstra (1973)
$U_2(SO_4)_3 \cdot 8H_2O$	orthorhombic	Chadha *et al.* (1980)
$(Cs, Rb)_2UO_2(SO_4)_2 \cdot 10H_2O$	orthorhombic	Weigel and Hellmann (1986)
$Cs_2NpO_2(SO_4)_2$	monoclinic	Fedosseev *et al.* (1999)
$Cs_2(NpO_2)_2(SO_4)_3$	tetragonal	Fedosseev *et al.* (1999)
$(Cs, Rb)_2NpO_2(SO_4)_2 \cdot nH_2O$ ($n = 0.5, 4, 10$)	orthorhombic	Weigel and Hellmann (1986)
$(NpO_2)_2SO_4 \cdot H_2O$	orthorhombic	Grigor'ev *et al.* (1993a)
$(NpO_2)_2SO_4 \cdot 2H_2O$	monoclinic	Budantseva *et al.* (1988)
$K_2NpO_2(SO_4)_2 \cdot 2H_2O$	monoclinic	Weigel and Hellmann (1986)
$Cs_2Np(SO_4)_3 \cdot 2H_2O$	monoclinic	Charushnikova *et al.* (2000a)
$Cs_3NpO_2(SO_4)_2 \cdot 2H_2O$	triclinic	Grigor'ev *et al.* (1991a)
$(NH_4)_2NpO_2SO_4 \cdot 2H_2O$	monoclinic	Fedosseev *et al.* (1999)
$NpO_2SO_4 \cdot 2.5H_2O$	monoclinic	Weigel and Hellmann (1986)
$Na_{10}Np_2(SO_4)_9 \cdot 4H_2O$	orthorhombic	Charushnikova *et al.* (2000b)
$Pu(SO_4)_2$	hexagonal	Mudher *et al.* (1999)
$(NH_4)_2Pu(SO_4)_3$	monoclinic	Mudher *et al.* (1999)
$NaPu(SO_4)_2 \cdot H_2O$	hexagonal	Iyer and Natarajan (1989)
$(K, Cs)_2PuO_2(SO_4)_2 \cdot 2H_2O$	monoclinic	Weigel and Hellmann (1986)
$(K, Rb)_4Pu(SO_4)_4 \cdot 2H_2O$	monoclinic	Mudher *et al.* (1988); Mudher and Krishnan (2000)
$PuO_2SO_4 \cdot 2.5H_2O$	monoclinic	Weigel and Hellmann (1986)
α-$Pu(SO_4)_2 \cdot 4H_2O$	orthorhombic	Jayadevan *et al.* (1982)
β-$Pu(SO_4)_2 \cdot 4H_2O$	orthorhombic	Jayadevan *et al.* (1982)
$NH_4Pu(SO_4)_2 \cdot 4H_2O$	monoclinic	Iyer and Natarajan (1990)
$Am_2(SO_4)_3 \cdot 8H_2O$	monoclinic	Burns and Baybarz (1972)

Water molecules can be directly bonded to the metal or take on a non-bonding role in the lattice. In the case of thorium(IV) sulfates, the number of water molecules in the lattice is variable by controlling the temperature of crystallization. The octahydrate is crystallized from neutral aqueous solution at 20–25°C, lower hydrates are obtained by drying at 100–110°C, and the anhydrous form is formed at 400°C. In the octahydrate, the coordination sphere around thorium is occupied by four oxygen atoms from two chelating sulfate groups and the oxygen atoms of six water molecules, resulting in bicapped square antiprismatic geometry. These polyhedra are linked by hydrogen bonding (Habash and Smith, 1983).

Protactinium sulfates are rare, probably due to the difficulties in handling this element. One example is $H_3PaO(SO_4)_3$ which has hexagonal symmetry, but decomposes to amorphous $H_3PaO(SO_4)_3$ at 375°C (Bagnall *et al.*, 1965). Uranyl sulfate structures, however, are more common because they constitute a widespread class of minerals. For example, in the cluster compound $Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$, the $[(UO_2)(SO_4)_4]^{6-}$ anion (Fig. 22.10) is composed of a uranyl pentagonal bipyramid that shares an edge with one sulfate tetrahedron and vertices of three tetrahedra (Burns and Hayden, 2002). Polymorphism is displayed in $2UO_2SO_4 \cdot 7H_2O$; the α and β forms are similar, but differ in the

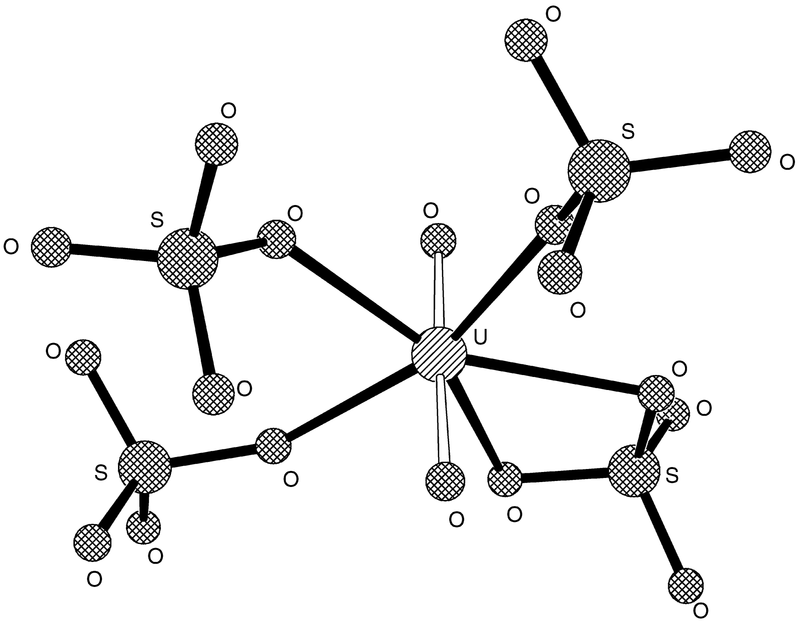

Fig. 22.10 *The uranyl sulfate cluster in the crystal structure of* $Na_{10}[(UO_2)(SO_4)_4](SO_4)_2 \cdot 3H_2O$ *(Burns and Hayden, 2002).*

way in which their chains are repeated and the orientation of their polyhedra (Zalkin *et al.*, 1978b).

Examples of neptunium and plutonium sulfate structures are also available. The compound $(NpO_2)_2SO_4 \cdot H_2O$ is a rare example of cation–cation interactions. Each linear NpO_2^+ unit is coordinated equatorially by three oxygen atoms from three sulfate groups as well as two oxygen atoms from two neighboring neptunyl groups, resulting in pentagonal bipyramidal polyhedra (Grigor'ev *et al.*, 1993a). Higher hydrated forms are also known, depending on the conditions of preparation (Budantseva *et al.*, 1988). The hexavalent actinide compounds of the composition $AnO_2SO_4 \cdot 2.5H_2O$ (An = U, Np, Pu) are isostructural with monoclinic symmetry. Two structural modifications are known for $Pu(SO_4)_2 \cdot 4H_2O$ (α and β), both of which are monoclinic; the latter modification has a lattice constant (*a*-axis) nearly twice as large as the former (Weigel and Hellmann, 1986).

The compound $Am_2(SO_4)_3 \cdot 8H_2O$, a rare americium sulfate, was studied using single-crystal X-ray diffraction. Each trivalent americium atom is coordinated by four oxygen atoms from four sulfate groups and by four water molecules; the resulting polyhedron is intermediate between an antiprism and a dodecahedron. Extensive hydrogen bonding links the polyhedra and the structure is isomorphous with the neodymium analog (Burns and Baybarz, 1972).

22.4 COORDINATION COMPOUNDS

Structural studies of coordination compounds of actinides in the solid state are quite numerous and diverse. Crystallographic information generated from X-ray and neutron diffraction techniques regarding the structural details of such compounds is too extensive to be comprehensively discussed herein. Thus, the following section comprising actinide coordination compounds will focus on two major areas: (1) structures containing carboxylic acid-derived acyclic ligands and (2) structures containing macrocyclic ligands including crown ethers, calixarenes, and porphyrins/phthalocyanines. Organoactinide compounds will be treated separately.

Actinide complexes with acyclic ligands are by no means limited to those involving carboxylic acids; a large number of crystal structures are available for those containing amides, phosphine oxides, and carbonyls, just to name a few. Due to the great diversity in this area, carboxylic acids were chosen owing to their extensive employment as actinide extraction ligands, ion-exchange media, and as agents in other practical applications. Their ability to act in both monodentate and bidentate modes and yield complexes of high coordination number has resulted in a plethora of structural characterizations, which will be illustrated in Section 22.4.1.

Macrocyclic ligands, including crown ethers, calixarenes, and porphyrins/phthalocyanines, have received a lot of attention due to their cyclic arrangement of donor atoms (including oxygen, nitrogen, and sulfur) for coordination to both lanthanide and actinide cations. The ability to vary the ring size of the macrocycle, as well as to alter the identity of the donor atoms (to tune hard/soft properties), has resulted in the generation of a large number of crystal structures that exhibit tremendous diversity, particularly with regard to the role of counter-ions for the generation of inclusion versus exclusion complexes. Examples of structurally characterized actinide/macrocycle complexes will be presented in Section 22.4.2.

Organoactinide structures involving cyclopentadienyl ligands, their derivatives, and related ligands, on account of their distinction from both acyclic and macrocyclic actinide complexes, will be the focus of Section 22.5. In addition, the chemistry of organoactinide complexes, including both synthesis and characterization, is the focus of Chapter 25.

22.4.1 Complexes with carboxylic acids

Carboxylic acids typically form stable coordination complexes with the large actinide ions via monodentate or bidentate donation through the carboxylate oxygen atoms, yielding complexes of high coordination number. Representative carboxylate ligands include monocarboxylate species such as formates, acetates, glycolates, and salicylates, dicarboxylate species such as oxalates and malonates, and pyridine or benzene derivatives containing three or more carboxylate functionalities. Several coordination modes are possible in carboxylic acid complexes with actinides, the major types of which are represented in Fig. 22.11 (for monocarboxylic acids). Carboxylic acid ligands can engage in both monodentate and bidentate coordination modes, as well as provide more than one bonding site per molecule. These features make carboxylic acids highly versatile ligands as evidenced in the high number of structural characterizations that have been made (Tables 22.21–22.23). Structural characteristics of representative examples will be described.

While a large number of carboxylic acid ligands exhibit the potential to chelate actinide cations, crystal structures have been most commonly determined of formates, acetates, oxalates, and malonates. This is due to the small $O \cdots O$ 'bite' distances and the overall relative compactness of the molecules, resulting in easy packing in the crystal lattice. Large or bulky chains attached to the (mono- or di-) carboxylate functionality tend to make crystallization and subsequent structural characterization difficult (Casellato *et al.*, 1978).

Formates are the simplest type of carboxylic acid, where the the R_1 group is a hydrogen atom. Actinide formates are typically prepared in solution using formic acid or a formate salt. Uranium(VI) diformate monohydrate crystallizes in the orthorhombic space group with the uranyl ion coordinated equatorially by five oxygen atoms, resulting in pentagonal bipyramidal geometry around the

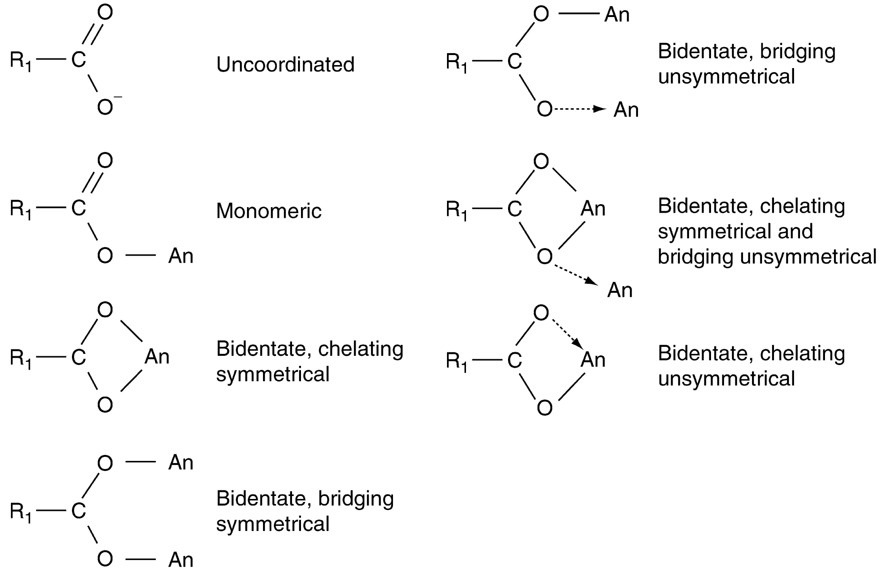

Fig. 22.11 *Summary of possible monocarboxylic acid bonding modes.* R_1 *can be a hydrocarbon radical or a proton* (*Casellato* et al., 1978).

uranium atom. The equatorial coordination is assigned to one oxygen atom from bound water and four oxygen atoms from the formate ligands, with these nodes forming infinite formate–uranium–formate chains, further stabilized by hydrogen bonding through bound water (Mentzen *et al.*, 1977).

The monoclinic $NaUO_2(HCOO)_3 \cdot H_2O$ lattice contains an interesting combination of structural motifs with two distinct types of formate bonding (Fig. 22.12). First, the uranyl motif contains equatorial pentagonal coordination through five formate oxygen atoms. The two uranyl oxygen atoms reside axially, resulting in a pentagonal bipyramid about uranium. The second motif has hexa-coordination around Na^+ using two oxygen atoms from water and four from formate ligands. Each uranium polyhedron is formed from three types of formate ligands. First, one type of formate bridges adjacent uranium centers, resulting in infinite formate–uranium–formate chains. Second, two infinite chains are bridged by a second type of formate, resulting in a uranium polyhedra 'layer'. Third, layers of sodium polyhedra and uranium polyhedra are bridged by a third type of formate ligand, resulting in an ..ABABA.. layering scheme (Claudel *et al.*, 1976, Mentzen, 1977).

Formate complexes with Th(IV) have also have been structurally investigated. For example, $Th(HCOO)_4 \cdot 3H_2O$ contains a central thorium atom with coordination number of ten, formally described as $[Th(HCOO)_4 \cdot 2H_2O]H_2O$. Each thorium is coordinated to eight oxygen atoms of eight separate bridging formate

Table 22.21 *Monocarboxylic acid compounds with actinides, by type.*

Structure	*References*
formate	
$Am(HCOO)_3$	Weigel and ter Meer (1967)
$Th(HCOO)_4$	Chevreton *et al.* (1968)
$An(HCOO)_4$, [$An = Th(IV)$, $Pa(IV)$, $U(IV)$, $Np(IV)$]	Hauck (1976)
$Th(HCOO)_4 \cdot 2/3H_2O$	Chevreton *et al.* (1968)
$Th(HCOO)_4 \cdot 3H_2O$	Chevreton *et al.* (1968); Arutyunyan *et al.* (1966b)
$UO_2(HCOO)(OH) \cdot H_2O$	Le Roux *et al.* (1979)
$UO_2(HCOO)_2 \cdot H_2O$	Mentzen *et al.* (1977)
$NaUO_2(HCOO)_3 \cdot H_2O$	Claudel *et al.* (1976); Mentzen (1977)
$(NH_4)_2UO_2(HCOO)_4$	Mentzen *et al.* (1978a)
$SrUO_2(HCOO)_4 \cdot (1 + x)H_2O$	Mentzen *et al.* (1978b)
$(NH_4)NpO_2(CHOO)_2$	Grigor'ev *et al.* (1994)
acetate	
$Th(CH_3COO)_4$	Eliseev *et al.* (1967)
$(CN_3H_6)_2[Th(CH_3COO)_6]$	Arutyunyan *et al.* (1966c)
$[UO_2(CH_3COO)_2Ph_3PO]_2$	Panattoni *et al.* (1969)
$UO_2(CH_3COO)_2(Ph_3PO)_2$	Graziani *et al.* (1967)
$UO_2(CH_3COO)_2Ph_3PO$	Graziani *et al.* (1967)
$[UO_2(CH_3COO)_2Ph_3AsO]_2$	Bandoli *et al.* (1968)
$UO_2(CH_3COO)_2(Ph_3AsO)_2$	Bandoli *et al.* (1968)
$Na[(UO_2)_2(\mu\text{-}OH)_2(CH_3COO)_2(OH)]$	Avisimova *et al.* (2001)
$UO_2(CH_3COO)_2 \cdot 2H_2O$	Howatson *et al.* (1975)
$NaUO_2(CH_3COO)_3$	Zachariasen and Plettinger (1959); Navaza *et al.* (1991)
$(C_6H_{15}N_4O_2)[UO_2(CH_3COO)_3] \cdot CH_3COOH \cdot H_2O$	Silva *et al.* (1999)
$U(CH_3COO)_4$	Jelenić *et al.* (1964)
$(NpO_2)_2(CH_3COO)_2(H_2O) \cdot C_2H_3N$	Charushnikova *et al.* (1995)
$NaNpO_2(CH_3COO)_3$	Zachariasen (1954)
$BaNpO_2(CH_3COO)_3 \cdot 2H_2O$	Burns and Musikas (1977)
$NaPuO_2(CH_3COO)_3$	Zachariasen (1954)
$NaAmO_2(CH_3COO)_3$	Zachariasen (1954)
propionate	
$MUO_2(CH_3CH_2COO)_3$, ($M = Cs, Rb, Tl, NH_4$)	Burkov *et al.* (1997)
$Ca[UO_2(C_2H_5COO)_3]_2 \cdot 6H_2O$	Benetollo *et al.* (1995)
glycolate	
$UO_2(CH_2OHCOO)_2$	Mentzen and Sautereau (1980)
$U(CH_2OHCOO)_4 \cdot 2H_2O$	Alcock *et al.* (1980b)
$NpO_2(CH_2OHCOO) \cdot H_2O$	Grigor'ev *et al.* (1995)
salicylate	
$[UO_2(NO_3)(C_7H_4O_3)(DMAP)]_2$	Nassimbeni *et al.* (1976)
$[H_3O][UO_2(C_7H_5O_3)_3] \cdot 5H_2O$	Alcock *et al.* (1989)
$Am(C_7H_5O_3)_3 \cdot H_2O$	Burns and Baldwin (1977)

Table 22.21 (*Contd.*)

Structure	*References*
benzoate	
$Na[UO_2(C_6H_5COO)_3]\cdot(C_6H_5COOH)\cdot H_2O$	Benetollo *et al.* (1995)
pyridine-2-carboxylate (*monopicolinate*)	
$[(UO_2)_3(C_5H_4NCOO)_2(NO_3)_2(H_2O)_2]\cdot 2H_2O$	Silverwood *et al.* (1998)
pyridine-3-carboxylate	
$UO_2(C_5H_4NCOO)_2(H_2O)_2$	Alcock *et al.* (1996a)
2,6-dihydroxybenzoate	
$[UO_2(C_6H_3(OH)_2COO)_2(H_2O)_2]\cdot 8H_2O$	Cariati *et al.* (1983)
amino acid	
$UO_2(CO_2CH_2NH_3)_4\cdot(NO_3)_2$ (glycine)	Alcock *et al.* (1985)
UO_2(γ-aminobutanoic acid)$_3(NO_3)_2\cdot$ H2O	Bismondo *et al.* (1985)
anthranilate (*1*), *pyrazinate* (*2*)	
$(H_3O)[UO_2(C_6H_4NH_2COO)_3]H_2O$ (1)	Alcock *et al.* (1996b)
$[UO_2(C_4H_3N_2COO)_2(H_2O)]\cdot 2H_2O$ (2)	Alcock *et al.* (1996b)

ligands, resulting in a distorted Archimedic antiprism. The remaining two coordination sites are occupied by oxygen atoms from two water molecules located in the square faces of the antiprism (Chevreton *et al.*, 1968).

Acetate ligands are carboxylates where R_1 is a methyl group, making them compact for packing in a crystal. The uranyl acetate dihydrate lattice contains a uranyl cation equatorially coordinated to an oxygen from a water molecule, two oxygen atoms from a chelating acetate ligand, and two oxygen atoms from two bridging acetate ligands, resulting in a distorted pentagonal bipyramidal geometry around the uranium center. The bridging acetates link the uranium centers together to form propagating chains, and adjacent chains are associated with one another through a lattice water molecule; this water participates in hydrogen bonding to the bound water of one chain and two acetate ligands of the neighboring chain (Howatson *et al.*, 1975).

Acetate complexes with uranyl incorporating phosphine oxides have also been structurally characterized and are significant with regards to separations processes. Certain types of phosphine oxides exhibit functional extractive abilities for actinides such as uranium and plutonium, making them invaluable for remediating acidic media and waste streams. The compound $UO_2(CH_3COO)_2(Ph_3PO)_2$ and the related arsine oxide analog $UO_2(CH_3COO)_2(Ph_3AsO)_2$ were found to be isomorphous by single-crystal X-ray diffraction (Graziani *et al.*, 1967; Bandoli *et al.*, 1968). The related compounds $[UO_2(CH_3COO)_2(Ph_3PO)]_2$ (Panattoni *et al.*, 1969) and $[UO_2(CH_3COO)_2(Ph_3AsO)]_2$ (Bandoli *et al.*, 1968) have also been isolated. The former structure consists of two seven-coordinate uranium centers. Each uranium has two axial uranyl

Table 22.22 *Dicarboxylic acid compounds with actinides, by type.*

Structure	*References*
oxydiacetate	
$[Th(SO_4)(CO_2CH_2OCH_2CO_2)(H_2O)_2] \cdot H_2O$	Graziani *et al.* (1983)
$Th(CO_2CH_2OCH_2CO_2)_2(H_2O)_4 \cdot 6H_2O$	Benetollo *et al.* (1984)
$Na_2[Th(CO_2CH_2OCH_2CO_2)_3] \cdot 2NaNO_3$	Benetollo *et al.* (1984)
$[UO_2(CO_2CH_2OCH_2CO_2)]_n$	Bombieri *et al.* (1972, 1974a)
$[C_2H_5NH_2(CH_2)_2NH_2C_2H_5][UO_2(CO_2CH_2OCH_2CO_2)_2]$	Jiang *et al.* (2002)
$[(CH_3)_2NH(CH_2)_2NH(CH_3)_2][UO_2(CO_2CH_2OCH_2CO_2)_2]$	Jiang *et al.* (2002)
$(C_6H_{13}N_4)_2[(UO_2)_2(CO_2CH_2OCH_2CO_2)_2(\mu\text{-}OH)_2] \cdot 2H_2O$	Jiang *et al.* (2002)
$Na_2[UO_2(CO_2CH_2OCH_2CO_2)_2] \cdot 2H_2O$	Bombieri *et al.* (1973)
iminodiacetate	
$[UO_2(CO_2CH_2NH_2CH_2CO_2)]_n$	Battiston *et al.* (1979)
$UO_2(CO_2CH_2NH_2CH_2CO_2)_2$	Bombieri *et al.* (1974b)
$(C_4H_{12}N_2)[(UO_2)_2(CO_2CH_2NHCH_2CO_2)_2(\mu\text{-}OH)_2] \cdot 8H_2O$	Jiang *et al.* (2002)
glutarate	
$UO_2(CO_2(CH_2)_3CO_2)Li(CO_2(CH_2)_3COOH) \cdot 4H_2O$	Benetollo *et al.* (1979)
succinate	
$UO_2(CO_2(CH_2)_2CO_2) \cdot DMSO$	Shchelokov *et al.* (1985)
$UO_2(CO_2(CH_2)_2CO_2) \cdot H_2O$	Bombieri *et al.* (1979)
oxalate	
$Ac_2(C_2O_4)_3 \cdot 10H_2O$	Weigel and Hauske (1977)
$K_4Th(C_2O_4)_4 \cdot 4H_2O$	Akhtar and Smith (1969)
$UO_2(C_2O_4) \cdot 3H_2O$	Jayadevan and Chackraburtty (1972)
$Na_3UO_2(C_2O_4)F_3 \cdot 6H_2O$	Dao *et al.* (1984)
$M_3[UO_2(C_2O_4)_2]F \cdot 2H_2O$ (M = Na, Rb, Cs)	Dao *et al.* (1984)
$M_3UO_2(C_2O_4)F_3 \cdot 2H_2O$ (M = K, Rb, Cs)	Dao *et al.* (1984)
$K_2UO_2(C_2O_4)F_2$	Chakravorti *et al.* (1978)
$K_2(UO_2)_2(C_2O_4)F_4$	Chakravorti *et al.* (1978)
$K_4UO_2(C_2O_4)_2F_2$	Chakravorti *et al.* (1978)
$K_3[UO_2(C_2O_4)_2]F \cdot 3H_2O$	Dao *et al.* (1984)
$K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$	Jayadevan *et al.* (1975)
$K_4U(C_2O_4)_4 \cdot 4H_2O$	Favas *et al.* (1983)
$K_6[(UO_2)_2(C_2O_4)_5] \cdot 10H_2O$	Legros and Jeannin (1976)
$Cs_2UO_2(C_2O_4)(SeO_4)$	Mikhailov *et al.* (2000a)
$Cs_4[UO_2(C_2O_4)_2(SO_4)] \cdot 2.7H_2O$	Mikhailov *et al.* (2000b)
$Ba_2[U(C_2O_4)_4(H_2O)] \cdot 7H_2O$	Spirlet *et al.* (1986, 1987a)
$(NH_4)_2[UO_2(C_2O_4)(SeO_4)] \cdot 1.5H_2O$	Mikhailov *et al.* (1996)
$(NH_4)_2[UO_2(O_2)(C_2O_4)(H_2O)] \cdot 2H_2O$	Baskin and Prasad (1964)
$(NH_4)_3[UO_2(NH_2O)(C_2O_4)_2] \cdot H_2O$	Shchelokov *et al.* (1984)
$(NH_4)_3[UO_2(C_2O_4)_2]F \cdot H_2O$	Dao *et al.* (1984)
$(NH_4)_2UO_2(C_2O_4)_2$	Alcock (1973a)
$(NH_4)_4UO_2(C_2O_4)_3$	Alcock (1973b)
$(NH_4)_2(UO_2)_2(C_2O_4)_3$	Alcock (1973c)

Table 22.22 (*Contd.*)

Structure	*References*
$(NH_4)_2(CH_6N_3)_4[(UO_2)_2(C_2O_4)_5] \cdot 2H_2O$	Chumaevskii *et al.* (1998)
$(N_2H_5)_2UO_2(C_2O_4)_2(H_2O)$	Poojary and Patil (1987)
$(N_2H_5)_6[(UO_2)_2(C_2O_4)_5] \cdot 2H_2O$	Govindarajan *et al.* (1986)
$Tl_2UO_2(C_2O_4)_2 \cdot 2H_2O$	Jayadevan *et al.* (1973)
$(NpO_2)_2C_2O_4 \cdot 6H_2O$	Grigor'ev *et al.* (1996)
$NpO_2(C_2O_4) \cdot 3H_2O$	Mefod'eva *et al.* (1981)
$Np(C_2O_4)_2 \cdot 6H_2O$	Grigor'ev *et al.* (1997)
$H_2Np_2(C_2O_4)_3(C_2O_4)_2 \cdot 9H_2O$	Charushnikova *et al.* (1998)
$NaNpO_2(C_2O_4) \cdot 3H_2O$	Tomilin *et al.* (1984)
$K_6(NpO_2)_2(C_2O_4)_5 \cdot nH_2O$ ($n = 2$–4)	Mefod'eva *et al.* (1981)
$Cs_2NpO_2(C_2O_4)_2 \cdot 2H_2O$	Mefod'eva *et al.* (1981)
$Cs_2(NpO_2)_2(C_2O_4)_3$	Mefod'eva *et al.* (1981)
$(NH_4)NpO_2(C_2O_4) \cdot 8/3H_2O$	Grigor'ev *et al.* (1991b)
$[Co(NH_3)_6][NpO_2(C_2O_4)_2] \cdot nH_2O$ ($n = 3, 4$)	Grigor'ev *et al.* (1991c)
$PuO_2(C_2O_4) \cdot 3H_2O$	Mefod'eva *et al.* (1981)
$Pu_2(C_2O_4)_3 \cdot 10H_2O$	Chackraburtty (1963)
$Am_2(C_2O_4)_3 \cdot 10H_2O$	Weigel and ter Meer (1967)
malonate	
$(C_2H_{10}N_2)_2[Th(CO_2CH_2CO_2)_4(H_2O)]$	Zhang *et al.* (2000)
$(C_4H_{12}N_2)_2[Th(CO_2CH_2CO_2)_4] \cdot H_2O$	Zhang *et al.* (2000)
$Li_2UO_2(CO_2CH_2CO_2)_2 \cdot nH_2O$ ($n = 1, 3$)	Herrero *et al.* (1977)
$Na_2UO_2(CO_2CH_2CO_2)_2 \cdot nH_2O$ ($n = 0, 2$)	Herrero *et al.* (1977)
$K_2UO_2(CO_2CH_2CO_2)_2 \cdot H_2O$	Herrero *et al.* (1977)
$(NH_4)_2UO_2(CO_2CH_2CO_2)_2 \cdot H_2O$	Rojas *et al.* (1979)
$[U(CO_2CH_2CO_2)_2(H_2O)_3]_n$	Zhang *et al.* (2000)
$MUO_2(CO_2CH_2CO_2)_2 \cdot 3H_2O$ ($M = Ba, Sr$)	Bombieri *et al.* (1980)
$(NpO_2)_2(CO_2CH_2CO_2) \cdot nH_2O$ ($n = 3, 4$)	Grigor'ev *et al.* (1993b,c)
methylmalonate	
$(C_4H_{12}N_2)_2[Th(CO_2CH(CH_3)CO_2)_4] \cdot 2H_2O$	Zhang *et al.* (2000)
$[\{Co(NH_3)_6\}\{UO_2(CO_2CH(CH_3)CO_2)(CO_2C(CH_3)_2CO_2)\}]_2Cl_2 \cdot 6H_2O$	Zhang *et al.* (2002a)
$(C_4H_{12}N_2)[UO_2(CO_2CH(CH_3)CO_2)_2(H_2O)] \cdot 1.5H_2O$	Zhang *et al.* (2002a)
$(C_4H_{14}N_2)[UO_2(CO_2CH(CH_3)CO_2)_2(H_2O)] \cdot 2H_2O$	Zhang *et al.* (2002a)
dimethylmalonate	
$(C_2H_{10}N_2)_2[Th(CO_2C(CH_3)_2CO_2)_4] \cdot 5H_2O$	Zhang *et al.* (2000)
$(C_{10}H_{26}N_2)[(UO_2)_2(CO_2C(CH_3)_2CO_2)_3]$	Zhang *et al.* (2002b)
$(C_2H_{10}N_2)[UO_2(CO_2C(CH_3)_2CO_2)_2(H_2O)] \cdot H_2O$	Zhang *et al.* (2002b)
$(C_6H_{16}N_2)[(UO_2)_3(CO_2C(CH_3)_2CO_2)_4(H_2O)_2] \cdot 3H_2O$	Zhang *et al.* (2002b)
$(C_7H_{20}N_2)[UO_2(CO_2C(CH_3)_2CO_2)_2] \cdot 3H_2O$	Zhang *et al.* (1998)
$[\{Co(NH_3)_6\}\{UO_2(CO_2C(CH_3)_2CO_2)_2\}Cl]_2 \cdot 7H_2O$	Zhang *et al.* (1998)
diethylmalonate	
$(C_4H_{12}N_2)[UO_2(CO_2C(C_2H_5)_2CO_2)_2(H_2O)] \cdot H_2O$	Zhang *et al.* (2002a)
$(C_{10}H_{26}N_2)[UO_2(CO_2C(C_2H_5)_2CO_2)_2(H_2O)] \cdot 2H_2O$	Zhang *et al.* (2002a)
$(C_{10}H_{26}N_2)[(UO_2)_3(CO_2C(C_2H_5)_2CO_2)_5] \cdot 2H_2O$	Zhang *et al.* (2002a)

Table 22.22 (*Contd.*)

Structure	*References*
pyridine-2,6-dicarboxylate (*dipicolinate*)	
$Th[C_5H_3N(COO)_2]_2(H_2O)_4$	Degetto *et al.* (1978)
$\{UO_2[C_5H_3N(COO)_2]\cdot H_2O\}_n$	Immirzi *et al.* (1975)
$U[C_5H_3N(COO)_2]_2(H_2O)_3\cdot 3.5H_2O$	Haddad *et al.* (1987)
$(Ph_4As)_2UO_2[C_5H_3N(COO)_2]_2\cdot 6H_2O$	Marangoni *et al.* (1974)
$(Ph_4As)_2U[C_5H_3N(COO)_2]_3\cdot 3H_2O$	Baracco *et al.* (1974)
$(UO_2)_3[C_5H_3N(COO)(COOH)]_2$ $[C_5H_3N(COO)_2]_2\cdot 2H_2O$	Cousson *et al.* (1993)
$UO_2(C_7H_3NO_5)\cdot 3H_2O$	Bombieri *et al.* (1977)
$UO_2[C_5H_3N(COO)_2]_2\cdot(C_5H_4NCOOH)\cdot 6H_2O$	Cousson *et al.* (1991)
fumarate (*1*), *maleate* (*2*)	
$UO_2(C_4H_4O_4)(H_2O)_2$ (1)	Bombieri *et al.* (1982)
$[UO_2(C_4H_2O_4)K(C_4H_3O_4)]$ (2)	Bombieri *et al.* (1981)

Table 22.23 *Tetracarboxylic and hexacarboxylic acid compounds with actinides, by type.*

Structure	*References*
1,2,4,5-benzenetetracarboxylate	
$(NH_4)_3[(NpO_2)_5(C_{10}O_8H_2)_2]\cdot 7H_2O$	Cousson (1985)
$[Na_3NpO_2(C_{10}O_8H_2)]_2\cdot 11H_2O$	Nectoux *et al.* (1984)
$UO_2(C_{10}O_8H_4)\cdot 2H_2O$	Cousson *et al.* (1986)
benzene hexacarboxylate	
$Na_4(NpO_2)_2(C_{12}O_{12})\cdot 8H_2O$	Nectoux *et al.* (1984); Cousson *et al.* (1984)

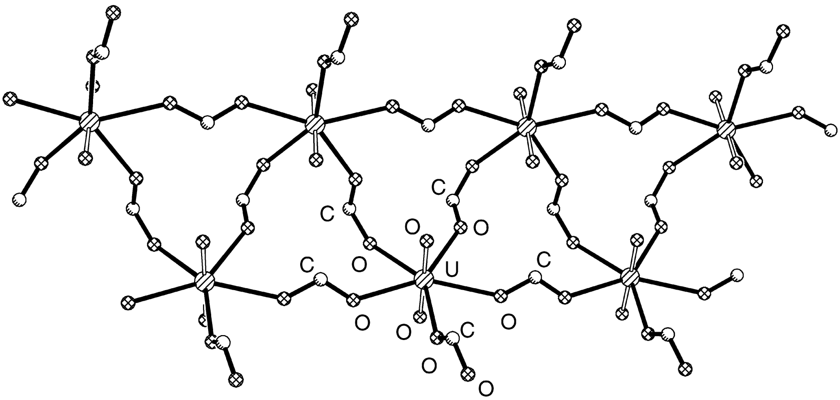

Fig. 22.12 *Crystal structure of anionic portion of* $NaUO_2(HCOO)_3\cdot H_2O$, *with* Na^+, H_2O, *and hydrogen atoms omitted* (*Claudel* et al., 1976). *The coordinates were obtained from the Cambridge Structural Database* (*refcode SURFOR*).

oxygen atoms and pentagonal equatorial coordination provided by a chelating acetate group, two oxygen atoms from bridging acetate groups, and an oxygen atom from a triphenyl phosphine oxide moiety. It is isomorphous with the arsenic-containing analog.

An example of a pentavalent actinide complex is illustrated (Fig. 22.13) in the single-crystal X-ray diffraction structure of $BaNpO_2(CH_3COO)_3 \cdot 2H_2O$. The anion contains a linear NpO_2^+ unit surrounded equitorially by three bidentate acetate groups, resulting in a hexagonal bipyramidal geometry around the neptunium center. The Ba^{2+} cation acts a crosslinker with shared coordination between six acetate oxygen atoms of three different neptunium polyhedra and the oxygen atoms of two lattice water molecules, resulting in a dodecahderal/square antiprism polyhedron. Neptunyl Np–O bond distances are 1.85(2) Å, while Np–$O_{acetate}$ distances range from 2.52(2) to 2.56(2) Å (Burns and Musikas, 1977).

Tetravalent thorium forms an anhydrous complex with four acetate ligands, $Th(CH_3COO)_4$, that is structurally isomorphous (Eliseev *et al.*, 1967) with the uranium(IV) analog (Jelenić *et al.*, 1964). Each thorium center is ten-coordinate;

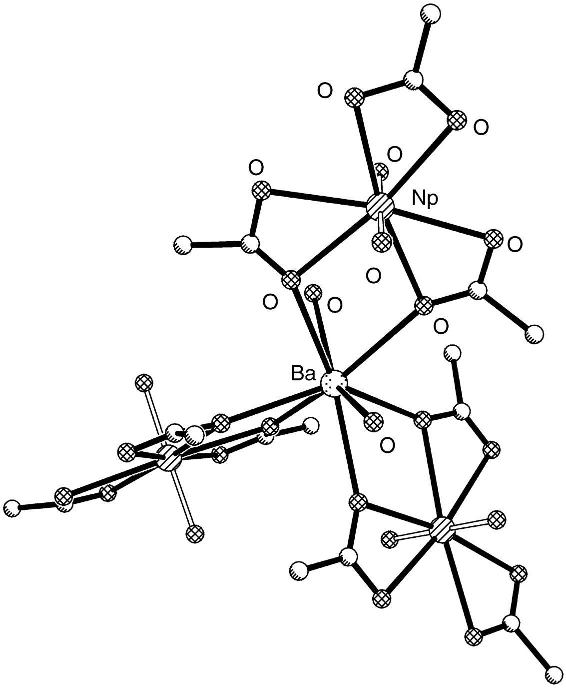

Fig. 22.13 *Crystal strucuture of* $BaNpO_2(CH_3COO)_3 \cdot 2H_2O$ *with hydrogen atoms omitted* (*Burns and Musikas,* 1977). *The coordinates were obtained from the Cambridge Structural Database* (*refcode BNPTAC*) (*Allen,* 2002).

eight oxygen atoms are provided by eight acetate ligands that bridge between adjacent thorium centers and the remaining two coordination sites are occupied by two of these acetate ligands acting in a tridentate manner (i.e., both oxygen atoms close to the metal center).

Dicarboxylate complexes with actinides are well studied, as evidenced by the large number of crystal structures present in the literature (Table 22.22). Crystallographic information for complexes with the simplest dicarboxylate, the oxalate ligand, is abundant, primarily due to its high affinity for actinides, the ability to form both four- and five-membered rings, and its potential to chelate in a tetradentate manner. An example of the tetradentate ability of oxalate is illustrated in $UO_2(C_2O_4) \cdot 3H_2O$. Each oxalate ligand, through its four oxygen donors, bridges two uranyl ions yielding five-membered rings; additional coordination is provided by the oxygen of a water molecule, making each uranium center hepta-coordinate and pentagonal bipyramidal. The remaining two water molecules, while not participants in direct uranium bonding, engage in hydrogen bonding to further stabilize the complex (Jayadevan and Chackraburtty, 1972).

The crystal structure of monoclinic $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$ shows the association of three separate oxalate ligands with a single uranyl cation (Fig. 22.14). Each linear uranyl fragment has six oxygen atoms bound equatorially from three oxalate ligands, forming three five-membered rings, with an average

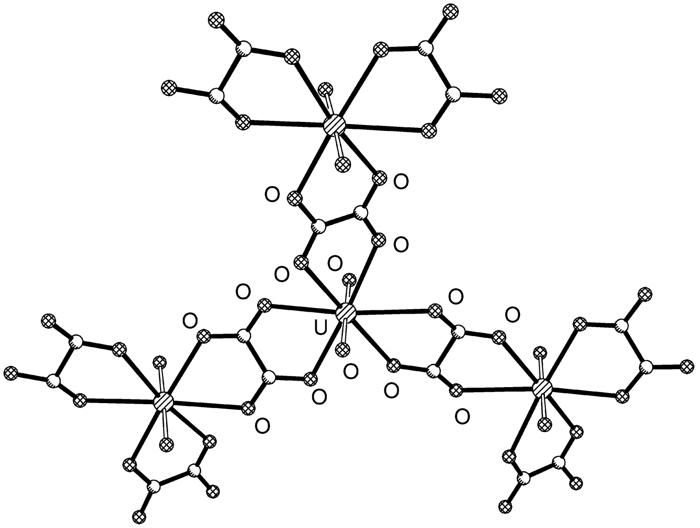

Fig. 22.14 *Crystal strucuture of anionic portion of* $K_2(UO_2)_2(C_2O_4)_3 \cdot 4H_2O$ *with* K^+, H_2O, *and hydrogen atoms omitted* (*Jayadevan* et al., 1975). *The coordinates were obtained from the Cambridge Structural Database* (*refcode KUROXT*).

U–O bond distance of 2.45(4) Å. The geometry around each uranium atom is hexagonal bipyramidal, with the equatorial hexagon being slightly puckered. Each oxalate group takes on a tetradentate role while associated with two uranyl cations, yielding infinite polymeric anions in the crystal lattice; the K^+ cations are associated with eight oxygen atoms from the oxalate ligands and the lattice water molecules within a sphere of about 3.2 Å (Jayadevan *et al.*, 1975).

Bridging oxalate coordination and the absence of uranium-bound water is observed in $K_6[(UO_2)_2(C_2O_4)_5] \cdot 10H_2O$; each uranyl cation in the dinuclear hexavalent anion is five-coordinate equatorially. Two oxalate ligands coordinate in a bidentate manner, forming two five-membered rings, and one oxalate bridges symmetrically, donating one oxygen atom to each uranium center. The pentagonal bipyramidal polyhedron around uranium has an average equatorial U–O bond distance of 2.38 Å (Legros and Jeannin, 1976).

Pyridine-2,6-dicarboxylic acid (pdca) can be multidentate through oxygen only or heteronuclear oxygen/nitrogen donation, and can form monomeric or polymeric metal-templated complexes. A repeating helical pattern is found in the single-crystal X-ray diffraction structure of $[UO_2\{C_5H_3N(COO)_2\} \cdot H_2O]_n$ where pseudo-planar pentagonal equatorial coordination around the linear uranyl ion is provided by two oxygens and one nitrogen from the pdca ligand, oxygen from a water molecule, and oxygen from a neighboring pdca ligand (Fig. 22.15). The bridging provided by the neighboring pdca ligand results in a polymeric structure that takes on a helical shape. In the crystal, all helices are of the same sense and possess a diameter of about 21 Å. Each helix is surrounded

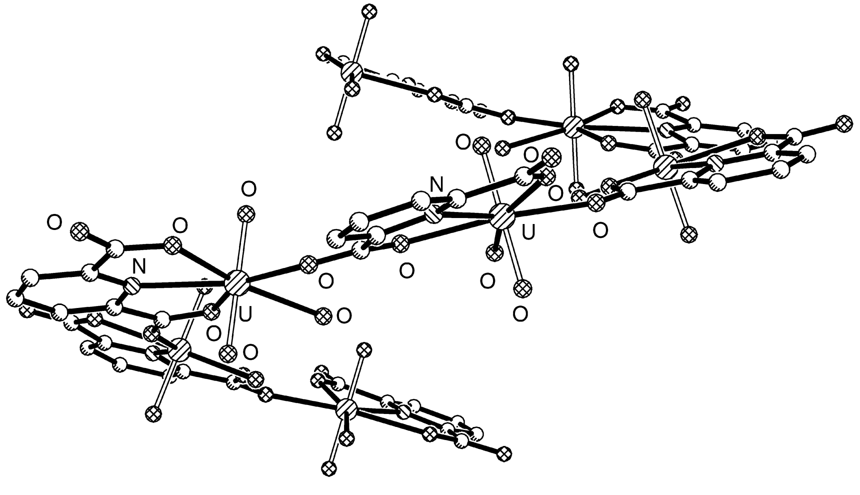

Fig. 22.15 *Crystal strucuture of* $[UO_2\{C_5H_3N(COO)_2\} \cdot H_2O]_n$ *with hydrogen atoms omitted* (*Immirzi* et al., 1975). *The coordinates were obtained from the Cambridge Structural Database* (*refcode PYDCUO*).

by six other helices that are associated with one another via hydrogen bonding between bound water and dangling C–O groups (Immirzi *et al.*, 1975).

Malonate ligands are dicarboxylates, structurally related to oxalates, where the caboxylate functionalities are joined by a methylene group. Several Th(iv) and U(vi) malonato complexes have been structurally characterized, once again taking advantage of the relatively compact nature of the malonate ligand for crystal packing. Malonate ligands have the ability to coordinate with actinides in bidentate, tridentate, and tetradentate modes, examples of which will be shown when available.

The structure of the bispiperazinium complex, $(C_4H_{12}N_2)_2[Th(CO_2CH_2CO_2)_4] \cdot H_2O$, contains an eight-coordinate thorium atom with four 1,5-bidentate malonate ligands, resulting in a monomeric anionic complex (Fig. 22.16). The geometry around the thorium is distorted square antiprismatic, with the Th–O bond distances ranging from 2.337(2) to 2.450(2) Å. The lattice water molecule is uncoordinated. The compounds $(C_2H_{10}N_2)_2[Th(CO_2CH_2CO_2)_4(H_2O)]$, $(C_4H_{12}N_2)_2[Th(CO_2CH(CH_3)CO_2)_4] \cdot 2H_2O$, and $(C_2H_{10}N_2)_2[Th(CO_2C(CH_3)_2\ CO_2)_4] \cdot 5H_2O$ have similar coordination around the thorium center with the exception that the former compound has a bound water, giving

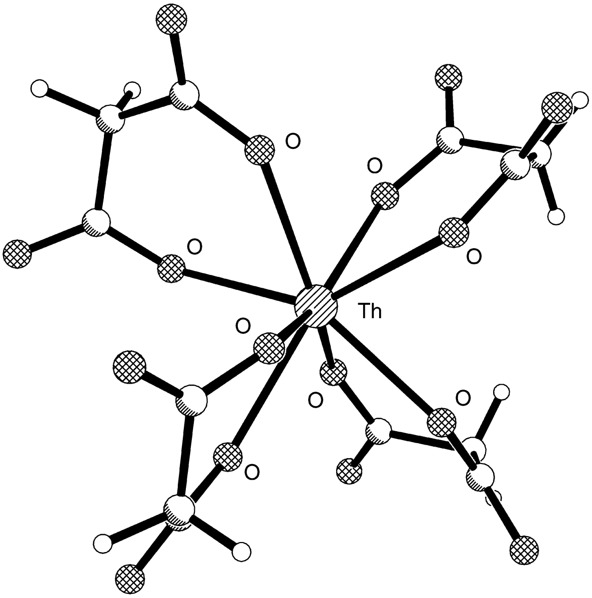

Fig. 22.16 *Crystal strucuture of anioic portion of* $(C_4H_{12}N_2)_2[Th(CO_2CH_2CO_2)_4] \cdot H_2O$ *with* $(C_4H_{12}N_2)^{2+}$*and* H_2O *omitted* (*Zhang* et al., 2000). *The coordinates were obtained from the Cambridge Structural Database* (*refcode WONKUF*).

the thorium a coordination number of nine and a mono-capped distorted square antiprismatic geometry. The latter two structures contain methylmalonate and dimethylmalonate ligands, respectively (Zhang *et al.*, 2000).

The structure of $[U(CO_2CH_2CO_2)_2(H_2O)_3]_n$, however, contains uranium with a coordination number of nine in a mono-capped square antiprismatic geometry. The coordination sphere is achieved through two 1,5-bidentate malonate ligands, each also bridging to an adjacent uranium through a carbonyl oxygen (thus the malonate ligands are tridentate) and oxygen atoms from three water molecules. The bridging character of the malonate ligands results in the formation of infinite chains. Chelating U–O bond distances are 2.315(4) and 2.434(4) Å, while the bridging U–O distance is 2.420(4) Å (Zhang *et al.*, 2000).

Two other types of malonate binding have also been observed using single-crystal X-ray diffraction. The structure of $(C_6H_{16}N_2)[(UO_2)_3(CO_2C(CH_3)_2CO_2)_4(H_2O)_2]\cdot 3H_2O$ (involving dimethylmalonate), has two distinct uranium sites. The first site shows hexagonal bipyramidal geometry around a single uranium center from two axial uranyl oxygen atoms, two *trans* equatorial water molecules, and two equatorial 1,3-bidentate malonate ligands. The second site shows two crystallographically equivalent uranium atoms, each also with hexagonal bipyramidal geometry. This geometry results from two axial uranyl oxygen atoms, a 1,3-bidenate malonate ligand that bridges the uranium atom at the first site, and two malonate ligands in a μ_2-1,3- and 1,5-bidentate arrangement. The malonate that bridges the two uranium sites is coordinated in a bis(1,3-bidentate) manner, making the ligand tetradenate and the overall structure infinite (Zhang *et al.*, 2002b).

Higher order carboxylate ligands (tetracarboxylate and hexacarboxylate) are shown in Table 22.23, the details of which will not be discussed here.

22.4.2 Complexes with macrocyclic ligands

(a) Crown ethers

Traditional crown ethers are cyclic polyether molecules that interact with the actinide cations in one of two fashions: either through an inner-sphere coordination mode, resulting in direct metal ion inclusion into the crown ether cavity, or through an outer-sphere coordination mode involving hydrogen bonds with the uranyl cation where the metal–crown interaction results in sandwich or polymeric structures. Crown ether derivatives where oxygen has been replaced with nitrogen (azacrowns) or sulfur (thiacrowns) have also been studied, thus taking advantage of the softer character of these elements. The complexation characteristics of crown ethers depend on a variety of factors, including size of cavity (size-fitting effect), nature of the heteroatoms present, as well as the type of counter ions, all of which are critical in obtaining inclusion versus exclusion complexes.

For inclusion complexes, the diameter of the crown ether molecule, and thus the ability for an actinide cation to fit within the cavity, increases from 12-crown-4, to 15-crown-5, to 18-crown-6. Crown ethers are neutral molecules; crystal structures showing metal ion complexation that results in inclusion usually have one or more poorly coordinating anions present to balance the charge on the cation. The formation of crown ether inclusion complexes, as indicated by the few structures available in the literature, takes careful matching of solvent and counter-ions to suitable macrocyclic cavity sizes (Bradshaw *et al.*, 1996). Representative structures of actinide inclusion complexes are shown in Table 22.24.

In UO_2(18-crown-6)$(CF_3SO_3)_2$, an inclusion complex between UO_2^{2+} and 18-crown-6, the trifluoromethanesulfonate anion is not directly bound to the complex, but rather effectively balances the overall charge (Deshayes *et al.*, 1994a). The linear uranyl fragment is perpendicular with respect to the crown plane and the six crown ether oxygen atoms coordinate the uranium atom equatorially, resulting in an overall hexagonal bipyramidal geometry. The average equatorial U–O bond distance is 2.50(5) Å. In the related structure (Fig. 22.17), UO_2(dicyclohexyl-18-crown-6)$(CF_3SO_3)_2$, uranyl insertion into dicyclohexano-18-crown-6 results in a similar 1:1 UO_2:crown inclusion complex where the geometry about the uranium atom is a hexagonal bipyramid (Deshayes *et al.*, 1994a). Here, the average equatorial U–O bond distance is slightly longer at 2.58(7) Å, indicating that the dicyclohexane rings of the crown ether result in a less flexible coordination environment.

The uranyl cation in the related inclusion complex UO_2(18-azacrown-6) $(CF_3SO_3)_2$ is bonded to all six nitrogen atoms of the crown in a hexagonal bipyramidal manner. The six nitrogen atoms in the azacrown ring are in a puckered plane with the uranium atom lying 0.066(1) Å out of this plane. The average U–N bond distance is 2.66(6) Å, indicating the relative weakness of

Table 22.24 *Inclusion compounds of actinides and crown ethers.*

Structure	*References*
UO_2(18-crown-6)$(CF_3SO_3)_2$	Deshayes *et al.* (1994a)
UO_2(18-crown-6)$(ClO_4)_2$	Dejean *et al.* (1987); Folcher *et al.* (1979)
$[UCl_3$(18-crown-6)$]_2[UO_2Cl_3(OH)(H_2O)] \cdot MeNO_2$	Bombieri *et al.* (1978a)
$U(BH_4)_3$(18-crown-6)$_{3/4}$	Moody *et al.* (1979)
UO_2(dicyclohexyl-18-crown-6)$(CF_3SO_3)_2$	Deshayes *et al.* (1994a)
UO_2(dicyclohexyl-18-crown-6)$(ClO_4)_2$	Navaza *et al.* (1984)
$[U(BH_4)_2$(dicyclohexyl-18-crown-6)$]_2[UCl_5(BH_4)]$	Dejean *et al.* (1987)
$[UCl_3$(dicyclohexyl-18-crown-6)$]_2[UCl_6]$	de Villardi *et al.* (1978)
UO_2(18-azacrown-6)$(CF_3SO_3)_2$	Nierlich *et al.* (1994)
UO_2(diaza-18-crown-6)(CF_3SO_3)	Thuéry *et al.* (1995a)
$[NpO_2$(18-crown-6)$](ClO_4)$	Clark *et al.* (1998b)

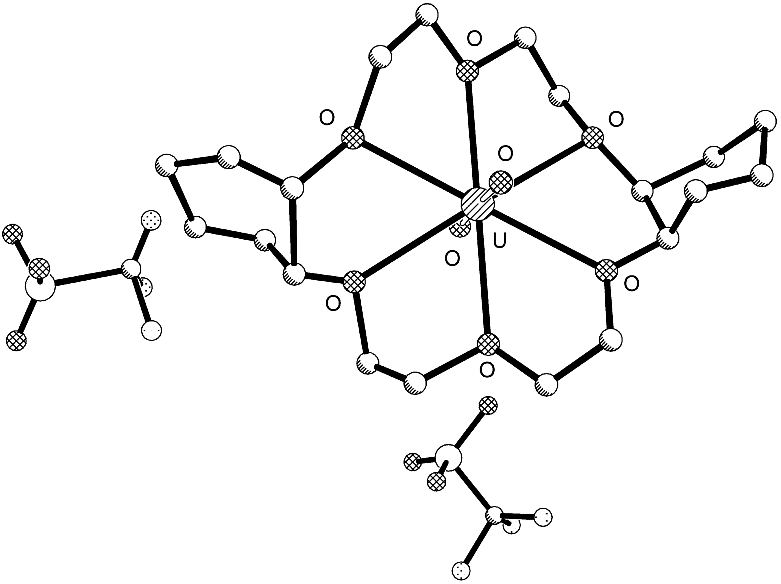

Fig. 22.17 *Crystal strucuture of* UO_2*(dicyclohexyl-*18*-crown-*6*)(*CF_3SO_3*)*$_2$ *with hydrogen atoms omitted (Deshayes* et al., 1994*a). The coordinates were obtained from the Cambridge Structural Database (refcode WIFTUA).*

the U–N bond compared to the U–O bond in the above complexes (Nierlich *et al.*, 1994).

The compound [U(BH_4)$_2$dicyclohexyl-18-crown-6]$_2$[UCl_5(BH_4)] contains U(III) macrocyclic coordination along with the coexistence of U(IV) in the same crystal. In the cationic portion, the U(III)(BH_4)$_2^+$ moiety resides in the crown ether cavity and the two BH_4 groups assume axial positions (B–U–B = 173(5)°). All six equatorial oxygen atoms participate in bonding, resulting in hexagonal bipyramidal geometry around uranium. The anion, $(UCl_5BH_4)^{2-}$ contains uranium in the 4+ oxidation state in a pseudo-octahedral environment (Dejean *et al.*, 1987). Other crown ether inclusion complexes of uranium include U(BH_4)$_3$(18-crown-6)$_{3/4}$, for which only marginal crystallographic data exist due to crystal disorder, making further structural characterization necessary (Moody *et al.*, 1979).

A rare example of a transuranium inclusion compound is [NpO_2(18-crown-6)](ClO_4). The NpO_2^+ cation resides within the crown ether cavity and the Np center is equatorially coordinated by the six coplanar oxygen atoms at an average distance of 2.594(10) Å, yielding a hexagonal bipyramidal coordination polyhedron (Fig. 22.18). The average Np–O distances of the *trans* oxo ligands are 1.800(5) Å, unusually short for the NpO_2^+ cation (Clark *et al.*, 1998b).

Despite the potential to favorably match crown ether cavities containing five and six donors to the UO_2^{2+} ion that prefers such equatorial coordination

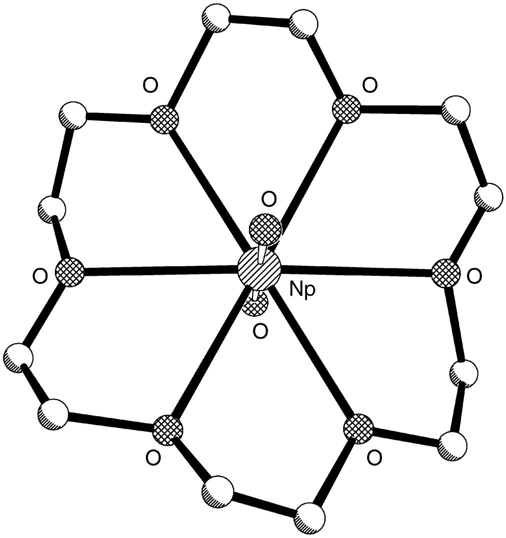

Fig. 22.18 *Crystal strucuture of* [*Np*O_2(18-*crown*-6)](*Cl*O_4) *with Cl*O_4^- *and hydrogen atoms omitted* (*Clark* et al., 1998*b*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode NICFUA*).

environments, the majority of actinide structures in the literature exhibit second sphere/outer sphere exclusion motifs (Thuéry *et al.*, 1995d). The result is the formation of 'supermolecules' usually involving complex hydrogen-bonded networks. Hydrogen bonding between the crown ether oxygen atoms and water molecules coordinated to the metal is commonly observed (but not always) (Rogers *et al.*, 1988). Table 22.25 summarizes representative second sphere/outer sphere actinide-crown ether exclusion complexes.

An interesting example of mistaken identity was observed in the case of $UO_2(NO_3)_2(H_2O)_2 \cdot$(12-crown-4). An initial study by Armağan (1977) contended, based on crystallographic data, that the compound was of the inclusion type. However, all previous and subsequent attempts to place uranyl in the relatively small cavity of 12-crown-4 were unsuccessful. Due to anomalies within the reported results, a follow-up study was done that established the structure as an exclusion complex; $UO_2(NO_3)_2$ nodes are connected to 12-crown-4 molecules through a hydrogen-bonded network enabled by the lattice water molecules (Ritger *et al.*, 1983).

One of the first examples of a hydrogen bonding-stabilized exclusion complex is that of $UO_2(NO_3)_2(H_2O)_2 \cdot 2H_2O \cdot$ (18-crown-6). Discrete $UO_2(NO_3)_2(H_2O)_2$ units are separated by crown ether molecules and linked together by hydrogen bonding through intermediary water molecules. Each uranium atom is coordinated to the *trans* uranyl oxygen atoms, two water molecules, and two bidentate nitrate groups (Eller and Penneman, 1976).

Table 22.25 *Exclusion (second sphere/outer sphere) compounds of actinides and crown ethers.*

Structure	*References*
9-crown-3, 12-crown-4	
UI_3(trithia-9-crown-3)(MeCN)$_2$	Karmazin *et al.* (2002)
$UO_2(SO_4)(H_2O)_2 \cdot$ (12-crown-4)$_{0.5} \cdot H_2O$	Rogers *et al.* (1991)
$UO_2(NO_3)_2(H_2O)_2 \cdot$ (12-crown-4)	Ritger *et al.* (1983)
[$UO_2Cl_2(H_2O)_2$(12-crown-4)] $\cdot$ (12-crown-4)	Rogers *et al.* (1989)
[Li(12-crown-4)]$_2$[UO_2Cl_4]	Danis *et al.* (2001)
[Li(12-crown-4)]$_2$[UO_2Br_4]	Danis *et al.* (2001)
[Na(12-crown-4)$_2$]$_2$[UO_2Cl_4] $\cdot$ 2MeOH	Rogers (1988)
15-crown-5	
$ThCl_4(MeOH)_2(OH_2)_2 \cdot$ (15-crown-5) $\cdot$ MeCN	Rogers and Benning (1988a)
$UO_2(NO_3)_2(H_2O)_2$(15-crown-5)	Gutberlet *et al.* (1989)
$UO_2Cl_2(H_2O)_3$(15-crown-5)	Hassaballa *et al.* (1988, 1998)
$(H_5O_2)[UO_2(H_2O)_2Cl_3] \cdot$ (15-crown-5)$_2$	Hassaballa *et al.* (1998)
[Na(15-crown-5)]$_2$[UO_2Cl_4]	Danis *et al.* (2001)
[Na(15-crown-5)]$_2$[UO_2Br_4]	Danis *et al.* (2001)
[(NH_4)(15-crown-5)$_2$]$_2$(UO_2Cl_4) $\cdot$ 2MeCN	Rogers *et al.* (1987a)
[$UO_2(H_2O)_5$][ClO_4]$_2 \cdot$ (15-crown-5)$_3 \cdot$ MeCN	Rogers *et al.* (1987b)
$UO_2(SO_4)(H_2O)_2 \cdot$ (benzo-15-crown-5)$_{0.5} \cdot 1.5H_2O$	Rogers *et al.* (1991)
$UO_2(NO_3)_2(H_2O)_2$(benzo-15-crown-5)	Deshayes *et al.* (1993)
[$UO_2(TTA)_2H_2O$]$_2$(benzo-15-crown-5)	Kannan *et al.* (2001)
[Na(benzo-15-crown-5)]$_2$(UO_2Cl_4)	Moody and Ryan (1979)
$UO_2(NO_3)_2(H_2O)_2$(benzo-15-crown-5)$_2$	Deshayes *et al.* (1993)
$UO_2(H_2O)_3(CF_3SO_3)_2 \cdot$ (benzo-15-crown-5)$_2$	Thuéry *et al.* (1995b)
[(H_5O_2)(H_9O_4)(benzo-15-crown-5)$_2$][UO_2Cl_4]	Rogers *et al.* (1991)
[(H_5O_2){(NO_2)$_2$benzo-15-crown-5}$_2$]$_2$ [{$UO_2(NO_3)_2$}$_2C_2O_4$]	Rogers *et al.* (1991)
[(NH_4)(benzo-15-crown-5)$_2$]$_2$[UCl_6] $\cdot$ 4MeCN	Rogers *et al.* (1987a)
[$UO_2(NO_3)_2$]$_2$(μ-H_2O)$_2$(monoaza-15-crown-5)$_2$	Cragg *et al.* (1988)
18-crown-6	
[$ThCl(OH)(H_2O)_6$]$Cl_4 \cdot$ (18-crown-6) $\cdot 2H_2O$	Rogers and Bond (1992)
[$ThCl_2(H_2O)_7$]$Cl_2 \cdot$ (18-crown-6) $\cdot 2H_2O$	Rogers (1989)
$ThCl_4(EtOH)_3(H_2O) \cdot$ (18-crown-6) $\cdot H_2O$	Rogers *et al.* (1988)
$Th(NCS)_4(H_2O)(HOCH_2CH_2OH)_2 \cdot$ (18-crown-6)	Rogers *et al.* (1998)
$Th(H_2O)_3(NO_3)_4 \cdot$ (18-crown-6)	Rogers *et al.* (1987c)
[(H_3O)(dicyclohexyl-18-crown-6)]$_2$[$Th(NO_3)_6$]	Ming *et al.* (1988)
$UO_2(SO_4)(H_2O)_3 \cdot$ (18-crown-6)$_{0.5}$	Rogers *et al.* (1991)
[(H_5O_2)$_2$(18-crown-6)][UO_2Cl_4]	Rogers *et al.* (1991)
[$UO_2(CH_3COO)(OH)(H_2O)$]$_2 \cdot$ (18-crown-6)	Mikhailov *et al.* (1997)
$UO_2(CH_3COO)_2(H_2O)_2 \cdot (H_2O)_2 \cdot$ (18-crown-6)	Mikhailov *et al.* (1997)
$UO_2(NO_3)_2(H_2O)_2$(18-crown-6)	Bombieri *et al.* (1978b)
$UO_2(NO_3)_2(H_2O)_2 \cdot 2H_2O \cdot$ (18-crown-6)	Eller and Penneman (1976)
$UO_2(H_2O)_5(CF_3SO_3)_2 \cdot$ (18-crown-6)	Deshayes *et al.* (1994b)
[$UO_2(H_2PO_4)_2(H_2O)$]$_2 \cdot$ (18-crown-6) $\cdot 5H_2O$	Danis *et al.* (2000)
$UO_2(H_2PO_4)_2(H_2O) \cdot$ (18-crown-6) $\cdot 3H_2O$	Danis *et al.* (2000)
[$U(SCN)_4(H_2O)_4$][18-crown-6]$_{1.5} \cdot 3H_2O \cdot (C_6H_{12}O)$	Charpin *et al.* (1977)
$UO_2(NCS)_2(H_2O)_3 \cdot$ (18-crown-6)$_{1.5} \cdot$ MeCN	Rogers *et al.* (1998)

Table 22.25 (*Contd.*)

Structure	*References*
$[(H_3O)(18\text{-crown-}6)]_2[\{UO_2(NO_3)_2\}_2C_2O_4]$	Rogers *et al.* (1991)
$[UO_2(H_2O)_5][ClO_4]_2 \cdot (18\text{-crown-}6)_2 \cdot 2MeCN \cdot H_2O$	Rogers *et al.* (1987b)
$[NH_4(18\text{-crown-}6)]_2[UCl_6] \cdot 2MeCN$	Rogers and Benning (1988b)
$[NH_4(18\text{-crown-}6)]_2[UO_2(NCS)_4(H_2O)]$	Ming *et al.* (1987a)
$[K(18\text{-crown-}6)]_2[UO_2(NCS)_4(H_2O)]$	Ming *et al.* (1987b)
$[K(18\text{-crown-}6)]_2[UO_2Cl_4]$	Danis *et al.* (2001)
$[K(18\text{-crown-}6)]_2[UO_2Br_4]$	Danis *et al.* (2001)
$[(UO_2)_2(OH)_2(H_2O)_6](ClO_4)_2$ $[\text{dicyclohexyl-18-crown-6}]_3 \cdot MeCN$	Navaza *et al.* (1984)
$UO_2Cl_4(\text{dicyclohexyl-18-crown-6} \cdot H_3O)_2$	Guang-Di *et al.* (1990)
$[UO_2(TTA)_2(\mu\text{-}H_2O)]_2(H_2O)_2(\text{dibenzo-18-crown-6})$	Kannan *et al.* (2001)
$[(NH_4)(\text{dibenzo-18-crown-6})]_2[(UO_2Cl_4) \cdot 2MeCN$	Rogers *et al.* (1987a)
24-crown-8	
$[(H_5O_2)(\text{dicyclohexyl-24-crown-8})]_2(UO_2Cl_4) \cdot MeOH$	Rogers and Benning (1991)
$[(H_5O_2)(\text{dicyclohexyl-24-crown-8})]_2(UCl_6) \cdot MeOH$	Rogers and Benning (1991)

The crystal lattice of the compound $[(H_5O_2)\{(NO_2)_2\text{benzo-15-crown-5}\}_2]_2[\{UO_2(NO_3)_2\}_2C_2O_4]$ contains discrete cation and anion pairs. The anion consists of two $UO_2(NO_3)_2$ groups (each nitrate is bidentate) bridged by a tetradentate oxalate group (forming two five-membered rings); each uranium center is surrounded by a hexagonal bipyramidal polyhedron of ligands. A single $H_5O_2^+$ ion resides between two 15-crown-5 molecules and is stabilized by hydrogen bonding to the ethereal oxygen atoms of the crown ether (Rogers *et al.*, 1991).

Inclusion of H_3O^+ is observed in the structure of $[(H_3O)(18\text{-crown-}6)]_2[\{UO_2(NO_3)_2\}_2C_2O_4]$; the H_3O^+ species resides in the cavity of the crown ether molecule, stabilized by hydrogen bonding (Fig. 22.19). This hydrogen bonding likely occurs with three crown ether oxygen atoms, giving the hydronium a pseudo-pyramidal geometry, residing 0.4 Å out of the plane. The discrete uranyl-containing anion adopts the same conformation as the former molecule, with alternate cation–anion–cation stacking (Rogers *et al.*, 1991).

In $UO_2(SO_4)(H_2O)_2 \cdot (12\text{-crown-}4)_{0.5} \cdot H_2O$, two *trans* uranyl oxygen atoms, two water molecules, and one oxygen each from three sulfate atoms coordinate each uranium atom, generating a pentagonal bipyramid. The sulfate anions bridge each uranium atom to two neighbors, thus forming polymeric double chains. Furthermore, the 18-crown-6 molecule and the uncoordinated water molecule form an organic layer that separates the layers of the uranium polymeric double chains; the layers are stabilized by a hydrogen-bonding network (Rogers *et al.*, 1991).

A series of five alkali metal/crown ether/uranyl halide sandwich exclusion complexes have been structurally characterized and each displays square

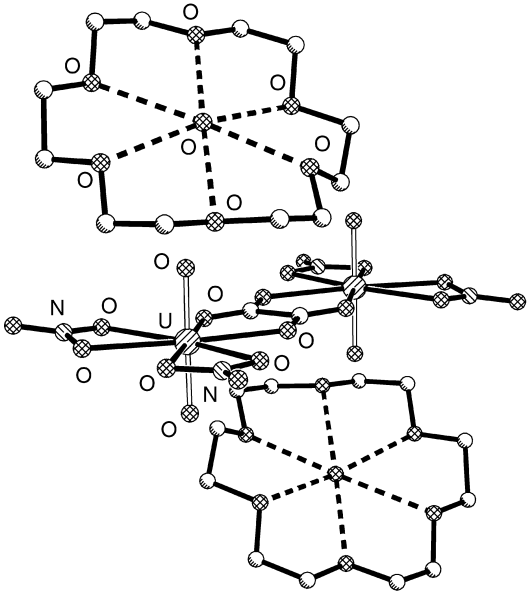

Fig. 22.19 *Crystal strucuture of* $[(H_3O)(18\text{-}crown\text{-}6)]_2[\{UO_2(NO_3)_2\}_2C_2O_4]$ *with hydrogen atoms omitted* (*Rogers* et al., 1991). *The coordinates were obtained from the Cambridge Structural Database* (*refcode SODFUM*).

bipyramidal $[UO_2X_4]^{2-}$ anions sandwiched between two [A(crown ether)]$^+$ cations (X = Cl, Br and A = Li, Na, K). Crown ethers of varying cavity size were investigated, including 18-crown-6, 15-crown-5, and 12-crown-4. The [K(18-crown-6)]$_2$[UO_2Cl_4] and [K(18-crown-6)]$_2$[UO_2Br_4] complexes display Type I bonding behavior where the K$^+$ cations form inclusion complexes with the crown ethers. Two uranium-bound halides coordinate in a bridging manner to each K$^+$ ion and the anionic unit is tilted with respect to the plane of the crown ether toward the K$^+$ ions to varying degrees (56° for Cl and 63° for Br) (Danis *et al.*, 2001).

The [Na(15-crown-5)]$_2$[UO_2Cl_4] has two crystallographically unique anionic units, one of which is Type I bonding, as described above, and the other Type II where only one uranium-bound chloride interacts with each Na$^+$ ion. Significant tilt of the anionic unit (31°) also occurs. In the Type I bonding, the linear uranyl unit of the anion is aligned parallel to the crown ether plane. If the halide in the aforementioned complex is changed from Cl to Br, a structural shift occurs to Type III bonding. Here, each crown-encapsulated Na$^+$ ion is bridged by one uranyl bromide and one uranyl oxygen. The linear unbound Br–U–Br unit is aligned parallel to the crown ether plane. Finally, [Li(12-crown-4)]$_2$[UO_2Cl_4] and [Li(12-crown-4)]$_2$[UO_2Br_4] both exhibit Type IV bonding and are both nearly isostructural. In both complexes, the bonding to each crown-encapsulated Li^+ is solely through the two uranyl oxygen atoms, resulting in a plane defined by uranium and its four halide atoms that separates the cationic units. The type of bonding exemplified in these structures can be described in terms of hard–soft acid–base theory; in the latter two complexes, the 'hard' Li^+ ion prefers exclusive interaction with the 'hard' uranyl oxygen atoms (Danis *et al.*, 2001).

Exclusion crown ether complexes of uranyl incorporating ligands that are important in uranium chemistry are also known. For example, thenoyl (trifluoroacetone) (HTTA), a β-diketone extractant that acts synergistically with crown ethers in extraction schemes, interacts directly with uranium in $[UO_2\ (TTA)_2H_2O]_2$(benzo-15-crown-5) and $[UO_2(TTA)_2(\mu\text{-}H_2O)]_2(H_2O)_2$(dibenzo-18-crown-6), where the crown ethers are second-sphere and third-sphere ligands, respectively (Fig. 22.20). In both complexes, each uranium attains pentagonal bipyramidal geometry, with equatorial coordination provided by two bidentate HTTA groups and a water molecule. In the former, the bound water hydrogen bonds to the crown ether, making it second sphere. In the latter, intermediate water molecules generate a hydrogen-bonding network (Kannan *et al.*, 2001).

Various forms of phosphate also play significant roles in both processing and environmental aspects of uranium chemistry. The structure of $[UO_2(H_2PO_4)_2(H_2O)]_2 \cdot$ (18-crown-6) $\cdot\ 5H_2O$ once again shows pentagonal bipyramidal geometry around uranium, as well as infinite, one-dimensional $[UO_2(H_2PO_4)_2(H_2O)]$ chains that are hydrogen-bonded to uncomplexed crown ether molecules

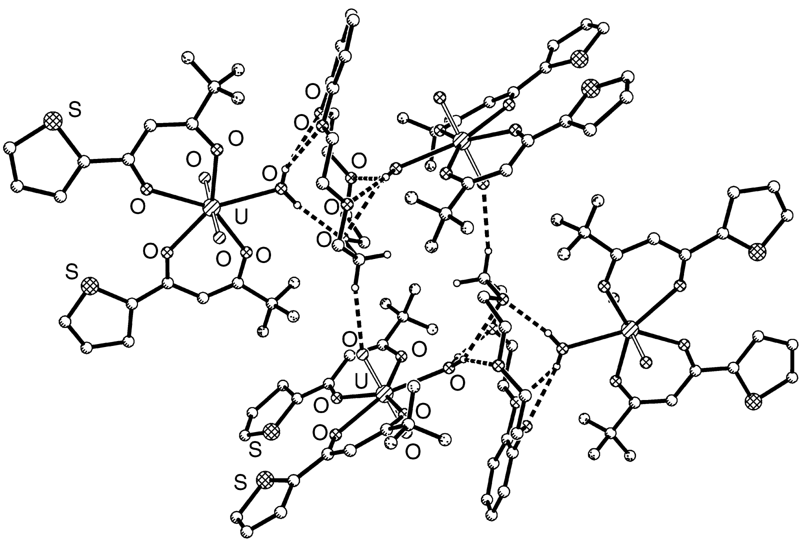

Fig. 22.20 *Crystal strucuture of* $[UO_2(TTA)_2H_2O]_2$(*benzo*-15-*crown*-5) *with hydrogen atoms omitted* (*Kannan* et al., 2001). *The coordinates were obtained from the Cambridge Structural Database* (*refcode RORXIF*).

through solvate lattice water molecules. Each of four $H_2PO_4^-$ units is bound $\mu-\eta^1$ to uranium. A similar situation is observed in the crystal structure of $UO_2(H_2PO_4)_2(H_2O)\cdot$(18-crown-6)$\cdot 3H_2O$ (Danis *et al.*, 2000).

Although fewer in number, thorium exclusion-type crown ether structures are also known. For example, the crystal structure of [(H_3O)(dicyclohexano-18-crown-6)]$_2$[$Th(NO_3)_6$] reveals the thorium atom resting at a center of symmetry and unbound to the crown ether donor atoms. The thorium is 12-coordinate due to bidentate coordination of the six nitrate anions, thus giving it a nearly perfect icosahedral geometry. The Th–O bond distances in this anionic unit range from 2.551 to 2.587 Å. Each H_3O^+ cation rests in the cavity of the crown ether molecules, stabilized by three hydrogen bonds, as well as ion–dipole interactions (Ming *et al.*, 1988).

(b) Calixarenes

The class of macrocyclic ligands known as calixarenes is structurally recognized by phenolic subunits joined in a cyclic fashion via methylene linkages; derivatives based on CH_2–X–CH_2 linkages are also commonly used, where X is O, NH, or S. Substitutions at the pendant phenol oxygen site are also possible. The latter types are of interest due to their less rigid character and larger number of potential donor sites. Calixarenes are highly diverse in terms of available ring sizes, making them excellent candidates for systematic analyses concerning their donor properties in binding to groups of metal ions, including lanthanides and actinides. Traditional calixarene chemistry allows for substitutions at either the lower or upper rim of the calixarene and the tuning of their physical properties. The lower rim of a calixarene comprises the cyclic arrangement of alcohol functionalities of the phenol unit. Typically, substitution is directed to the upper rim, leaving the lower rim unsubstituted, thus comprising the class of ‘phenolic calixarenes’. Due to the variety of ring sizes available, actinide complexes with calixarenes can be either inclusion or exclusion complexes with the coordination based on considerations such as ligand type, ring diameter, and metal ion radius. For a general overview of phenolic calixarene f-element coordination chemistry, the reader is referred to a review from Thuéry *et al.* (2001d); representative single-crystal X-ray diffraction structures from the literature will be reviewed herein, the likes of which are summarized in Table 22.26.

The complexes formed between $UO_2^{2+}$and triply deprotonated *p-tert*-butylhexahomotrioxacalix[3]arene, studied by Thuéry *et al.* (1999a) show the lowest coordination number (five) observed for a uranyl complex (Fig. 22.21). In the presence of the deprotonating agents triethylamine and DABCO, two isomorphous inclusion-type complexes are formed where the uranyl is located in the center of the lower rim of the calixarene. The uranyl cation is bound in the equatorial plane to the three deprotonated phenolic oxygen atoms with an average U–O_{eq} bond distance of 2.20(3) Å, yielding pseudo-trigonal

Table 22.26 *Representative actinide-calix[n]arene compounds, by type.*

Structure	*References*
calix[3]*arenes*	
[HNEt$_3$][UO$_2$(*p*-methylhexahomotrioxacalix[3]arene–3H)]	Masci *et al.* (2002a)
[HN^{n}Pr$_3$][UO$_2$(*p*-*tert*-butylhexahomotrioxacalix[3]arene–3H)] · MeOH	Masci *et al.* (2002a)
[H$_3$N^{n}Bu][UO$_2$(*p*-*tert*-butylhexahomotrioxacalix[3]arene–3H)]	Masci *et al.* (2002a)
[H$_2$N^{n}Bu$_2$][UO$_2$(*p*-*tert*-butylhexahomotrioxacalix[3]arene–3H)] · MeOH	Masci *et al.* (2002a)
(C$_6$H$_{14}$N)[UO$_2$(*p*-*tert*-butylhexahomotrioxacalix[3]arene–3H)] · 2MeOH · H$_2$O	Masci *et al.* (2002a)
[UO$_2$(*p*-*tert*-butylhexahomotrioxacalix[3]arene–3H)(HNEt$_3$)] · 3H$_2$O	Thuéry *et al.* (1999a)
[UO$_2$(*p*-*tert*-butylhexahomotrioxacalix[3]arene–3H)(HDABCO)] · 3MeOH	Thuéry *et al.* (1999a)
[UO$_2$(NO$_3$)$_2$(*p*-chloro-*N*-benzylhexahomotriazacalix[3]arene)] · pyr · CHCl$_3$	Thuéry *et al.* (2001a)
calix[4]*arenes*	
[UO$_2$(NO$_3$)$_2$(*p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene)] · 0.5MeOH · H$_2$O	Thuéry *et al.* (2001a)
[HNEt$_3$]$_2$[UO$_2$(*p*-*tert*-butyltetrahomodioxacalix[4]arene–4H)] · CHCl$_3$ · MeCN	Thuéry *et al.* (2001a)
[{UCl(*tert*-butylcalix[4]arene–4H)}$_3$(μ$_3$-oxo)] · 11.5pyr	Leverd and Nierlich (2000)
[HNEt$_3$]$_2$[UO$_2${bis(homo-oxa)-*p*-*tert*-butylcalix[4]arene–4H}] · 2H$_2$O	Harrowfield *et al.* (1991a)
[Hpyr][(UO$_2$)$_2$(*p*-methyloctahomotetraoxacalix[4]arene–4H)(OH)(H$_2$O)] · 2.5pyr	Thuéry *et al.* (2001b)
[(UO$_2$)$_2$(1-acid-3-diethylamide substituted calix[4]arene–2H)$_2$] · 10MeCN · 2MeOH	Beer *et al.* (1998)
[UO$_2$(calix[4]arene–1H)$_2$(DMF)$_{3.7}$(DMSO)$_{0.3}$] · [calix[4]arene(DMF)] · 1.5DMF	Asfari *et al.* (2001)
[HNEt$_3$]$_2$[UO$_2$(*p*-*tert*-butyltetrathiacalix[4]arene–4H)(DMF)] · 2DMF	Asfari *et al.* (2001)
[HNEt$_3$]$_2$[UO$_2$(*p*-*tert*-butyltetrathiacalix[4]arene–4H)(MeCN)] · ~ 1.7DMSO	Asfari *et al.* (2001)
[Hpyr]$_2$[UO$_2$(*p*-methyl-tetrahomodioxacalix[4]arene–4H)] · 3H$_2$O	Masci *et al.* (2002b)
[HNEt$_3$]$_2$[UO$_2$(*p*-phenyl-tetrahomodioxacalix[4]arene–4H)] · 2CHCl$_3$	Masci *et al.* (2002b)
[H$_3$N^{n}Bu]$_2$[UO$_2$(*p*-phenyl-tetrahomodioxacalix[4]arene–4H)] · (H$_3$N^{n}Bu) · (CH$_3$COO) · 2H$_2$O	Masci *et al.* (2002b)
[UO$_2$(*p*-methyl-*N*-benzyl-tetrahomodiazacalix[4]arene–2H)] · 2CHCl$_3$ · MeCN	Thuéry *et al.* (2001c)
calix[5]*arenes*	
[Hpyr]$_2$[{U(*tert*-butylcalix[5]arene–5H)}$_2$(μ$_2$-oxo)] · 4pyr	Leverd and Nierlich (2000)
[{U(*tert*-butylcalix[5]arene–5H)}$_2$(μ$_2$-oxo)]$_2$ · 5pyr	Leverd and Nierlich (2000)

Table 22.26 (*Contd.*)

Structure	*References*
[HNEt$_3$]$_2$[UO$_2$(*p-tert*-butylcalix[5]arene–4H)] · 2MeOH	Thuéry and Nierlich (1997)
calix[6]*arenes*	
[U(*tert*-butylcalix[6]arene–3H)$_2$] · (Hpyr)$_2$Cl$_2$ · 10pyr	Leverd and Nierlich (2000)
[U{(*tert*-butylcalix[6]arene–4H)LaCl$_2$(pyr)$_4$}$_2$]	Leverd *et al.* (2002)
[UO$_2$(*p-tert*-butylcalix[6]arene–4H)]$_2$ · 2(HNEt$_3$) · 2(H$_3$O) · 6MeCN	Thuéry *et al.* (1996)
[HNEt$_3$]$_2$[UO$_2$(*p-tert*-butyltetrahomodioxacalix[6]arene–4H)] · 3MeCN	Thuéry *et al.* (2001b)
[Hpyr]$_3$[Cs][(UO$_2$Cl$_2$)$_2$(*tert*-butylcalix[6]arene–4H)] · 7pyr	Leverd *et al.* (1998)
[(UO$_2$)$_2$Li(OH)(*p-tert*-butylhexahomotrioxacalix[6]arene–6H)(pyr)][Li(H$_2$O)$_3$(pyr)] · (Hpyr) · H$_2$O · 4.5pyr	Thuéry and Masci (2004)
[UO$_2$K(*p-tert*-butylhexahomotrioxacalix[6]arene–3H)(H$_2$O)$_2$]$_2$ · 14pyr	Thuéry and Masci (2004)
calix[7]*arenes*	
[(UO$_2$)$_6$(*p*-benzylcalix[7]arene–7H)$_2$(O)$_2$(HDABCO)$_6$] · 3MeCN · CH$_3$Cl · 5MeOH · 3H$_2$O	Thuéry *et al.* (1999b)
[HNEt$_3$]$_2$[UO$_2$(*p-tert*-butylcalix[7]arene–4H)] · MeNO$_2$ · MeOH	Thuéry *et al.* (1998)
[HNEt$_3$]$_2$[UO$_2$(*p-tert*-butylcalix[7]arene–4H)] · MeCN · 2H$_2$O	Thuéry *et al.* (1998)
calix[8]*arenes*	
[Th$_4$(*p-tert*-butylcalix[8]arene–7H)(*p-tert*-butylcalix[8]arene–6H)(DMSO)$_4$(OH)$_3$(H$_2$O)] · (DMSO) · 2H$_2$O	Harrowfield *et al.* (1991b)
[HNEt$_3$]$_2$[(UO$_2$)$_4$(*p-tert*-butyloctahomotetraoxacalix[8]arene–8H)(OH)$_2$(H$_2$O)$_4$] · 1.5NEt$_3$ · 2.5H$_2$O · MeOH	Thuéry *et al.* (2001b)
[(HNEt$_3$)$_2$(OH)][(UO$_2$)$_2$(*p-tert*-butylcalix[8]arene–4H)(OH)] · 2NEt$_3$ · 3H$_2$O · 4MeCN	Thuéry *et al.* (1995c)
[HNEt$_3$]$_5$[(UO$_2$)$_2$(*p-tert*-butylcalix[8]arene–4H)(OH)]$_2$ · 3OH · 3MeCN	Thuéry *et al.* (1995d)
[NMe$_4$][(UO$_2$)$_3$(OH)(*p-tert*-butylcalix[8]arene–6H)(DMSO)$_2$]	Thuéry *et al.* (2001d)
[(UO$_2$)$_4$O$_4$(*p-tert*-butyloctahomotetraoxacalix[8]arene)] · 10MeOH	Thuéry and Masci (2003)
[(UO$_2$)$_2$(pyr)$_4$(*p-tert*-butyloctahomotetraoxacalix[8]arene–4H)] · pyr	Thuéry and Masci (2003)
calix[9, 12]*arenes*	
[HNEt$_3$]$_3$[(UO$_2$)$_2$(*p-tert*-butylcalix[9]arene–5H)(CO$_3$)]	Thuéry *et al.* (2001d)
[HNEt$_3$]$_2$[{(UO$_2$)$_2$(NO$_3$)(pyr)}$_2$(*tert*-butylcalix[12]arene–8H)] · 9pyr	Leverd *et al.* (2000)

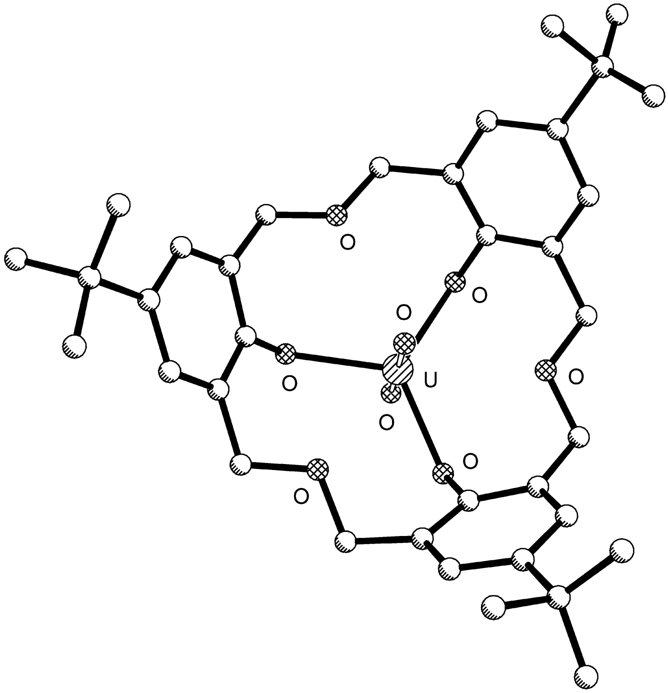

Fig. 22.21 *Crystal strucuture of* $[UO_2(\text{p-tert-}butylhexahomotrioxacalix[3]arene\text{–}3H)(HDABCO)]\cdot 3MeOH$ *with MeOH, HDABCO, and hydrogen atoms omitted* (*Thuéry* et al., 1999*a*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode BINKOY*).

bipyramidal geometry around the uranium atom. The oxa-linkages that connect the phenolic units do not take part in the bonding; thus, the five-coordinate environment around uranium is the lowest ever observed. The overall conformation of the calixarene ligand is cone-shaped, and the uranyl is slightly displaced from the plane formed by the three bonding phenolic oxygen atoms. This displacement is counter-ion-dependent, with triethylamine and DABCO resulting in 0.186(4) and 0.248(3) Å displacements, respectively (Thuéry *et al.*, 1999a).

The trigonal equatorial coordination environment around uranium in the two aforementioned complexes changes with alterations to the upper rim as well as the deprotonating agent. Maintaining the *tert*-butyl substitution at the upper rim and changing the deprotonation agent to H_2NBu preserves the trigonal equatorial coordination around uranium; however, in the presence of NPr_3, a distorted tetragonal coordination is observed, with an ether oxygen also taking part in the bonding. Distorted tetragonal coordination is also observed with a methyl substitution and triethylamine. Higher degrees of equatorial coordination are also possible. A *tert*-butyl substitution with 4-methylpiperidine as the deprotonating agent results in distorted pentagonal coordination aided by the participation of two ether oxygen atoms; an intermediate coordination environment (between tetragonal and pentagonal) occurs with $HNBu_2$ (Masci *et al.*, 2002a).

Calix[4]arene-based actinide complexes are plentiful in the literature, owing to the larger cavity size of the ligand and larger number of potential donor sites. Tetrahomodioxa- and tetrahomodiazacalix[4]arene uranyl structures typically show 1:1 complexes with different complexation modes. The complexation of UO_2^{2+} with *p-tert*-butyltetrahomodioxacalix[4]arene in the presence of triethylamine yields an inclusion complex where the uranyl is bound equatorially in the plane of four deprotonated phenolic oxygen atoms, with the two calixarene ether oxygen atoms taking on a non-bonding role (3.832(4) and 3.820(4) Å from uranium). The geometry around uranium is square bipyramidal with an average $U–O_{eq}$ bond distance of 2.28(3) Å (Thuéry *et al.*, 2001a).

The uranyl/*p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene complex, on the other hand, is of the exclusion type. Interestingly, the complex forms in the absence of base, resulting in a neutral 1:1 complex, where the uranyl is bound to two phenolic oxygens (zwitterionic form) of the calixarene and to two nitrate counter-ions. The uranyl cation rests above the plane of the four phenolic oxygen atoms at a distance of 1.543(8) Å, with the two bound $U–O_{phenol}$ distances at 2.234(9) and 2.269(8) Å. The nitrate anions have different coordination modes, one being mondentate and the other bidentate. The differences observed between the dioxa- and diaza-complexes are presumably due to electrostatic repulsion between the uranyl and the ammonium groups of the diazacalixarene (Thuéry *et al.*, 2001a).

A unique inclusion complex between *p*-methyloctahomotetraoxacalix[4]arene and two uranyl cations has also been structurally characterized (Fig. 22.22). The doubly bridged dinuclear cation rests in the calixarene cavity with the bridging provided by a hydroxide and one oxygen atom from a water molecule. Pentagonal bipyramidal geometry around each uranium results from the two axial uranyl oxygen atoms, the two bridging oxygen atoms, two deprotonated phenolic oxygen atoms, and a single ether oxygen atom. The mean $U–O_{phenoxide}$ bond distances are 2.25(2) Å, while the mean $U–O_{ether}$ distances are significantly longer at 2.67(2) Å (Thuéry *et al.*, 2001b).

The reaction of UO_2^{2+} with *p-tert*-butycalix[5]arene in the presence of triethylamine generates an inclusion complex. The uranyl is bound equatorially to the five phenolic oxygen atoms of the lower rim of the calixarene, generating an overall pentagonal bipyramidal geometry around the uranium atom. Interestingly, only four of the five phenolic sites are deprotonated, suggesting that uranyl ion has an acid-enhancing effect. The $U–O_{eq}$ bond distances vary greatly; three in the range 2.25–2.30 Å, a fourth at 2.571(7) Å, and the longest at 2.836(8) Å. The large variation in the range of $U–O_{eq}$ bond lengths may be due to the calixarene cavity being too large for ideal coordination of the uranyl ion. Finally, the calixarene itself takes on the common cone conformation and

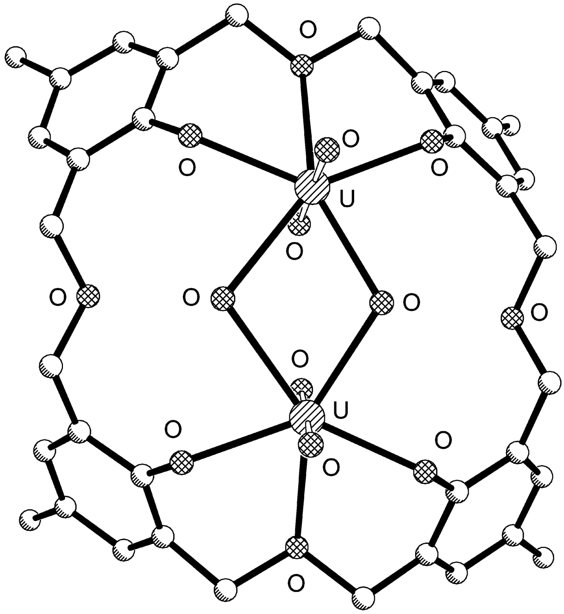

Fig. 22.22 *Crystal strucuture of* [*Hpyr*][(UO_2)$_2$(p-*methyloctahomotetraoxacalix*[4]*arene–*4*H*)(*OH*)(H_2O)] · 2.5*pyr with Hpyr, pyr, and hydrogen atoms omitted* (*Thuéry* et al., 2001*b*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode QOPMIR*).

one of the protonated triethylamine molecules sits in the cavity of the cone, coordinated with an axial uranyl oxygen atom (Thuéry and Nierlich, 1997).

Single crystals of larger calix[*n*]arenes, where $n = 6, 7, 8, 9$, or 12, complexed with actinides have also been isolated and their structures determined. While uranium–calixarene complexes are the most common in the literature, a novel Th(IV) structure with *p-tert*-butylcalix[8]arene has also been solved (DMSO solvate). The structure contains two different calixarene ligands, each with varying degrees of deprotonation (both seven and six protons), bound to four thorium atoms. While the structure itself is very complicated, it is obvious that the two calixarenes attain two different conformations, with one being in a 'propeller' conformation and the other a 'crown'. The two calixarenes form four cone-shaped cavities, the apices of which are defined by a plane of four phenolic oxygen atoms; each cavity is subsequently associated with a single thorium atom. Each thorium center is associated with five phenolic oxygen atoms, three of which are mondentate while the remaining two take on bridging interactions. DMSO and hydroxide molecules also contribute to the bonding (Harrowfield *et al.*, 1991b).

A related uranyl complex incorporating *p-tert*-butylcalix[8]arene is bimetallic and contains only a single calixarene ligand (Fig. 22.23). Here, each uranyl ion

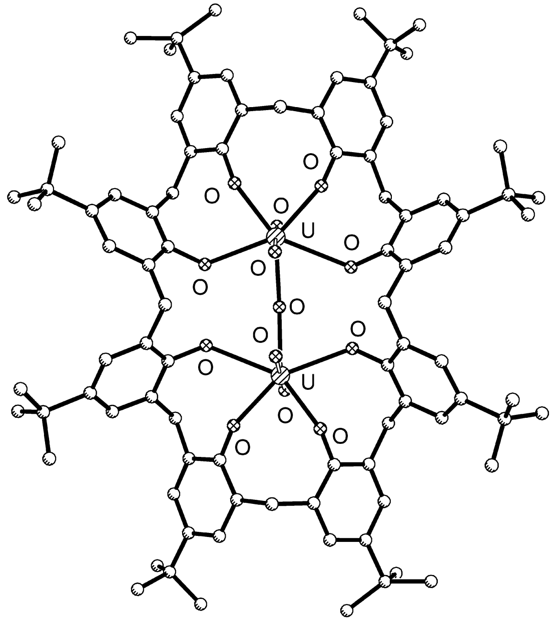

Fig. 22.23 *Crystal strucuture of* $[(HNEt_3)_2(OH)][(UO_2)_2(\text{p-tert-}butylcalix[8]arene{-}4H)(OH)] \cdot 2NEt_3 \cdot 3H_2O \cdot 4MeCN$ *with* $[(HNEt_3)_2(OH)]^+$, NEt_3, H_2O, *MeCN, and hydrogen atoms omitted (Thuéry* et al., 1995c). *The coordinates were obtained from the Cambridge Structural Database (refcode ZAMJIG).*

resides in the cavity of the calixarene, making it an inclusion complex, and each is bound equatorially to four phenolic oxygen atoms, two of which are deprotonated. The uranyl ions are also linked via a bridging hydroxide, thus making the overall geometry around each heptacoordinate uranium atom distorted pentagonal bipyramidal. The equatorial U–O bond lengths at the protonated sites are 2.619(9) and 2.476(9) Å, while the corresponding lengths at the deprotonated sites are 2.218(9) and 2.20(1) Å. Two protonated triethylamine molecules are also associated with the complex, each being hydrogen-bonded to a separate axial uranyl oxygen atom. The overall conformation of the bound calixarene has been described as a ‘pleated loop’ (Thuéry *et al.*, 1995c).

The largest calixarene complex of an actinide to date for which a single-crystal X-ray diffraction structure is known is that between *tert*-butylcalix[12]arene and UO_2^{2+} (Fig. 22.24). The resulting inclusion complex contains two uranyl bimetallic units; the uranyl ions in each unit are bridged by a tridentate nitrate ligand. Each bimetallic unit is bound to five phenolic oxygen sites, four of which are deprotonated. One uranyl in each unit is bound to three of the oxygen atoms, while the second is bound to the remaining two and a pyridine molecule (through nitrogen). The resulting geometry around each uranium atom is pentagonal bipyramidal. The four shorter $U{-}O_{eq}$ bond lengths at each bimetallic

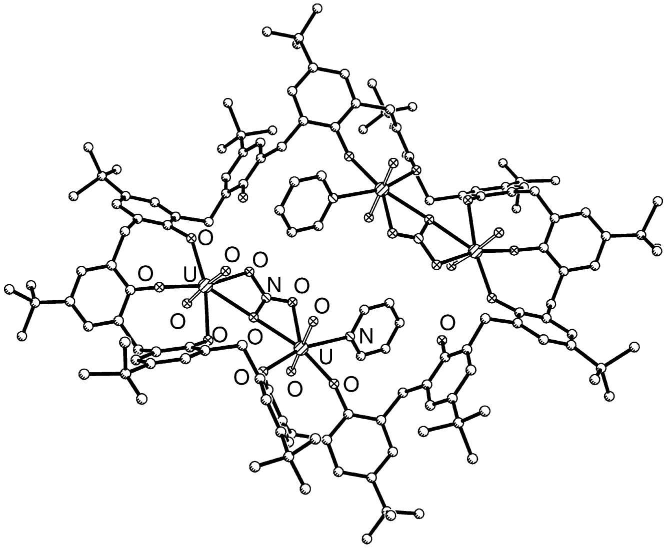

Fig. 22.24 *Crystal strucuture of* $[HNEt_3]_2[\{(UO_2)_2(NO_3)(pyr)\}_2(\text{tert-}butylcalix[12]arene\text{–}8H)]\cdot 9pyr$ *with* $[HNEt_3]^+$*, pyr(unbound), and hydrogen atoms omitted (Leverd* et al., 2000)*. The coordinates were obtained from the Cambridge Structural Database (refcode MALGEL).*

unit are about 2.2 Å and correspond to the four deprotonated phenolic sites; the fifth longer bond length at the protonated site is 2.62(3) Å (Leverd *et al.*, 2000).

(c) Porphyrins/phthalocyanines

The macrocyclic ligands commonly referred to as porphyrins are ubiquitous in nature. They are structurally described as an arrangement of four pyrrole units linked together in a cyclic manner at the 2- and 5-positions by methine bridges, forming an aromatic, 22-π electron system. The iron-containing porphyrin, commonly known as heme, comprises the primary binding site in hemoglobin that is responsible for dioxygen transport throughout the body. While traditional porphyrins contain only nitrogen-donor atoms, pyrrole-derived macrocycles have also been synthesized that contain pyrrole, furan, and thiophene subunits solely, or combinations thereof. In addition, extensive chemistries have been developed in the synthesis of expanded, contracted, and isomeric porphyrins, the details of which have been described elsewhere. Expanded porphyrins will hereafter be defined as containing at least 17 atoms in a conjugated manner and three pyrrole or pyrrole-like subunits (Sessler and Weghorn, 1997). Porphyrins have been extensively studied as templates for metal ion coordination; the addition of base, such as triethylamine, for the deprotonation of nitrogen sites allows for tetradentate or higher coordination to the metal centers, often times facilitating electronic transitions in the visible portion of the electromagnetic spectrum that give rise to a wide range of observable color changes. In addition, traditional nitrogen-containing porphyrins give rise to unique coordination complexes with metals that prefer oxygen or sulfur atom donation (Girolami *et al.*, 1994).

Traditionally, oxygen and sulfur atoms, when incorporated into ligand support molecules, have been the atoms of choice for coordination to metal centers; thus, the use of pyrrole-derived porphyrins provides a unique opportunity to study the binding to actinide ions in a non-traditional manner (i.e. all nitrogen atoms) and the subsequent effect on electronic and structural (using X-ray crystallography) motifs. Only a small number of porphyrin–actinide crystal structures have been reported in the literature, indicative of the inherent difficulty in synthesizing these kinds of complexes (as well as the precursors). These structures contain the expanded porphryins, characterized by a bigger core size to accommodate the actinide cations that are considerably larger in diameter than the more commonly used transition metals (Sessler *et al.*, 2001a).

Crystallographic studies of porphyrin- and polypyrrolic-derived ligands with actinides have been limited to tetravalent, pentavalent, and hexavalent cations, including Th(IV), U(IV), Np(V), and U(VI). Table 22.27 lists representative structurally characterized actinide phthalocyanine/porphyrin complexes. The claimed ‘first’ structural determination of an actinide porphyrin complex was

Table 22.27 *Phthalocyanine and porphyrin compounds of the actinides.*

Structure	*References*
phthalocyanines	
Th(phthalocyanine)$_2$	Kobayashi (1978)
U(phthalocyanine)$_2$	Gieren and Hoppe (1971)
U(diphthalocyanine)$_2$I$_{5/3}$	Janczak and Kubiak (1999)
U(diphthalocyanine)$_2$I$_2$	Anczak *et al.* (2000)
UO$_2$(superphthalocyanine)	Day *et al.* (1975)
porphyrins	
Th(tetraphenylporphyrin)$_2 \cdot C_7H_8$	Girolami *et al.* (1988)
[Th(tetraphenylporphyrin)$_2$][SbCl$_6$] $\cdot 2C_7H_8 \cdot CH_2Cl_2$	Girolami *et al.* (1988)
[Th(tetraphenylporphyrin)(OH)$_2$]$_3 \cdot 2H_2O \cdot 3C_7H_{16}$	Kadish *et al.* (1988)
Th(octaethylporphyrin)$_2$	Girolami *et al.* (1994)
Th(octaethylporphyrin)(acetylacetonate)$_2$	Dormond *et al.* (1986)
U(tetraphenylporphyrin)Cl$_2$(THF)	Girolami *et al.* (1987)
UO$_2$(pentaphyrin)	Burrell *et al.* (1991a)
UO$_2$[hexaphyrin(1.0.1.0.0.0)]	Sessler *et al.* (2001b)
UO$_2$(monooxasapphyrin)	Sessler *et al.* (1998)
UO$_2$(β-methoxysapphyrin)	Burrell *et al.* (1991b)
UO$_2$(grandephyrin)	Sessler *et al.* (2002)
UO$_2$(alaskaphyrin)(CHCl$_3$)$_4$	Sessler *et al.* (1992)
[HNEt$_3$]NpO$_2$[hexaphyrin(1.0.1.0.0.0)]	Sessler *et al.* (2001b)

for U(tpp)Cl_2(THF) with U(IV) and doubly deprotonated tetraphenylporphyrin (tpp). X-ray analysis indicates an exclusion complex, where the U(IV) rests above the plane of the porphyrin (defined by four nitrogen atoms) by 1.29 Å; the two chloride ions and a THF molecule are bound to the metal. The porphyrin itself is not rigorously planar, but rather 'saucer-shaped' to promote bonding of the four nitrogens to uranium. Overall, the coordination geometry about uranium consists of what may be described as a 4:3 piano-stool configuration, with the porphyrin comprising the base of the stool. The U–N bond lengths are 2.41(1) Å, while the U–Cl and U–O bond distances are 2.63(1) and 2.50(1) Å, respectively (Girolami *et al.*, 1987). The structure of Th(octaethylporphyrin)(acetylacetonate)$_2$, incidentally, was reported by Dormond *et al.* in 1986.

The structure of UO_2(pentaphyrin) contains an expanded pentadentate porphyrin that takes on a characteristic saddle-shaped geometry with a uranyl ion located at the center. The uranyl ion is bound symmetrically through uranium to all five nitrogen atoms of the ligand, resulting in a nearly ideal, centrally coordinated pentagonal bipyramid, with U–N and U–O bond distances averaging 2.541(3) and 1.756(5) Å, respectively. Distortions from planarity are due to the oversized diameter of the ligand cavity, thus yielding to the bonding requirements of the uranyl ion (Burrell *et al.*, 1991a).

The complexes of both UO_2^{2+} and NpO_2^+ with hexaphyrin(1.0.1.0.0.0) contain the ligand in its oxidized, aromatic form; the crystal structure of the latter is provided in Fig. 22.25. The linear uranyl ion is completely encapsulated within the porphyrin and is oriented perpendicularly to the plane of the six nitrogen atoms; each nitrogen participates in bonding to the uranium, resulting in a distorted hexagonal bipyramid due to non-centered placement of uranium within the macrocycle cavity. The average U–N bond distance is 2.63(1) Å (considerably longer than U–N distances observed in the former pentaphyrin structure) and U–O distances are 1.760(2) Å (typical for the uranyl cation) (Sessler *et al.*, 2001b).

The analogous NpO_2^+ structure reveals less distortion in the ligand geometry as compared to the uranyl complex, presumably due to a better intrinsic 'fit' between the larger NpO_2^+ cation and the hexaaza ligand core. The geometry around the neptunium center, as in the uranium complex, is roughly a hexagonal bipyramid. The two Np–O bond distances [1.762(1) and 1.826(1) Å] are short for the NpO_2^+ cation (1.85 Å in simple metal salts); the difference in length of these bonds is presumably due to a short-contact interaction between a triethylammonium cation nitrogen atom and a neptunyl oxygen atom. In addition, Np–N bond distances average 2.77(2) Å, nearly 0.14 Å longer than in the corresponding uranyl complex (Sessler *et al.*, 2001b).

Thorium–porphyrin compounds are also relatively common in the literature; for example, Th(IV) and octaethylporphyrin (oep) in the presence of acetylacetonate yield Th(oep)(acac)$_2$. The geometry about the Th(IV) center in the crystal structure is described as a nearly ideal octa-coordinated Archimedean antiprism

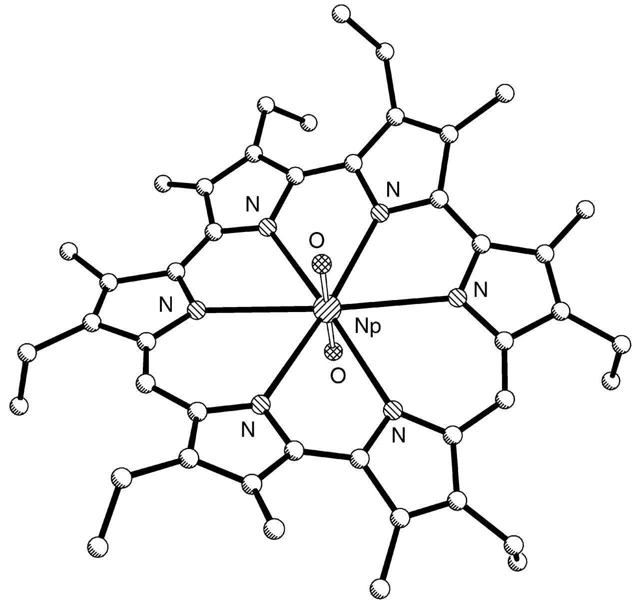

Fig. 22.25 *Crystal strucuture of* [*HNEt*$_3$]*NpO*$_2$[*hexaphyrin*(1.0.1.0.0.0)] *with* [*HNEt*$_3$]$^+$ *and hydrogen atoms omitted* (*Sessler* et al., 2001*b*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode QIVCON*).

provided by the four pyrrolic nitrogen atoms and the four oxygen atoms of the two acetylacetonato ligands. The Th(IV) ion is observed to rest closer to the acteylacetonato oxygen atoms than the nitrogen atoms of the porphyrin, making it an exclusion complex. The Th–N and Th–O bond distances average 2.50 and 2.40 Å, respectively, and the geometry of the acetylacetonate ligand is consistent with known carboxylic acid complexes of related type (Dormond *et al.*, 1986).

The neutral Th(tetraphenylporphyrin)$_2 \cdot C_7H_8$ and its oxidized π-radical cation in the form of [Th(tpp)$_2$][SbCl$_6$] are quite similar and have average Th–N bond distances of 2.55(1) and 2.52(2) Å, respectively. Both metal centers are displaced from the mean plane formed by the pyrrolic nitrogen atoms with an average displacement distance of 1.47 Å for the neutral and 1.45 Å for the cation. The overall geometry around thorium in both the neutral and cationic species may be described as distorted square antiprismatic. Slight differences in the interplanar spacings and twists angles further distinguish the two (Girolami *et al.*, 1988).

Phthalocyanines are porphyrin-like macrocycles (aza rather than methine bridge) and may be described as tetrabenzo-tetraazaporphyrins that, unlike porphyrins, are typically prepared via a metal-templated condensation using phthalonitrile and its derivatives (Sessler and Weghorn, 1997). The

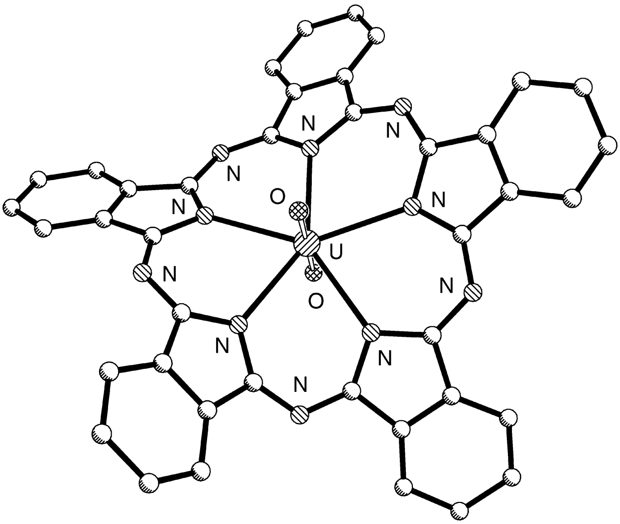

Fig. 22.26 *Crystal strucuture of UO_2(superphthalocyanine) with hydrogen atoms omitted* (*Day* et al., 1975). *The coordinates were obtained from the Cambridge Structural Database* (*refcode CIMINU10*).

uranyl-templated condensation reaction with *o*-dicyanobenzene has yielded an expanded, cyclic five-subunit complex with uranyl known as a 'uranyl superphthalocyanine' (Fig. 22.26). The crystal structure of the UO_2(superphthalocyanine) complex reveals a linear uranyl ion pentacoordinated to the five nitrogen donors of the ligand, creating a near ideal compressed pentagonal bipyramid. The linear [179(1)°] uranyl fragment has an average U–O bond distance of 1.744(8) Å, consistent with other uranyl structures. The average U–N bond distance is 2.524(9) Å and is consistent with other seven-coordinate uranyl/nitrogen complexes. A side-profile of the complex reveals severe distortions from planarity, inherently due to steric strain within the ligand upon metal binding (Day *et al.*, 1975).

22.5 ORGANOACTINIDE COMPOUNDS

Historically, organoactinide chemistry had its origins in the era of the Manhattan Project with unsuccessful attempts to synthesize volatile compounds such as tetraethyl uranium for isotopic enrichment in the gaseous diffusion operations. The synthesis of the unique sandwich compound, uranocene, in 1968, more than previous strides in actinide chemistry with cyclopentadienyl ligands, truly marked the beginning of the organoactinide era, evidenced by the exponential growth thereafter. The subsequent exploration of organoactinide complexes has mainly focused on π-electron interactions with the cyclopentadienyl and cyclooctatetraenyl ligands and their derivatives, resulting in complexes that take advantage of the potential for high coordination numbers as compared to d-block elements. In addition to the π-bonding ability of these ligands, coordinative saturation of the actinide center can be approached with a variety of other σ- or π-donating ligands (including halides, alkyls, and others), thus introducing a seemingly endless number of possibilities for studying coordination, ligand activation, or reactivity (Marks, 1982a).

Organometallic complexes of lanthanide ions are largely ionic in nature, due to poor overlap between the 4f orbitals and ligand molecular orbitals. As a result, all the lanthanides favor the trivalent oxidation state and display similar chemical reactivity, with differences being primarily due to differences in ionic radii. The 5f electrons of the early actinides, however, are not completely shielded by the 6s and 6p electrons, resulting in a significant radial extension of the 5f orbitals that allows for overlap with ligand orbitals and a covalent bonding contribution. Despite this small covalent contribution, ionic character predominates; in fact, in the later actinides, contraction of the 5f orbitals due to increased nuclear charge results in less metal–ligand orbital overlap and in the predominance of the trivalent oxidation state (Bombieri *et al.*, 1998).

The interest surrounding organoactinide chemistry is based on the unique properties of actinide ions (e.g., larger size) that cause them to interact with ligands to produce chemistry that is wholly different from that observed with the d-elements. The larger size of the actinide ions permits coordination numbers (as high as 12) and polyhedra that are unknown or highly unusual for d-elements. This implies a greater control over coordinative unsaturation and a greater number of reactive species can be coordinated and maintained in spatially unusual orientations (Marks, 1982a).

The tremendous growth of organoactinide chemistry since 1968 has resulted in the structural characterization of a wide range of complexes, far too many to be comprehensively presented in this section. The following sections present representative examples, primarily organized in a tabular form, that give the reader an idea of the classes of bonding, as well as the diversity and complexity of organoactinide structural chemistry with brief synopses of select complexes where appropriate. For a more comprehensive treatment of the chemistry and characterization of these compounds, the reader is referred to Chapter 25 of this work, or the annual lanthanide/actinide surveys that are listed in Table 22.28.

22.5.1 Cyclopentadienyl–actinide compounds

Organoactinide complexes of the cyclopentadienyl ligand (η^5-C_5H_5 or Cp) commonly occur as $An(\eta^5\text{-}C_5H_5)_4$, $An(\eta^5\text{-}C_5H_5)_3X$, $An(\eta^5\text{-}C_5H_5)_2X_2$, and $An(\eta^5\text{-}C_5H_5)X_3$ where X is a halogen atom, an alkyl, hydride, or alkoxy group, NCS, BH_4, or other ligands with oxygen, nitrogen, or phosphorus donor sites of varying denticity. Typically, the aromatic nature of the Cp ring

Table 22.28 *Annual lanthanide and actinide organometallic surveys* (1964–1998).

Year	*Reference*	*Year*	*References*
1964–1970	Hayes and Thomas (1971)	1983	Rogers and Rogers (1990)
1971	Calderazzo (1973)	1984–1986	Rogers and Rogers (1991)
1972	Calderazzo (1974)	1987–1990	Rogers and Rogers (1992a)
1973	Marks (1974)	1990	Rogers and Rogers (1992b)
1974	Marks (1975)	1991	Rogers and Rogers (1993)
1975	Marks (1976)	1992	Kilimann and Edelmann (1995)
1976	Marks (1977)	1993	Richter and Edelmann (1996)
1977	Marks (1978)	1994	Gun'ko and Edelmann (1996)
1978	Marks (1979a)	1995	Edelmann and Gun'ko (1997)
1979	Marks (1980)	1996	Edelmann and Lorenz (2000)
1980	Marks (1982b)	1997	Hyeon and Edelmann (2003a)
1981	Ernst and Marks (1987)	1998	Hyeon and Edelmann (2003b)
1982	Ernst (1990)	1999	Gottfriedsen and Edelmann (2005)
		2000	Hyeon *et al.*, (2005)

Table 22.29 *Representative tetrakis–cyclopentadienyl organoactinide complexes.*

Structure	*References*
Cp_4An (An = Th, U, Np)	Kanellakopulos and Bagnall (1972)
Cp_4Th	Maier *et al.* (1993)
Cp_4U	Burns (1974)

lends itself to a η^5 (pentahapto) bonding mode to the actinide metal via its π-electrons. The following discussion will focus on structural motifs present in representative compounds of mono-, bis-, tris-, and tetrakis-cyclopentadienyl organoactinide complexes (Marks, 1979b).

(a) Tetrakis–cyclopentadienyl complexes

The Cp_4An complexes, shown in Table 22.29, are very few in number and are prepared by heating $AnCl_4$ with KCp. A single-crystal X-ray diffraction study of Cp_4U revealed four identical Cp rings arranged in a tetrahedral fashion around the uranium atom with an average U–C distance of 2.538 Å (Burns, 1974). The single-crystal structure of Cp_4Th is isostructural with the uranium analog with a slightly longer average Th–C distance of 2.606 Å (Maier *et al.*, 1993). The arrangement of Cp ligands around the thorium center is illustrated in Fig. 22.27. Furthermore, powder X-ray diffraction techniques have confirmed the isostructural nature of the Th, U, and Np complexes (Kanellakopulos and Bagnall, 1972).

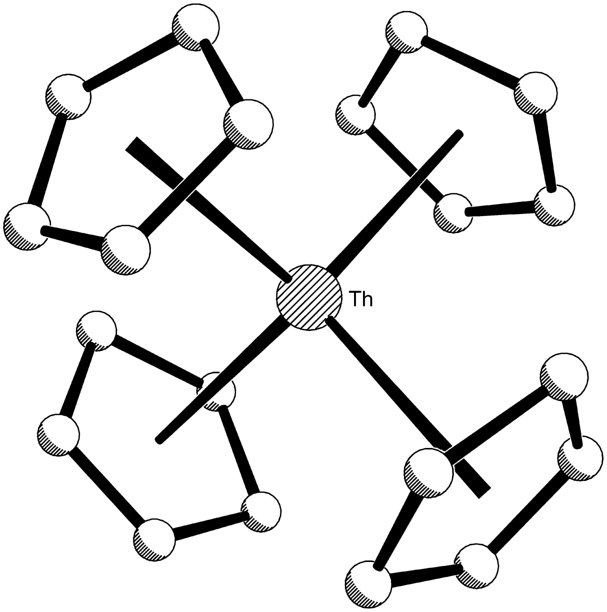

Fig. 22.27 *Crystal strucuture of Cp_4Th with hydrogen atoms omitted* (*Maier* et al., 1993). *The coordinates were obtained from the Cambridge Structural Database* (*refcode LANTEZ*).

(b) Tris-cyclopentadienyl complexes

The tris-cyclopentadienyl complexes of the actinides are known for Th, U, Pu, Am, Cm, Bk, and Cf, but not all have been structurally characterized. The uranium and thorium compounds can be prepared by different methods, including reduction of the tetravalent derivatives or photo-induced β-hydride elimination reactions of Cp_3An–alkyl compounds (Bruno *et al.*, 1982a). The thorium version is a unique example of thorium in the rare trivalent oxidation state and some structural data are available (Kanellakopulos *et al.*, 1974). The uranium complex is a strong Lewis acid and readily favors the formation of adducts with a variety of Lewis bases (Marks, 1982a). Powder diffraction data are available for the Cm, Bk, and Cf compounds, evidence that the trivalent oxidation state is preferred for the heavier actinide elements (Cm, Bk, Cf) (Laubereau and Burns, 1970a,b).

The predominance of Cp_3AnX compounds over Cp_3An (where An is U or Th and X is an anion, Lewis base, or another Cp ring) in organoactinide chemistry depicts the degree to which the tetravalent oxidation state of the metal is preferred over the trivalent state in these complexes, or in cases where the trivalent oxidation state is maintained, the high Lewis acid character of the precursor (Bombieri *et al.*, 1998). In all the Cp_3AnX compounds, the Cp rings are bound in the traditional η^5 (pentahapto) mode to the actinide cation(s) and the complexes have irregular tetrahedral structure (although there are exceptions). Structural analysis has confirmed that this molecular arrangement exists for other complexes in which the X is varied, revealing not only the retention of the irregular tetrahedral structure, but also the aromatic nature of the Cp rings and the regularity of the An–C bond length.

A series of tris-cyclopentadienyl actinide complexes are tabularized in Table 22.30. The series of Cp_3UX complexes, where X is a halide (F, Cl, Br, I), have been structurally characterized (Wong *et al.*, 1965; Ryan *et al.*, 1975; Spirlet *et al.*, 1989; Rebizant *et al.*, 1991). While each has the same distorted tetrahedral environment around the uranium center, none are isostructural, despite the chloride and bromide being geometrically equivalent (both monoclinic, $P2_1/n$). A neutron diffraction structure of the chloride is also available which shows disorder of the Cp rings as well as a crystallographic phase transition between 80 and 100 K (Delapalme *et al.*, 1988). A structure of the iodide derivative is shown in Fig. 22.28.

A large number of compounds exhibit σ-bonding at the fourth site, such as $Cp_3U(n\text{-}C_4H_9)$, $Cp_3U(p\text{-}CH_2C_6H_4Me)$ (Perego *et al.*, 1976), or $Cp_3U[MeC(CH_2)_2]$ (Halstead *et al.*, 1975), with U—C_σ bond distances of 2.426(23), 2.541(15), and 2.48(3) Å, respectively. In the latter complex, while π-bonding of the methylallyl group is possible, the structure clearly indicates σ-type interactions with the metal center. The result is a distorted tetrahedral geometry with approximate C_{3v} symmetry. An interesting case exists with $[Cp_2Th(\eta^5{:}\eta^1\text{-}C_5H_4)]_2$, where the two Cp_2Th centers are bridged by two $\eta^5{:}\eta^1\text{-}C_5H_4$ ligands, each pentahapto to one thorium and monohapto (σ-bonded) to its neighbor (Baker *et al.*, 1974).

Another interesting situation arises in the pyrazolate complex, $Cp_3U(N_2C_3H_3)$, where endo-bidentate η^2-coordination through both nitrogen atoms to the uranium center is observed; the U–N distances are 2.40 and 2.36 Å (Fig. 22.29). In this compound, the ionic nature of the U–N bond suggests that the N–N bond is involved in a non-directional association with the uranium atom; the resulting geometry may be described as a flattened tetrahedron with bonds joining the uranum atom with the center of the three Cp ligands and the midpoint of the N–N pyrazolate bond (Eigenbrot and Raymond, 1981).

The reaction of $Cp_3U \cdot THF$ with the potentially bidentate phosphine ligand, $Me_2P(CH_2)_2PMe_2$, yields the complex $(Cp_3U)_2[Me_2P(CH_2)_2PMe_2]$ where the phosphine ligand adopts an unusual role (Zalkin *et al.*, 1987a). Here, the phosphine acts as a bridging ligand between each Cp_3U fragment rather that chelating in a bidentate mode through each phosphorus atom. In doing so, the steric repulsions are minimized and the coordination number of the uranium is reduced by one, resulting in an 'economical arrangement'. The U–P bond distance is 3.022(2) Å and the U–$Cp_{centroid}$ distance is 2.52(1) Å, both of which

Table 22.30 *Representative tris-cyclopentadienyl organoactinide complexes and derivatives.*

Structure	*Non-Cp Donors (# per center)*	*References*
Cp		
Cp_3Th	–	Kanellakopulos *et al.* (1974)
Cp_3An (An = Cm, Bk, Cf)	–	Laubereau and Burns (1970a,b)
$[(Cp_3U)_2(\mu\text{-}H)][Na(THF)_2]$	H	Le Maréchal *et al.* (1989a)
$Cp_3U(HBBN)$	H(2)	Zanella *et al.* (1987b)
$Cp_3U(BH_4)$	H(3)	Zanella *et al.* (1988)
Cp_3UF	F	Ryan *et al.* (1975)
Cp_3UCl	Cl	Wong *et al.* (1965); Delapalme *et al.* (1988)
$(Cp_3UClCp_3)[Na(18\text{-}crown\text{-}6)(THF)_2]$	Cl	Le Maréchal *et al.* (1989b)
Cp_3UBr	Br	Spirlet *et al.* (1989)
Cp_3UI	I	Rebizant *et al.* (1991)
$[Cp_2Th(\eta^5{:}\eta^1\text{-}C_5H_4)]_2$	C	Baker *et al.* (1974)
$Cp_3U(C{\equiv}CH)$	C	Atwood *et al.* (1976)
$Cp_3U[C{\equiv}CPh]$	C	Atwood *et al.* (1973)
$Cp_3U(n\text{-}C_4H_9)$	C	Perego *et al.* (1976)
$[Cp_3U\text{-}n\text{-}C_4H_9][LiC_{14}H_{28}N_2O_4]$	C	Arnaudet *et al.* (1986)
$Cp_3U(p\text{-}CH_2C_6H_4Me)$	C	Perego *et al.* (1976)
$Cp_3U[MeC(CH_2)_2]$	C	Halstead *et al.* (1975)
$Cp_3U(CHPMe_2Ph)$	C	Cramer *et al.* (1981, 1983)
$Cp_3U(CHPMe_3)$	C	Cramer *et al.* (1988a)
$Cp_3U(CNC_6H_{11})$	C	Kanellakopulos and Aderhold (1973)
$Cp_2Cp^*U(CH_2Ph)$	C	Kiplinger *et al.* (2002a)
$Cp_3U(NCR)$ (R = ^{n}Pr, ^{i}Pr)	N	Adam *et al.* (1993)
Cp_3UNPh_2	N	Cramer *et al.* (1987a)
$Cp_3U(NCS)$	N	Spirlet *et al.* (1993a)
$Cp_3UNC(Me)CHP(Me)(Ph)_2$	N	Cramer *et al.* (1984a)
$Cp_3U(NPPh_3)$	N	Cramer *et al.* (1988b)
$Cp_3U(NCBH_3)(NCMe)$	N(2)	Adam *et al.* (1990)
$[Cp_3U(NCMe)_2]_2[UO_2Cl_4]\cdot(C_4H_6)_2$	N(2)	Bombieri *et al.* (1983a)
$[Cp_3U(NCMe)_2][CpThCl_4(NCMe)]$	N(2); Cl(4), N	Rebizant *et al.* (1987)
$[Cp_3U(NCMe)_2][BPh_4]$	N(2)	Aslan *et al.* (1988)
$Cp_3U(NCS)(NCMe)$	N(2)	Aslan *et al.* (1988); Fischer *et al.* (1978)
$Cp_3U(N_2C_3H_3)$	N(2)	Eigenbrot and Raymond (1981)
$[Ph_4As][Cp_3U(NCS)_2]$	N(2)	Bombieri *et al.* (1983b)
$Cp_3U(OR)$ (R = $C(CF_3)_2CCl_3$, Ph)	O	Knösel *et al.* (1987); Spirlet *et al.* (1990a)
$Cp_3U(THF)$	O	Wasserman *et al.* (1983)
$Cp_3U(OSiPh_3)$	O	Porchia *et al.* (1989)
$Cp_3Np(OPh)$	O	De Ridder *et al.* (1996a)
$(Cp_3U)_2(Me_2P(CH_2)_2PMe_2)$	P	Zalkin *et al.* (1987a)
$Cp_3U(SMe)$	S	Leverd *et al.* (1996)

Table 22.30 (*Contd.*)

Structure	*Non-Cp Donors (# per center)*	*References*
Cp		
$Cp_3U[\eta^2\text{-MeC=N}(C_6H_{11})]$	C, N	Zanella *et al.* (1985)
$Cp_3U[(NEt_2)C=N(C_6H_3Me_2\text{–}2,6)]$	C, N	Zanella *et al.* (1987a)
$Cp_3U(NPh)(O)CCHPMe_2Ph$	O, N	Cramer *et al.* (1987b)
$Cp_3U(\eta^2\text{-OCCH})P(Me)(Ph)_2$	C, O	Cramer *et al.* (1982)
*Cp**		
$(Cp^*)_3ThH$	H	Evans *et al.* (2001)
$(Cp^*)_3UX$ (X = F, Cl)	F; Cl	Evans *et al.* (2000)
$(Cp^*)_3U(CO)$	C	Evans *et al.* (2003a)
$(Cp^*)_3U(\eta^1\text{-}N_2)$	N	Evans *et al.* (2003b)
MeCp, Me_4Cp, $PhCH_2Cp$		
$(Me_4Cp)_3UCl$	Cl	Cloke *et al.* (1994)
$(PhCH_2Cp)_3UCl$	Cl	Leong *et al.* (1973)
$(Me_4Cp)_3U(CO)$	C	Parry *et al.* (1995)
$(MeCp)_3U(NH_3)$	N	Rosen and Zalkin (1989)
$(MeCp)_3U(NPh)$	N	Brennan and Andersen (1985)
$(MeCp)_3U[N(CH_2CH_2)_3CH]$	N	Brennan *et al.* (1988a)
$(MeCp)_3U(C_7H_{10}N_2)$	N	Zalkin and Brennan (1987)
$(MeCp)_3U(OPPh_3)$	O	Brennan *et al.* (1986b)
$[(MeCp)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-PhNCO}]$	O; C, N	Brennan and Andersen (1985)
$(MeCp)_3U(PMe_3)$	P	Brennan and Zalkin (1985)
$(MeCp)_3U[P(OCH_2)_3CEt]$	P	Brennan *et al.* (1988a)
$(MeCp)_3U(C_4H_8S)$	S	Zalkin and Brennan (1985)
$[(MeCp)_3U]_2[\mu\text{-S}]$	S	Brennan *et al.* (1986b)
$[(MeCp)_3U]_2[\mu\text{-}\eta^1,\eta^2\text{-}CS_2]$	S; C, S	Brennan *et al.* (1986a)
Cp′, Cp″, Cp^{tt}, $(SiMe_3)_2CHCp$		
$(Cp'')_3Th$	–	Blake *et al.* (1986a, 2001)
$(Cp^{tt})_3Th$	–	Blake *et al.* (2001)
$(Cp')_3U$	–	Zalkin *et al.* (1988a)
$(Cp'')_3ThCl$	Cl	Blake *et al.* (1998)
$(Cp^{tt})_3ThCl$	Cl	Blake *et al.* (1998)
$(Cp'')_2(Cp^*)ThCl$	Cl	Blake *et al.* (1998)
$[(SiMe_3)_2CHCp]_3ThCl$	Cl	Blake *et al.* (1998)
$(Cp'')_3UCl$	Cl	Blake *et al.* (1998)
$(Cp')_3UCH=CH_2$	C	Schock *et al.* (1988)
$[Na(18\text{-crown-}6)][(Cp')_3U\text{-}N_3\text{-}U(Cp')_3]$	N	Berthet *et al.* (1991a)
$[(Cp')_3U]_2[\mu\text{-O}]$	O	Berthet *et al.* (1991b)

* Semicolons used to differentiate coordination to different metal centers or different structures.

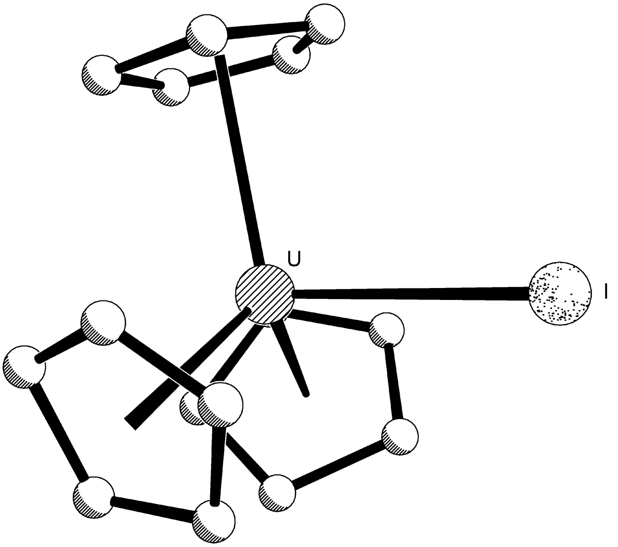

Fig. 22.28 *Crystal strucuture of* Cp_3UI *with hydrogen atoms omitted* (Rebizant et al., 1991). *The coordinates were obtained from the Cambridge Structural Database* (*refcode JIKGOZ*).

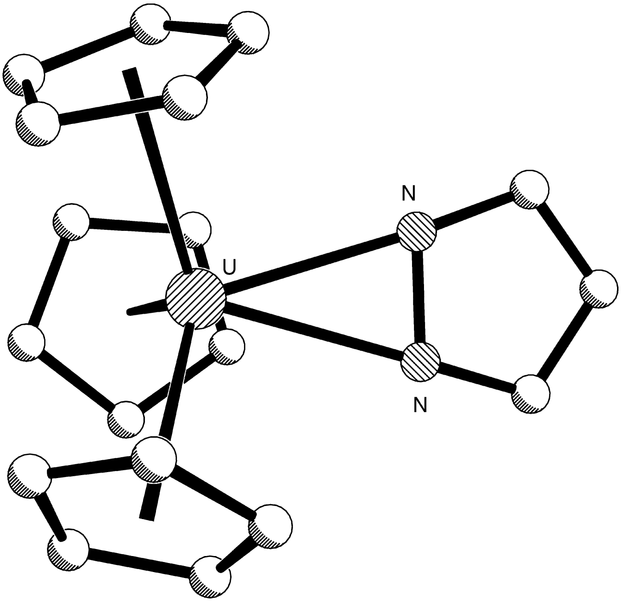

Fig. 22.29 *Crystal strucuture of* $Cp_3U(N_2C_3H_3)$ *with hydrogen atoms omitted* (*Eigenbrot and Raymond,* 1981). *The coordinates were obtained from the Cambridge Structural Database* (*refcode CPYRZU*).

are comparable to the distances observed in the (MeCp)$_3$U(PMe$_3$) complex of 2.972(6) and 2.52(1) Å, respectively (Brennan and Zalkin, 1985).

Several novel tris-cyclopentadienyl complexes have also been studied structurally. In the anionic portion of [Ph$_4$As][Cp$_3$U(NCS)$_2$], the uranium center is surrounded by a trigonal planar arrangement of Cp ligands in the equatorial plane, and the thiocyanate ligands occupy axial positions with U–N bond distances of 2.46 and 2.50 Å (Bombieri *et al.*, 1983a). The first example of the opposite situation, a cationic organoactinide species, was observed in [Cp$_3$U(NCMe)$_2$]$_2$[UO$_2$Cl$_4$] · (C$_4$H$_6$)$_2$, formed from the reaction of Cp$_3$UCl in MeCN with gaseous butadiene and traces of O$_2$ (Fig. 22.30). The cation contains uranium in the tetravalent oxidation state with trigonal bipyramidal geometry (D$_{3h}$), while the anion has hexavalent uranium with approximate D$_{2h}$ symmetry (Bombieri *et al.*, 1983b). Another cationic organoactinide species is evident in [Cp$_3$U(NCMe)$_2$][CpThCl$_4$(NCMe)] with the familiar trigonal bipyramidal geometry. An interesting aspect of this structure is the simultaneous presence of tetravalent thorium in the anion with octahedral coordination (Rebizant *et al.*, 1987).

In the compound Cp$_3$U(NPh)(O)CCHPMe$_2$Ph, η^2 coordination of the oxygen and nitrogen atoms of the neutral ligand creates a four-membered ring. The U–N and U–O bond lengths are 2.45(1) and 2.34(1) Å, respectively, indicating the presence of single bonds which are typical for donor atoms carrying a partial negative charge. Due to the sterically crowded nature of the uranium center, the formation of this *cis*-Cp$_3$UXY-type compound is quite rare; its highly crowded nature is evident in the small ligand bite distance (2.22(2) Å), elongated U–C$_{Cp}$ bonds (average 2.84(2) Å vs 2.72 Å for Cp$_3$UBr), and compressed Cp$_{centroid}$–U–Cp$_{centroid}$ angles (Cramer *et al.*, 1987b).

A rare instance of a neptunium-containing organometallic complex (with tetravalent neptunium) is Cp$_3$Np(OPh). Considering the oxygen atom and the centers of the three Cp ligands as vertices, the structure has flattened tetrahedral geometry and near C$_{3v}$ symmetry (De Ridder *et al.*, 1996a). The Np–O bond

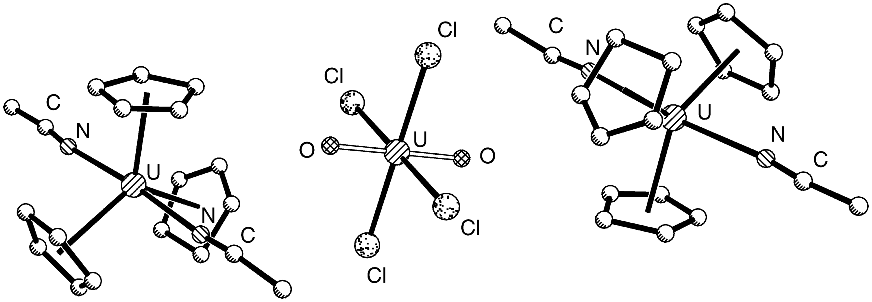

Fig. 22.30 *Crystal strucuture [Cp$_3$U(NCMe)$_2$]$_2$[UO$_2$Cl$_4$] · (C$_4$H$_6$)$_2$ with (C$_4$H$_6$) and hydrogen atoms omitted (Bombieri* et al., *1983b). The coordinates were obtained from the Cambridge Structural Database (refcode BUJPOL).*

distance is 2.136(7) Å, considerably shorter than that in $CpNpCl_3(OPMePh_2)_2$ of 2.277(6) Å (Bagnall *et al.*, 1986). $Cp_3Np(OPh)$ is isostructural with its uranium analog $Cp_3U(OPh)$; the U–O bond distance is slightly shorter, however, at 2.119(7) Å, and the flattened tetrahedral geometry is maintained (Spirlet *et al.*, 1990a).

The structure of $[(MeCp)_3U]_2[\mu\text{-}S]$ shows sulfur occupying a bridging role between two $(MeCp)_3U$ moieties, with an average U–S distance of 2.60(1) Å, one of the shortest ever observed. The most interesting aspect of this structure is the bent U–S–U angle of 164.9(4)°. These observed structural features are consistent with a class of bridging sulfur transition metal complexes with nearly linear M–S–M angles (159–180°) and M–S bond lengths shorter than expected for a M–S single bond. This trend suggests that the bridging sulfur may act as a π-donor or π-acceptor towards the metal center; an alternative explanation, however, is an electrostatic one, where steric repulsion due to the bulky $(MeCp)_3U$ groups accounts for the observed structural features (Brennan *et al.*, 1986b).

The first example of end-on binding of N_2 has been observed in the structure of $(Cp^*)_3U(\eta^1\text{–}N_2)$. A solution of $(Cp^*)_3U$ under N_2 at 80 psi darkens with the precipitation of hexagonal crystals of the desired compound. Binding is reversible, with quantitative regeneration of $(Cp^*)_3U$ upon lowering the pressure to 1 atm. The three Cp* ligands are bound pentahapto to the uranium center, with the remaining coordination site filled by N_2, resulting in a trigonal pyramidal geometry (Evans *et al.*, 2003b). The U–N bond distance of 2.492(10) Å is comparable to the 2.485(9) Å $U\text{–}C_{CO}$ distance observed in $(Cp^*)_3U(CO)$. Here, the $C{\equiv}O$ ligand is isoelectronic with N_2 and also binds end-on to the uranium center through carbon (Evans *et al.*, 2003a). The isostructural nature of the two compounds is illustrated in Fig. 22.31.

(c) Bis-cyclopentadienyl complexes

Like the tris-compounds, the prevalance of $Cp_2(Th,U)X_2$ compounds over $Cp_2(Th,U)X$ compounds reveals the large preference for the tetravalent oxidation state in these complexes. However, the $Cp_2(Th,U)X_2$ are considerably unstable compared to transition metal and lanthanide analogs towards intermolecular ligand redistribution (Bombieri *et al.*, 1998). For example, Cp_2UCl_2, produced by the reaction of TlCp and UCl_4 in the presence of 1,2-dimethoxyethane (DME), is actually a mixture of Cp_3UCl and $CpUCl_3(DME)$ (Ernst *et al.*, 1979).

The pentamethylcyclopentadienyl ligand (Cp*) has been utilized in organoactinide chemistry to circumvent many of the problems encountered with the unstable $Cp_2(Th,U)X_2$ compounds. As compared to the unsubstituted analog (Cp), Cp* provides increased covalent character of the Cp–M bond, stronger π-donor ability, kinetic stabilization due to steric shielding of the metal, and increased thermal stability. In addition to inhibiting the formation of polymeric structures, the Cp* improves many solution chemistry properties, including

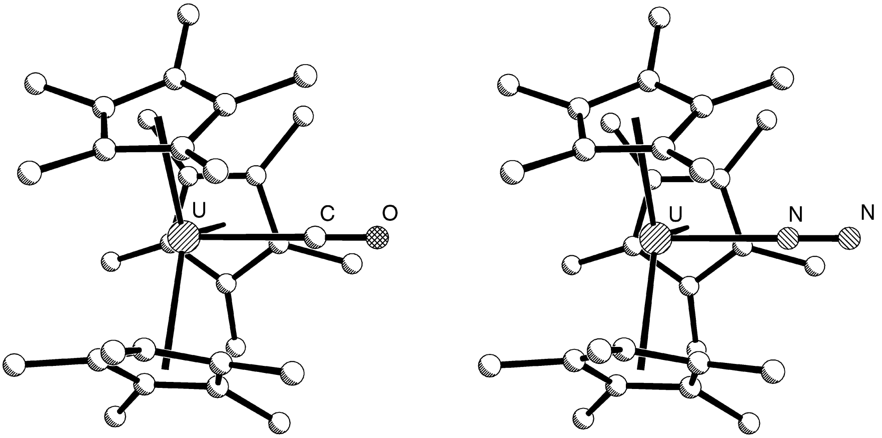

Fig. 22.31 *Crystal strucutures of* ($Cp^*)_3U(CO)$ (*Evans* et al., 2003*a*) *and* $(Cp^*)_3U(\eta^1\text{-}N_2)$ (*Evans* et al., 2003*b*) *with hydrogen atoms omitted. The coordinates were obtained from the Cambridge Structural Database* (*refcodes IMUVAN and ENABUQ*).

crystallizability, thus promoting its widespread use in organoactinide chemistry (Bombieri *et al.*, 1998).

The addition of methyl groups to the Cp rings promotes coordinative unsaturation of the actinide metal by preventing the binding of other sterically demanding ligands. In addition, the methyl groups stabilize the organoactinide complexes with respect to ligand redistribution reactions, a feature that dominates the solution chemistry of unsubstituted f-element metallocenes. Ligand rearrangement prevents the cystallization of the Cp_2UCl_2 and $(Cp^*)(Cp)UCl_2$, as well as $[(^t Bu)Cp]_2UCl_2$ and $(Cp')_2UCl_2$ (Lukens *et al.*, 1999). In contrast, the $(Cp^*)_2UCl_2$ complex (Fig. 22.32) has normal, monomeric pseudotetrahedral ‘bent-sandwich’ configuration and has no tendency to undergo ligand redistribution to form the unknown $(Cp^*)_3UCl$ (Spirlet *et al.*, 1992a).

A large number of representative bis-cyclopentadienyl actinide complexes are listed in Table 22.31, again illustrating the magnitude and diversity of organoactinide structural chemistry. The list is dominated by Cp* ligands (and other Cp derivative with bulky substituents), a tribute to its prevalence in organometallic chemistry and its usefulness in preventing ligand redistribution.

The series of compounds $Cp_2ThX_2(Me_2P(CH_2)_2PMe_2)$, where X = Cl, Me, or $CH_2C_6H_5$, have been synthesized and structurally characterized. The chloro derivative (Fig. 22.33) was synthesized from the reaction of sodium cyclopentadienide with $ThCl_4 \cdot (CH_3)_2PCH_2CH_2P(CH_3)_2$ in THF at 203 K. The latter two derivatives were synthesized from the reaction of the chloro derivative with methyllithium and benzyllithium, respectively, at 228 K. In accordance with Keppert’s rules, the monodentate ligand with the shortest bond distance in each

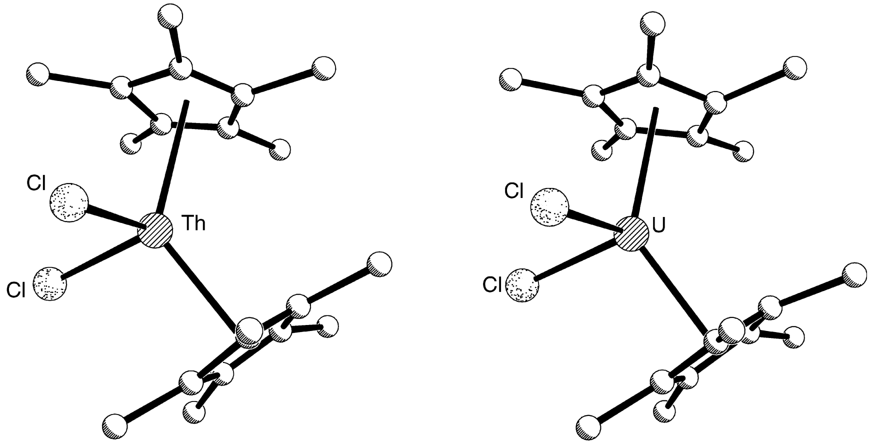

Fig. 22.32 *Crystal strucutures of* $(Cp^*)_2ThCl_2$ *and* $(Cp^*)_2UCl_2$ *with hydrogen atoms omitted* (*Spirlet* et al., 1992*a*). *The coordinates were obtained from the Cambridge Structural Database* (*refcodes VUJRAT and VUJPUL*).

structure (the Th–$Cp_{centroid}$ bond) occupies the site *trans* to the bidentate $Me_2P(CH_2)_2PMe_2$ ligand, thus making the bulky Cp ligands *cis* to one another. This is, in many ways, counter-intuitive in that the bulky Cp ligands should prefer a *trans* configuration to each other to lessen steric hindrance. The average Th–P bond lengths in the above three compounds are 3.147(1), 3.121(1), and 3.19(3) Å, respectively (Zalkin *et al.*, 1987b,c).

The compounds $(Cp^*)_2UCl_2(C_3H_4N_2)$, $(Cp^*)_2UCl(C_3H_3N_2)$, and $(Cp^*)_2U(C_3H_3N_2)_2$ exhibit two bonding modes for the pyrazole/pyrazolate ligand. In the first compound, the pyrazole ligand acts as a neutral donor, with donation to the uranium center occurring through only a single nitrogen atom. In the latter two complexes, the pyrazole ligand is in the form of the pyrazolate anion and donates two nitrogen atoms per ligand to the uranium center. In the mono-chloro complex, the geometry can be approximated as tetrahedral by considering the two Cp* centroids, the chloride, and the midpoint of the N–N bond as corners. The U–N nitrogen bond length trend is supported by the nature of the ligand: the longest U–N bonds (2.607(8) Å average) occur for the neutral pyrazole ligand, while the anionic ligand yields the shortest U–N bonds. In the monopyrazolate complex, the two U–N bond lengths are 2.351(5) and 2.349(5) Å, while the dipyrazolate distances are 2.403(4), 2.360(5), 2.363(9), and 2.405(5) Å. Interestingly, in the latter case, the two 'internal' U–N bonds are shorter (greater crowding) than the two 'external' bonds. The pyrazolate U–N bond lengths are consistent with the $Cp_3U(N_2C_3H_3)$ structure (1.36, 1.40 Å) (Eigenbrot and Raymond, 1982).

Table 22.31 *Representative bis-cyclopentadienyl organoactinide complexes and derivatives.*

Structure	*Non-Cp donors (# per center)*	*References*
Cp		
$Cp_2U(BH_4)_2$	H(6)	Zanella *et al.* (1977)
$[\{Cp_2U(\mu\text{-}Cl)\}_3(\mu_3\text{-}Cl)_2][\{CpUCl_2\}_2(\mu\text{-}Cl)_3]\cdot 2(CH_2Cl_2)$	Cl(4); Cl(5)	Arliguie *et al.* (1994a)
$Cp_2ThX_2(Me_2P(CH_2)_2PMe_2)$ ($X = Me, Cl, CH_2C_6H_5$)	C(2), P(2); Cl(2), P(2)	Zalkin *et al.* (1987b,c)
$[Cp_2U(\mu\text{-}CH)(CH_2)P(Ph)_2]_2\cdot(C_2H_5)_2O$	C(3)	Cramer *et al.* (1978, 1980)
$M\text{-}[Cp_2U(\mu\text{-}S\text{-}CH)(CH_2)P(Ph)_2]_2\cdot C_5H_{12}$	C(3)	Cramer *et al.* (1980)
$Cp_2Th[(CH_2)(CH_2)PPh_2]_2$	C(4)	Cramer *et al.* (1995a)
*Cp**		
$[(Cp^*)_2Th(H)(\mu\text{-}H)]_2$	H(3)	Broach *et al.* (1979)
$[K(18\text{-}crown\text{-}6)][(Cp^*)_2U(Cl)H_6Re(PPh_3)_2]\cdot 0.5(C_6H_6)$	H(3), Cl	Cendrowski-Guillaume *et al.* (1994)
$(Cp^*)_2U(H)(Me_2P(CH_2)_2PMe_2)$	H, P(2)	Duttera *et al.* (1982)
$(Cp^*)_2MCl_2$ ($M = Th, U$)	Cl(2)	Spirlet *et al.* (1992a)
$[(Cp^*)_2U(\mu\text{-}Cl)]_3$	Cl(2)	Manriquez *et al.* (1979)
$[Li(TMED)][(Cp^*)_2UCl(NC_6H_5)]$	Cl, N	Arney and Burns (1995)
$(Cp^*)_2Th(Cl)(HNC(Me)NC(Me)CHCN)$	Cl, N(2)	Sternal *et al.* (1987)
$(Cp^*)_2UCl(\eta^2\text{-}(N,N')\text{-}MeNN{=}CPh_2)$	Cl, N(2)	Kiplinger *et al.* (2002b)
$(Cp^*)_2UCl_2(C_3H_3N_2)$	Cl, N(2)	Eigenbrot and Raymond (1982)
$(Cp^*)_2UCl_2(C_3H_4N_2)$	Cl(2), N	Eigenbrot and Raymond (1982)
$(Cp^*)_2UCl_2(HNPPh_3)$	Cl(2), N	Cramer *et al.* (1989)
$(Cp^*)_2UCl_2(HNSPh_2)$	Cl(2), N	Cramer *et al.* (1995b)
$(Cp^*)_2ThCl[O_2C_2(CH_2CMe_3)(PMe_3)]$	Cl, O(2)	Moloy *et al.* (1983)
$[(Cp^*)_2ThCl\{\mu\text{-}CO(CH_2CMe_3)CO\}]_2$	Cl, O(2)	Fagan *et al.* (1980)
$(Cp^*)_2ThCl[\eta^2\text{-}COCH_2CMe_3]$	Cl, C, O	Fagan *et al.* (1980)
$(Cp^*)_2ThBr_2(THF)$	Br(2), O	Edelman *et al.* (1995)
$[(Cp^*)_2Th(Me)][B(C_6F_5)_4]$	C	Yang *et al.* (1991)
$(Cp^*)_2Th[(CH_2)_2SiMe_2]$	C(2)	Bruno *et al.* (1982b)
$(Cp^*)_2Th(CH_2SiMe_3)_2$	C(2)	Bruno *et al.* (1983)
$(Cp^*)_2Th(CH_2CMe_3)_2$	C(2)	Bruno *et al.* (1986)
$(Cp^*)_2Th(\eta^4\text{-}C_4H_6)$	C(4)	Smith *et al.* (1986)
$[(Cp^*)_2Th(Me)(THF)_2][BPh_4]$	C, O(2)	Lin *et al.* (1987)
$[(Cp^*)_2U(Me)(OTf)]_2$	C, O(2)	Kiplinger *et al.* (2002b)
$(Cp^*)_2U(N\text{-}2,4,6\text{-}{}^tBu_3C_6H_2)$	N	Arney and Burns (1995)
$(Cp^*)_2U(NC_6H_5)_2$	N(2)	Arney *et al.* (1992)
$(Cp^*)_2U[NH(C_6H_3Me_2\text{–}2,6)]_2$	N(2)	Straub *et al.* (1996)
$(Cp^*)_2U(NCPh_2)_2$	N(2)	Kiplinger *et al.* (2002c)
$(Cp^*)_2U(NSPh_2)_2$	N(2)	Ariyaratne *et al.* (2002)
$(Cp^*)_2U(C_3H_3N_2)_2$	N(4)	Eigenbrot and Raymond (1982)
$[(Cp^*)_2Th(\mu\text{-}O_2C_2Me_2)]_2$	O(2)	Manriquez *et al.* (1978)

Table 22.31 (*Contd.*)

Structure	*Non-Cp donors (# per center)*	*References*
*Cp**		
$(Cp^*)_2U(\eta^2\text{-}(N,N')\text{-MeNN=CPh}_2)(OTf)$	O, N(2)	Kiplinger *et al.* (2002b)
$[(Cp^*)_2U(OMe)]_2(\mu\text{-PH})$	O, P	Duttera *et al.* (1984)
$(Cp^*)_2Th(PPh_2)_2$	P(2)	Wrobleski *et al.* (1986a)
$(Cp^*)_2U(SMe)_2$	S(2)	Lescop *et al.* (1999)
$(Cp^*)_2Th[S(CH_2)_2Me]_2$	S(2)	Lin *et al.* (1988)
$[Na(18\text{-crown-}6)][(Cp^*)_2U(S^tBu)(S)]$	S(2)	Ventelon *et al.* (1999)
$(Cp^*)_2U(S^tBu)(S_2CS^tBu)$	S(3)	Lescop *et al.* (1999)
$(Cp^*)_2ThS_5$	S(4)	Wrobleski *et al.* (1986b)
MeCp		
$[(MeCp)_2U]_2(\mu\text{-NR})_2$ $(R = Ph, SiMe_3)$	N(2)	Brennan *et al.* (1988b)
Cp′, Cp″, Cp^{tt}, *(*^{t}*Bu)*$_2$*Cp*		
$(Cp'')_2UX_2$ $(X = BH_4, Cl, OAr)$	H(6); Cl(2); O(2)	Hunter and Atwood (1984)
$(Cp'')_2UX_2$ $(X = BH_4, Br, I)$	H(6); Br(2); I(2)	Blake *et al.* (1995)
$[({}^tBu)_2Cp]_2UX_2$ $(X = F, Cl)$	F(2); Cl(2)	Lukens *et al.* (1999)
$[(Cp'')_2UF(\mu\text{-F})]_2$	F(3)	Lukens *et al.* (1999)
$[(Cp'')_2U(\mu\text{-BF}_4)(\mu\text{-F})]_2$	F(4)	Hitchcock *et al.* (1984)
$(Cp'')_2MCl_2$ $(M = Th, U)$	Cl(2)	Blake *et al.* (1995)
$(Cp'')_2U(\mu\text{-Cl})_2Li(PMDETA)$	Cl(2)	Blake *et al.* (1988a)
$(Cp'')_2U(\mu\text{-Cl})_2Li(THF)_2$	Cl(2)	Blake *et al.* (1988b)
$[PPh_4][(Cp'')_2UCl_2]$	Cl(2)	Blake *et al.* (1988a)
$[\{({}^tBu)_2Cp\}_2U]_2(\mu\text{-Cl})_2$	Cl(2)	Zalkin *et al.* (1988b)
$[(Cp'')_2U(\mu\text{-X})]_2$ $(X = Cl, Br)$	Cl(2); Br(2)	Blake *et al.* (1986b)
$(Cp'')_2UX_2$ $(X = Cl, Me)$	Cl(2); C(2)	Lukens *et al.* (1999)
$[(Cp^{tt})_2Th(Cl)\{CH(SiMe_3)_2\}]$	Cl, C	Edelman *et al.* (1995)
$(Cp'')_2UCl[CN(C_6H_3Me_2)]_2$	Cl, C(2)	Zalkin and Beshouri (1989a)
$(Cp'')_2UCl(NCSiMe_3)_2$	Cl, N(2)	Zalkin and Beshouri (1989b)
$[({}^tBu)_2Cp]_2Th(\mu,\eta^3\text{-P}_3)Th(Cl)[({}^tBu)_2Cp]_2$	Cl, P(3)	Scherer *et al.* (1991)
$(Cp'')_2UBr(CN^tBu)_2$	Br, C(2)	Beshouri and Zalkin (1989)
$[(Cp')_2U(\mu\text{-O})]_3$	O(2)	Berthet *et al.* (1993)
$[(Cp'')_2U(\mu\text{-O})]_2$	O(2)	Zalkin and Beshouri (1988)
$[({}^tBu)_2Cp]_2Th(\mu,\eta^3,\eta^3\text{-P}_6)Th[({}^tBu)_2Cp]_2$	P(3)	Scherer *et al.* (1991)
$[({}^tBu)_2Cp]_2Th(\mu,\eta^{2:1:2:1}\text{-As}_6)Th[({}^tBu)_2Cp]_2$	As(3)	Scherer *et al.* (1994)

* Semicolons used to differentiate coordination to different metal centers or different structures.

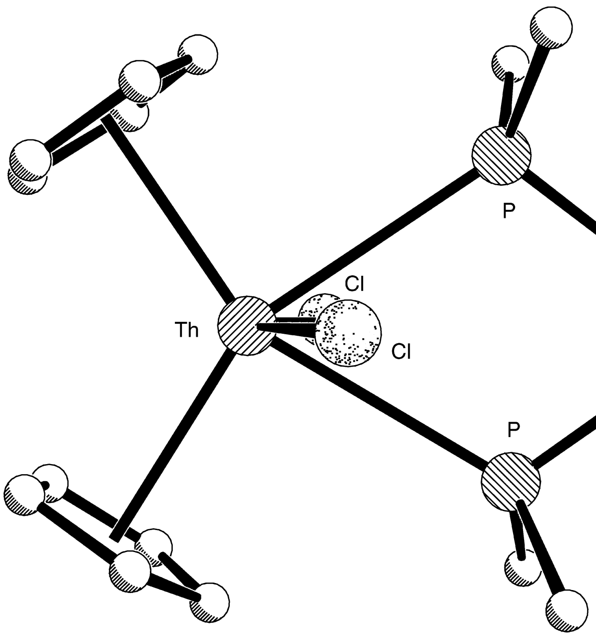

Fig. 22.33 *Crystal strucuture of* $Cp_2ThCl_2(Me_2P(CH_2)_2PMe_2)$ *with hydrogen atoms omitted* (*Zalkin* et al., 1987*b*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode BIXVOT10*).

The first example of an organoactinide polysulfide reveals the unique twist-boat conformation of a ThS_5 ring, generated by the reaction of $(Cp^*)_2ThCl_2$ with Li_2S_5. The crystal structure of $(Cp^*)_2ThS_5$ (Fig. 22.34) is unique compared to transition metal analogs, such as Cp_2TiS_5, Cp_2ZrS_5, and Cp_2HfS_5, which strictly exhibit a MS_5 chair conformation. This anomaly in conformation is likely due to the coordination of four ring sulfur atoms to the uranium center, rather than two. Two types of bonding are thought to occur: two Th–S bonds at 2.768(4) Å are ionic in nature and two at 3.036(3) Å are dative in nature (Wrobleski *et al.*, 1986b).

Many polynuclear bis-organoactinide complexes with bridging hydride, halide, and oxo groups are known. For example, the single-crystal neutron diffraction structure of the dimeric compound $[(Cp^*)_2Th(H)(\mu\text{-}H)]_2$, one of the first examples of an actinide hydride complex, contains both bridging and terminal hydrides. Two $(Cp^*)_2Th(H)$ moieties, each containing a terminal hydride, are connected by two bridging hydrides; the terminal and bridging Th–H distances are 2.03(1) and 2.29(3) Å, respectively, with a Th–Th separation of 4.007(8) Å (Broach *et al.*, 1979).

The trimeric bridging halide complex, $[(Cp^*)_2U(\mu\text{-}Cl)]_3$, contains three $(Cp^*)_2U$ units, each connected by a bridging chloride and pseudotetrahedral

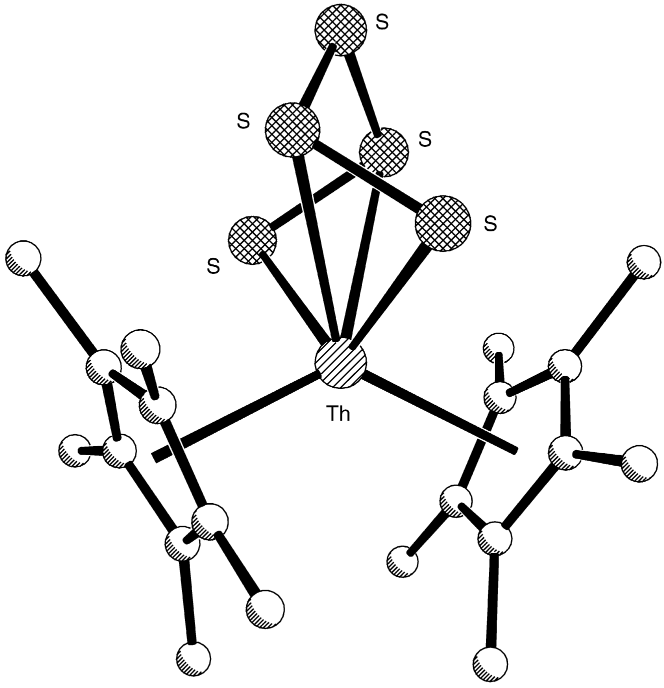

Fig. 22.34 *Crystal strucuture of* $(Cp^{*})_2ThS_5$ *with hydrogen atoms omitted* (*Wrobleski* et al., 1986*b*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode DIJRET*).

geometry around each uranium. The cyclic –U–Cl–U–Cl–U–Cl– moiety comprises a nearly planar six-membered ring, with average U–Cl, U–C, and U–U distances of 2.901(5), 2.76(3), and 5.669(2) Å, respectively (Manriquez *et al.*, 1979). Finally, the bridging oxo complex, $[(Cp'')_2U(\mu\text{-}O)]_2$, contains two $(Cp'')_2U$ units connected by two bridging oxo ligands and a geometry similar to the chloro complex (Fig. 22.35). The average U–O and U–C distances are 2.213(8) and 2.77(4) Å, respectively. The average U–$Cp_{centroid}$ distance is 2.496 Å (Zalkin and Beshouri, 1988). For further examples of bridging complexes, the reader is referred to Table 22.31.

(d) Mono-cyclopentadienyl complexes

Mono-cyclopentadienyl organoactinide complexes, while less common, are typically Lewis-base adducts of the type $CpAnX_3L_n$. These complexes are usually sterically and electronically unsaturated, making their synthesis and subsequent crystallization quite challenging. Representative complexes for which structural data are available are listed in Table 22.32. The structures of

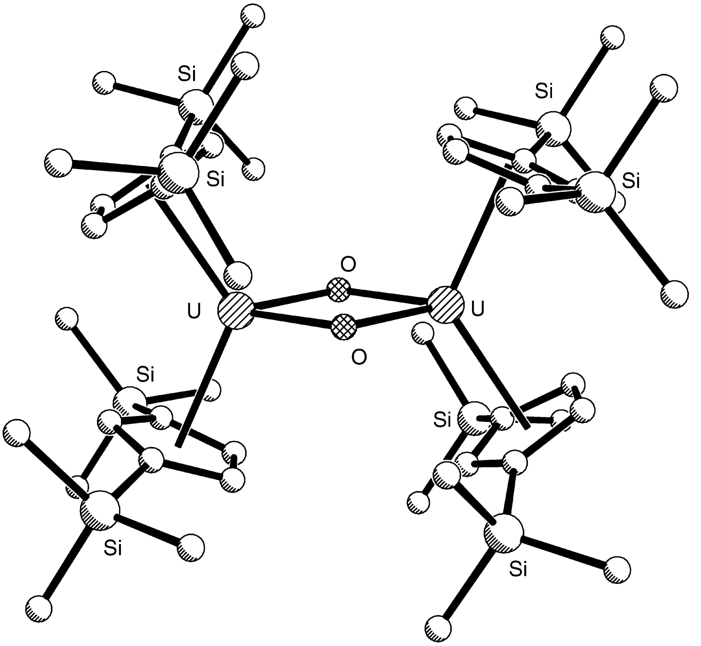

Fig. 22.35 *Crystal strucuture of* $[(Cp'')_2U(\mu\text{-}O)]_2$ *with hydrogen atoms omitted* (*Zalkin and Beshouri,* 1988). *The coordinates were obtained from the Cambridge Structural Database* (*refcode GIFNIS*).

$CpUCl_3(OPPh_3)_2 \cdot THF$ (Bombieri *et al.*, 1978c; Bagnall *et al.*, 1984) and $CpUCl_3[OP(NMe_2)_3]_2$ (Bagnall *et al.*, 1984) show an octahedral environment around the uranium centers with the neutral ligands occupying the *cis* coordination sites. In addition, the chlorine ligands are arranged in a *mer* fashion (as opposed to a *fac* arrangement) and the Cp ligands are *trans* to one of the neutral ligands. One of the few neptunium-containing organoactinide complexes, $CpNpCl_3(OPMePh_2)_2$, is analogous to the uranium structures described above (Fig. 22.36) (Bagnall *et al.*, 1986).

The compound $[CpU(CH_3COO)_2]_4O_2$ has four seven-coordinate uranium centers, each with distorted pentagonal bipyramidal geometry. The pentagonal arrangement around a given uranium center is defined by five oxygen atoms from four different acetate ligands. Two bridging acetates are monodentate simultaneously with respect to two neighboring uranium atoms. The remaining two bridging acetate groups take on a more complex role, each joining two neighboring uranium centers, with one oxygen being mondentate toward one uranium and the other oxygen being bidentate toward both uranium atoms. The remaining coordination sites are occupied by bridging oxo ligands (joining two pairs of uranium atoms), providing the apex of each pentagonal bipyramid,

Table 22.32 *Representative mono-cyclopentadienyl organoactinide complexes.*

Structure	*Non-Cp donors (# per center)*	*References*
Cp		
$CpU(BH_4)_3$	H(9)	Baudry *et al.* (1989a)
$[CpTh_2(O\text{-}^iPr)_7]_3$	O(5)	Barnhart *et al.* (1995b)
$CpUCl(acac)_2(OPPh_3)$	Cl, O(5)	Baudin *et al.* (1988)
$CpUCl_3(OPPh_3)_2 \cdot THF$	Cl(3), O(2)	Bombieri *et al.* (1978c); Bagnall *et al.* (1984)
$CpUCl_3[OP(NMe_2)_3]_2$	Cl(3), O(2)	Bagnall *et al.* (1984)
$CpNpCl_3(OPMePh_2)_2$	Cl(3), O(2)	Bagnall *et al.* (1986)
$CpU[(CH_2)(CH_2)PPh_2]_3$	C(6)	Cramer *et al.* (1984b)
$[Cp(CH_3COO)_5U_2O]_2$	O(6)	Brianese *et al.* (1989)
$[CpU(CH_3COO)_2]_4O_2$	O(6)	Rebizant *et al.* (1992)
*Cp**		
$[Na(THF)_6][Cp^*U(BH_4)_3]_2$	H(9)	Ryan *et al.* (1989)
$[Cp^*(Cl)(HNSPh_2)U(\mu^3\text{-}O)(\mu^2\text{-}O)U(Cl)(HNSPh_2)]_2$	Cl, N, O(3)	Cramer *et al.* (1995b)
$Cp^*UI_2(THF)_3$	I(2), O(3)	Avens *et al.* (2000)
$Cp^*UI_2(pyr)_3$	I(2), N(3)	Avens *et al.* (2000)
$Cp^*U(CH_2Ph)_3$	C(6)	Kiplinger *et al.* (2002a)
$Cp^*U(\eta^3\text{-}2\text{-}MeC_3H_4)_3$	C(9)	Cymbaluk *et al.* (1983)
$Cp^*[(Me_3Si)_2N]Th(\mu_2\text{-}OSO_2CF_3)_3Th[N(SiMe_3)(SiMe_2CH_2)]Cp^*$	C, N, O(3); N, O(3)	Butcher *et al.* (1995)
$Cp^*U[N(SiMe_3)_2]_2$	N(2)	Avens *et al.* (2000)
$[Cp^*U(NEt_2)_2(THF)_2]BPh_4$	N(2), O(2)	Berthet *et al.* (1995)
Cp''', MeCp		
$[(Cp'''ThCl_3)_2NaCl(OEt_2)]_2$	Cl(5)	Edelman *et al.* (1995)
$Cp'''UCl_2(THF)(\mu\text{-}Cl)_2[Li(THF)_2]$	Cl(4), O(1)	Edelman *et al.* (1987)
$(MeCp)UCl_3(THF)_2$	Cl(3), O(2)	Ernst *et al.* (1979)

* Semicolons used to differentiate coordination to different metal centers or different structures.

and each pentahapto Cp ligand occupies the remaining apex (Rebizant *et al.*, 1992).

A cyclic hexameric thorium organoactinide complex (Fig. 22.37) is evident in the structure of $[CpTh_2(O\text{–}^iPr)_7]_3$. Interestingly, the Cp ligands in this structure take on a bridging role between three $[Th_2(O\text{–}^iPr)_7]$ units, each pentahapto to its neighboring thorium atoms. Each thorium center has distorted octahedral geometry provided by a Cp ligand and five $O\text{–}^iPr$ groups, two of which are bound to a thorium atom and the remaining three bridge between two thorium atoms (Barnhart *et al.*, 1995b).

The two thorium atoms in the triflate-bridged compound isolated by Butcher *et al.* (1995) have different coordination numbers (Fig. 22.38). Each thorium atom has one Cp* ligand bound in a pentahapto fashion and the two centers are

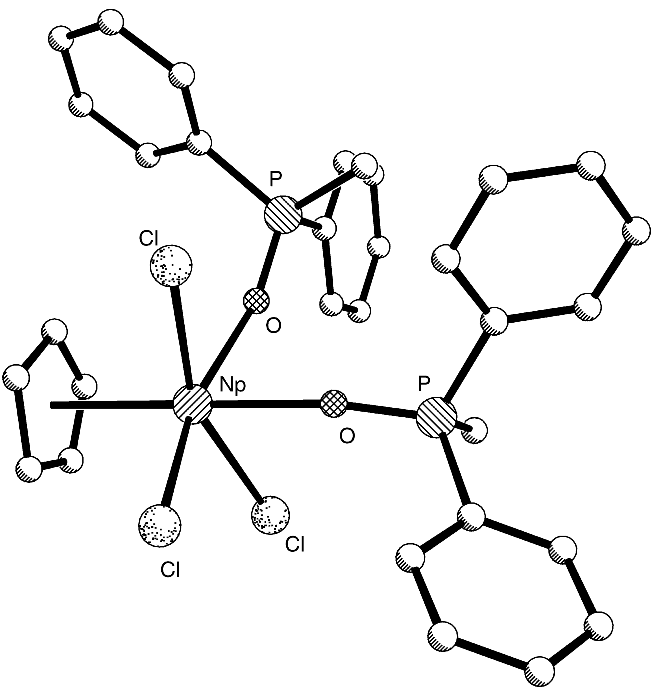

Fig. 22.36 *Crystal strucuture of $CpNpCl_3(PMePh_2O)_2$ with hydrogen atoms omitted* (*Bagnall* et al., 1986). *The coordinates were obtained from the Cambridge Structural Database* (*refcode DIXCOC*).

joined by three bridging triflate ligands. One thorium center is coordinated to a cyclometalated amide ligand in a bidenate manner through both nitrogen, and interestingly, carbon, resulting in a hexacoordinate thorium atom (Th–N= 2.26(4) Å, Th–C=2.43(5) Å). The remaining thorium center has a bis-(trimethylsilyl)amide ligand bound in a monodentate fashion only through the nitrogen atom (Th–N=2.24(3) Å), resulting in pentacoordinate thorium.

22.5.2 Cyclooctatetraene–actinide compounds

A milestone in the field of organometallics that effectively marked the beginning of organoactinide chemistry was the synthesis (Streitweiser and Müller-Westerhoff, 1968) and subsequent structural characterization of uranocene. The pursuit of uranocene was a direct result of the idea that it would be analogous to ferrocene with the additional benefit of studying the contribution of f-orbitals to the bonding. Like ferrocene, uranocene is a sandwich complex of D_{8h} symmetry in which the uranium(IV) ion is positioned between two octahapto (η^8-C_8H_8) cyclooctatetraene (COT) dianions. Although eclipsed in

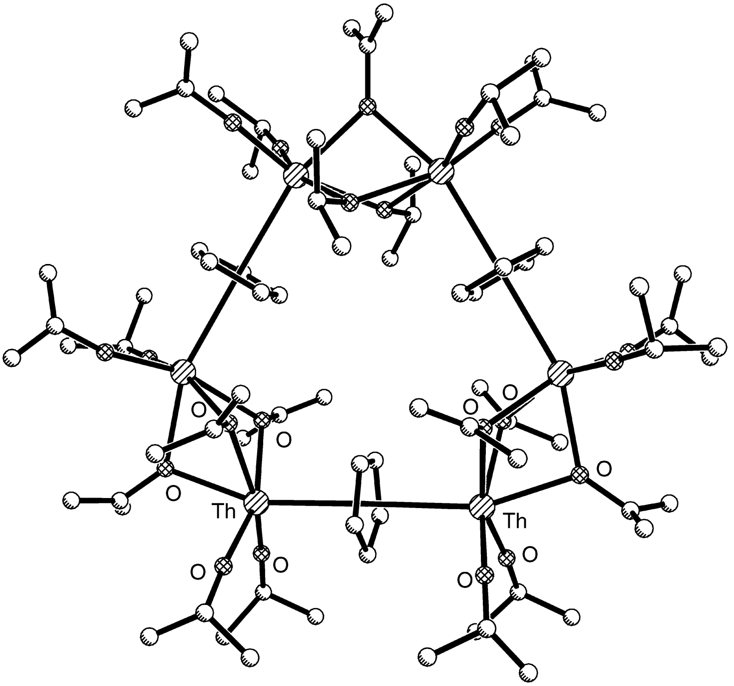

Fig. 22.37 *Crystal strucuture of* $[CpTh_2(O\text{-}^iPr)_7]_3$ *with hydrogen atoms omitted* (*Barnhart* et al., 1995*b*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode ZEJYES*).

uranocene, the COT rings have the potential of being either eclipsed or staggered (Zalkin and Raymond, 1969; Avdeef *et al.*, 1972). The thorium analog of uranocene, commonly referred to as thorocene, is isostructural, and both are extremely air-sensitive (Avdeef *et al.*, 1972). Both structures consist of the central metal atom participating in symmetrical π-bonding to the COT ligands, related by a crystallographic inversion center. The average Th–C and U–C bond distances are 2.701(4) and 2.647(4) Å, respectively; the corresponding metal-to-centroid distances are 2.004 and 1.924 Å. Spectroscopic studies with uranocene seem to indicate at least some π-interactions between the molecular orbitals of the COT ligands and the 5f orbitals of the metal.

Neptunocene, a transuranic metallocene, is isostructural with both thorocene and uranocene, with an average Np–C bond distance of 3.630(3) Å (De Ridder *et al.*, 1996b). Powder diffraction data are available for both $(COT)_2Pa$ and $(COT)_2Pu$ that indicate protactinocene is isostructural with the lower actinide analogs and plutonocene is isomorphous with the series (Karraker *et al.*, 1970; Starks *et al.*, 1974). Incorporation of the COT ligand is not limited to metallocenes. In fact, a host of other examples containing COT are listed in Table 22.33.

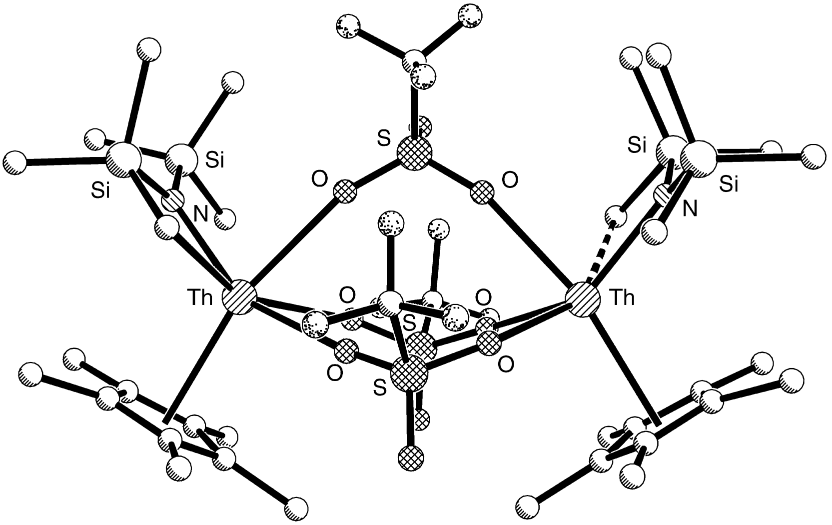

Fig. 22.38 *Crystal strucuture of* $Cp^*[(Me_3Si)_2N]Th(\mu_2\text{-}OSO_2CF_3)_3Th[N(SiMe_3)(SiMe_2CH_2)]Cp^*$ *with hydrogen atoms omitted* (*Butcher* et al., 1995). *The coordinates were obtained from the Cambridge Structural Database* (*refcode ZANJIH*).

A mixed cyclopentadiene/cyclooctatetraene complex is observed in the crystal structure of (COT)(Cp*)U(Me_2bpy) (Schake *et al.*, 1993). The binding of the COT and Cp* rings are η^8 and η^5, respectively, and the bipyridine adduct is bidentate through both nitrogen atoms. The resulting geometry around the uranium is a distorted tetrahedron with a Cp*–U–COT bond angle (from centroids of ligands) of 138.2°, comparable to what is observed in the thorium complexes, (COT)Cp*Th[$CH(SiMe_3)_2$] and (COT)Th(Cp*)(μ-Cl)$_2$Mg($CH_2{}^t$Bu)(THF) · 0.5PhMe (Gilbert *et al.*, 1989).

Butenouranocene, $[C_8H_6(CH_2)_2]_2U$, contains a cyclooctatetraene derivative appended with a cyclobuteno ring (Fig. 22.39). The uranium ion is sandwiched between the two eclipsed rings, but centered on the cyclooctatetraene rings, with an overall C_{2h} symmetry. The average U–C distance of 2.64(2) Å (Zalkin *et al.*, 1979) is comparable to uranocene (2.65 Å) and similar structures.

22.5.3 Other (indenyl, arene, etc.) compounds

Representative organoactinide complexes containing ligands not covered in previous sections are listed in Table 22.34 and include various indenyl, arene, and miscellaneous structures, including bridged Cp ligands. The indenyl ligand, $C_9H_7^-$, is formally analogous to $C_5H_5^-$, yet is more sterically demanding (both substituted and unsubstituted) and can coordinate in pentahapto, trihapto, and monohapto modes (Bombieri *et al.*, 1998).

Table 22.33 *Representative cyclooctatetraenyl organoactinide complexes.*

Structure	*Non-Cp donors (# per center)*	*References*
(COT)$_2$Th	–	Avdeef *et al.* (1972)
(COT)$_2$U	–	Zalkin and Raymond (1969); Avdeef *et al.* (1972)
(Me$_4$COT)$_2$U	–	Hodgson and Raymond (1973)
(Ph$_4$COT)$_2$U	–	Templeton *et al.* (1977)
[C$_8$H$_6$(CH$_2$)$_2$]$_2$U	–	Zalkin *et al.* (1979)
[C$_8$H$_6$(CH$_2$)$_3$]$_2$U	–	Zalkin *et al.* (1982)
[C$_8$H$_6$(CH)$_4$]U	–	Zalkin *et al.* (1985)
(COT)$_2$An (An = Pa, Np, Pu)	–	Karraker *et al.* (1970); Starks *et al.* (1974)
(COT)$_2$Np	–	De Ridder *et al.* (1996b)
K(COT)$_2$An · (THF)$_2$ (An = Np, Pu)	–	Karraker and Stone (1974)
K(COT)$_2$Pu · [CH$_3$O(CH$_2$)$_2$]$_2$O	–	Karraker and Stone (1974)
(COT)U(η^5-C$_4$Me$_4$P)(BH$_4$)(THF)	H(3), O	Cendrowski-Guillaume *et al.* (2002)
[(COT)U(BH$_4$)(μ-OEt)]$_2$	H(3), O(2)	Arliguie *et al.* (1992)
(COT)U(BH$_4$)$_2$(OPPh$_3$)	H(6), O	Baudry *et al.* (1990a)
(COT)(Cp*)Th(μ-Cl)$_2$Mg(CH$_2$^{t}Bu)(THF) · 0.5PhMe	Cl(2)	Gilbert *et al.* (1989)
(COT)UCl$_2$(pyr)$_2$	Cl(2), N(2)	Boussie *et al.* (1990)
(COT)ThCl$_2$(THF)$_2$	Cl(2), O(2)	Zalkin *et al.* (1980)
(COT)(Cp*)Th[CH(SiMe$_3$)$_2$]	C	Gilbert *et al.* (1989)
[(COT)U(mdt)]$_2$	C(2), S(4)	Arliguie *et al.* (2003)
(COT)U(mdt)(pyr)$_2$	C(2), N(2), S(2)	Arliguie *et al.* (2003)
(COT)Th[N(SiMe$_3$)$_2$]$_2$	N(2)	Gilbert *et al.* (1988)
(COT)(Cp*)U(Me$_2$bpy)	N(2)	Schake *et al.* (1993)
(μ-η^8,η^8-COT)U$_2$(NC[^{t}Bu]Mes)$_6$	N(3)	Diaconescu and Cummins (2002)
[(COT)U]$_2$[μ-η^4,η^4-HN(CH$_2$)$_3$N(CH$_2$)$_2$N(CH$_2$)$_3$NH]	N(4)	Le Borgne *et al.* (2000)
[(COT)Cp*U(THF)$_2$]BPh$_4$	O(2)	Berthet *et al.* (1995)
[(COT)U(O^{i}Pr)(μ-O^{i}Pr)]$_2$	O(3)	Arliguie *et al.* (1992)
(COT)U(MeCOCHCOMe)$_2$	O(4)	Boussie *et al.* (1990)
[Na(18-crown-6)(THF)$_2$][(COT)U(S^{t}Bu)$_3$]	S(3)	Leverd *et al.* (1994)
[(COT)U(μ-S^{i}Pr)$_2$]$_2$	S(4)	Leverd *et al.* (1994)
[Na(18-crown-6)(THF)][(COT)U(C$_4$H$_4$S$_4$)$_2$]	S(4)	Arliguie *et al.* (2000)

The π-bonding of indenyl ligands to the Th(IV) center in (C$_9$H$_7$)$_4$Th occurs in an η^3 manner, where the five-membered rings of each indenyl ligand form the apices of a distorted tetrahedron. The indenyl bonding occurs through the three non-bridging carbons of each five-membered ring, giving thorium a

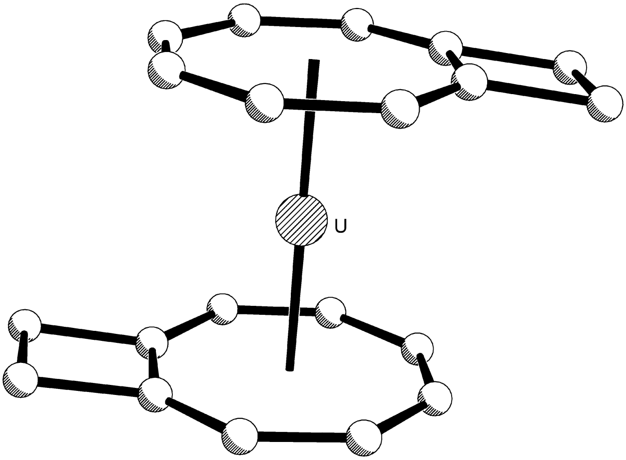

Fig. 22.39 *Crystal strucuture of* $[C_8H_6(CH_2)_2]_2U$ *with hydrogen atoms omitted* (*Zalkin* et al., 1979). *The coordinates were obtained from the Cambridge Structural Database* (*refcode CBOCTU*).

coordination number of 12. The lengthening of the distance between thorium and the remaining two bridging carbons of the five-membered ring is likely a consequence of localization of charge at these sites (Rebizant *et al.*, 1986a,b). This is similar to what is observed in $(C_{12}H_{13})_3ThCl$ (containing a trimethyl indenyl ligand) (Spirlet *et al.*, 1982) and $(C_9H_7)_3UCl$. In the latter case, the three shorter U–C bond distances range from 2.67(1) to 2.77(1) Å, while the two longer bonds are in the range of 2.79(1)–2.89(1) Å, suggesting trihapto bonding. However, the authors suggest the possibility of pentahapto bonding if one considers steric interferences from chloride and the six-membered ring (Burns and Laubereau, 1971). The trihapto indenyl coordination mode is also reported in the bromide and iodide analogs of the uranium complex (Spirlet *et al.*, 1987b; Rebizant *et al.*, 1988).

Pentahapto coordination of the indenyl ligand is apparent in the structures of several complexes, including $(C_9H_7)_3U$ (Meunier-Piret *et al.*, 1980a), $(C_9H_7)_2U(BH_4)_2$ (Rebizant *et al.*, 1989), and $(C_9H_7)UBr_3(THF)(OPPh_3)$ (Meunier-Piret *et al.*, 1980b). In the tri-indenyl uranium complex (Fig. 22.40), the U–C_{indenyl} bond distances to the five-membered ring are very similar; for instance, these distances for one of the indenyl rings are 2.846, 2.802, 2.845, 2.833, and 2.804 Å, with no bridging/non-bridging correlation. The first example of monhapto indenyl coordination is in the structure of $(C_{15}H_{19})_3ThCl$, where the hexamethyl indenyl ligand is σ-bonded through one carbon of each five-membered ring to thorium (Spirlet *et al.*, 1992b).

Arene complexes of the actinides are very few (and limited to uranium); those for which structures are available show η^6 π-bonding of the aromatic ring

Table 22.34 *Representative other organoactinide complexes.*

Structure	*Other donors (# per center)*	*References*
indenyl		
pentahapto (η^5)		
$(C_9H_7)_3U$	–	Meunier-Piret *et al.* (1980a)
$(C_9H_7)_2U(BH_4)_2$	H(6)	Rebizant *et al.* (1989)
$(C_9H_7)UX_3(THF)_2$ (X = Cl, Br)	Cl(3), O(2); Br(3), O(2)	Rebizant *et al.* (1983, 1985)
$(C_9H_7)UBr_3(THF)(OPPh_3)$	Br(3), O(2)	Meunier-Piret *et al.* (1980b)
trihapto (η^3)		
$(C_9H_7)_4Th$	–	Rebizant *et al.* (1986a,b)
$(C_{11}H_{11})_3ThCl$	Cl	Spirlet *et al.* (1990b)
$(C_{12}H_{13})_3ThCl$	Cl	Spirlet *et al.* (1982)
$(C_9H_7)_3UCl$	Cl	Burns and Laubereau (1971)
$(C_{12}H_{13})_3UCl$	Cl	Meunier-Piret and Van Meerssche (1984)
$(C_9H_7)_3UBr$	Br	Spirlet *et al.* (1987b)
$[(C_9H_7)UBr_2(NCMe)_4]_2[UBr_6]$	Br(2), N(4)	Beeckman *et al.* (1986)
$[\{(C_9H_7)UBr(NCMe)_4\}_2(\mu\text{-}O)][UBr_6]$	Br, N(4), O	Beeckman *et al.* (1986)
$(C_9H_7)_3UI$	I	Rebizant *et al.* 1988)
$(C_{11}H_{11})_3ThCH_3$	C	Spirlet *et al.* (1993b)
$(C_9H_7)_3U(OCH_2CF_3)$	O	Spirlet *et al.* (1993c)
monohapto (*σ-bonded*)		
$(C_{15}H_{19})_3ThCl$	Cl	Spirlet *et al.* (1992b)
arenes		
$(C_6Me_6)U(BH_4)_3$	H(9)	Baudry *et al.* (1989b)
$[(C_6Me_6)UCl_2]_2(\mu\text{-}Cl)_3(AlCl_4)$	Cl(5)	Cotton and Schwotzer (1985)
$[(C_6Me_6)UCl_2(\mu\text{-}Cl)_3Cl_2U(C_6Me_6)][AlCl_4]$	Cl(5)	Campbell *et al.* (1986)
$(C_6Me_6)UCl_2(\mu\text{-}Cl)_3UCl_2(\mu\text{-}Cl)_3Cl_2U(C_6Me_6)$	Cl(5); Cl(8)	Campbell *et al.* (1986)
$(C_6H_6)U(AlCl_4)_3$	Cl(6)	Cesari *et al.* (1971)
$(C_6Me_6)U(AlCl_4)_3$	Cl(6)	Cotton and Schwotzer (1987)
$[U_3(\mu^3\text{-}Cl)_2(\mu^2\text{-}Cl)_3(\mu^1,\eta^2\text{-}AlCl_4)_3(\eta^6\text{-}C_6Me_6)_3][AlCl_4]$	Cl(6)	Cotton *et al.* (1986)
$[U(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)_3]_2$	O(3)	Van Der Sluys *et al.* (1988)

Table 22.34 (*Contd.*)

Structure	*Other donors (# per center)*	*References*
ring-bridged		
$LiU_2Cl_5[CH_2(C_5H_4)_2]_2(THF)_2$	Cl(4)	Secaur *et al.* (1976)
$[Me_2Si(C_5Me_4)_2]U(\mu\text{-}Cl_4)[Li(TMEDA)]_2$	Cl(4)	Schnabel *et al.* (1999)
$[CH_2(C_5H_4)_2]UCl_2(bipy)$	Cl(2), N(2)	Marks (1977)
$\mu\text{-}[2,6\text{-}CH_2C_5H_3NCH_2](\eta^5\text{-}C_5H_4)_2UCl_2$	Cl(2), N	Paolucci *et al.* (1991)
$(Cp^*)(C_5H_4CH_2)U(NAd)(NHAd)$	N(2)	Peters *et al.* (1999)
$[\{Me_2Si(C_5Me_4)(C_5H_4)\}U(\mu\text{-}NPh)]_2$	N(2)	Schnabel *et al.* (1999)
other	*type*	
$[U(C_3H_5)_2(O^iPr)_2]_2$	allyl	Brunelli *et al.* (1979)
$[Li(THF)_4]_2[(C_2B_9H_{11})_2UCl_2]$	dibarbollide	Fronczek *et al.* (1977)
$[U(BH_4)(THF)_5][U(BH_4)_3(\mu\text{-}\eta^7,\eta^7\text{-}C_7H_7)U(BH_4)_3]$	cycloheptatrienyl	Arliguie *et al.* (1994b)
$[K(18\text{-}crown\text{-}6)][U(\eta\text{-}C_7H_7)_2]$	cycloheptatrienyl	Arliguie *et al.* (1995)
$K_2(\mu\text{-}\eta^6,\eta^6\text{-}C_{10}H_8)[U(NC[^tBu]Mes)_3]_2$	napthalene	Diaconescu and Cummins (2002)
$(Me_4Fv)_2FeThCl_2$	fulvalene	Scott and Hitchcock (1995)
$[(\eta^5\text{-}C_4Me_4P)(\mu\text{-}\eta^5\text{-}C_4Me_4P)U(BH_4)]_2$	phospholyl	Gradoz *et al.* (1994)
$(\eta^5\text{-}C_4Me_4P)_2U(BH_4)_2$	phospholyl	Baudry *et al.* (1990b)
$(\eta\text{-}2,4\text{-}Me_2C_5H_5)U(BH_4)_3$	dimethylpentadienyl	Baudry *et al.* (1989a)

* Semicolons used to differentiate coordination to different metal centers or different structures.

(C_6H_6) to the metal center. For example, in the complexes $(C_6H_6)U(AlCl_4)_3$ (Cesari *et al.*, 1971) and $(C_6Me_6)U(AlCl_4)_3$ (Cotton and Schwotzer, 1987), the hexahapto arene ligands are bound to the uranium centers along with three bidentate $AlCl_4$ ligands (through chlorine), resulting in pentagonal bipyramidal structures (Fig. 22.41). In the case of $[(C_6Me_6)UCl_2]_2(\mu\text{-}Cl)_3(AlCl_4)$, as well as other U(III)–benzene complexes, the U–benzene (centroid) distances are considerably longer than in traditional anionic π-ligands. This is a strong indication of the relatively weak bonds that form in these types of complexes with the neutral arene ligand (Cotton and Schwotzer, 1985).

22.6 SUMMARY

The actinide structures that have been presented herein represent a fraction of known f-element compounds that have been studied by neutron and X-ray diffraction techniques. However, this treatment is by no means exhaustive as it

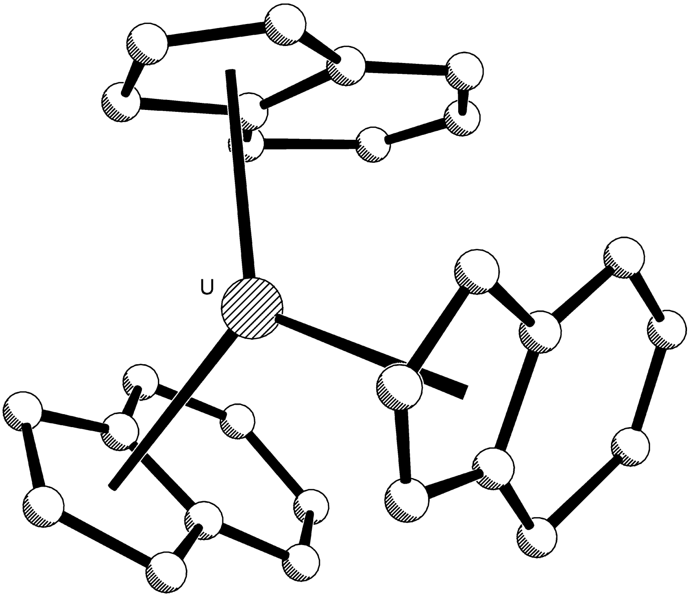

Fig. 22.40 *Crystal strucuture of* $(C_9H_7)_3U$ *with hydrogen atoms omitted* (*Meunier-Piret* et al., 1980*a*). *The coordinates were obtained from the Cambridge Structural Database* (*refcode TRINUR*).

would require several more chapters of comparable length. It should be apparent that the study and structural characterization of actinide compounds continues to play an important role in understanding the nature of this fascinating row of elements. While it is true that most simple and fundamental actinide compounds have been structurally characterized over the past 50 years, these studies are only the 'tip of the iceberg' in terms of what can and has yet to be discovered.

Due to the complex nuclear wastes that exist at many sites, the intricacies of environmental actinide migration and interaction phenomena, the task-specific nature of fuel processing schemes for the recovery of heavy elements, and a continued fundamental academic interest in these elements, advances in actinide chemistry will continue to be increasingly important into the foreseeable future. These advances must necessarily be accompanied by more complex structural analyses that will achieve a more thorough understanding of the chemical behavior of the actinides.

The development of more advanced X-ray and neutron diffraction instrumentation, along with the use of more exotic techniques such as extended X-ray absorption fine-structure (EXAFS) spectroscopy and even highly advanced *ab initio* quantum mechanics tools based on relativistic theory, will be

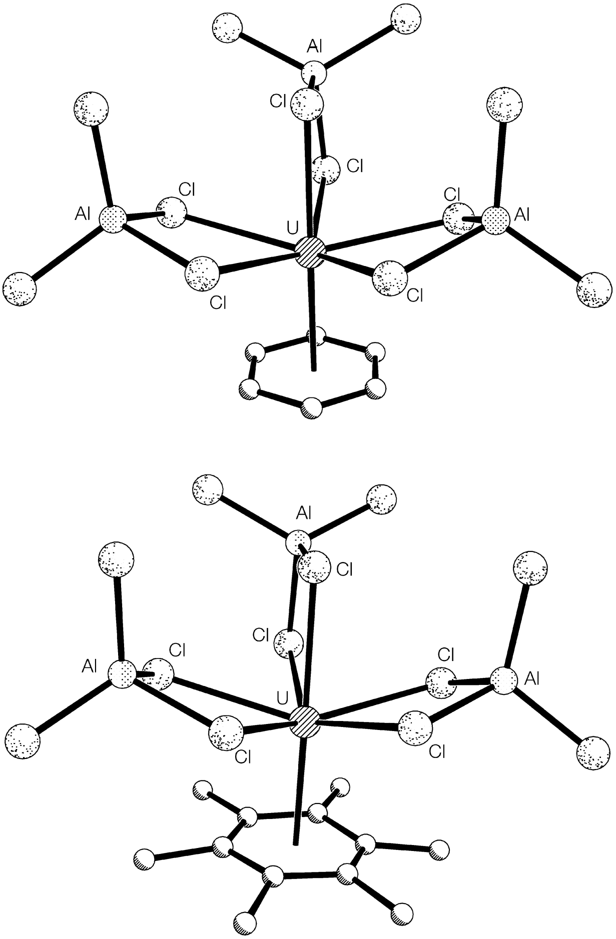

Fig. 22.41 *Crystal strucutures of* $(C_6H_6)U(AlCl_4)_3$ (*Cesari* et al., 1971) *and* $(C_6Me_6)U(AlCl_4)_3$ (*Cotton and Schwotzer,* 1987) *with hydrogen atoms omitted. The coordinates were obtained from the Cambridge Structural Database* (*refcodes BNZUAL and FODRUL*).

paramount in moving forward. These techniques will continue to assist in the elucidation of the critical aspects of actinide electronic structure and bonding, such as the role of 5f electrons in covalent interactions, that are still widely studied and debated. Nonetheless, the actinides are a series of elements unlike any other that will continue to provide ample challenges for chemists worldwide and push the limits of existing technology, particularly in the area of structural determination.

ABBREVIATIONS

Acac	acetylacetonato = 2,4-pentanedionato
BBN	9-borabicyclo(3.3.1)nonane
bipy	2,2′-bipyridyl
$^n\mathrm{Bu}$	butyl = C_4H_9–
$^t\mathrm{Bu}$	*tert*-butyl = $(CH_3)_3C$–
$(^t\mathrm{Bu})\mathrm{Cp}$	$\eta^5\text{-}C_5H_4(^t\mathrm{Bu})$
$(^t\mathrm{Bu})_2\mathrm{Cp}$	$\eta^5\text{-}C_5H_3(^t\mathrm{Bu})_2$–1,3
COT	$\eta^8\text{-}C_8H_8$
Cp	$\eta^5\text{-}C_5H_5$
Cp*	$\eta^5\text{-}C_5(CH_3)_5$
Cp'	$\eta^5\text{-}C_5H_4[Si(CH_3)_3]$
Cp''	$\eta^5\text{-}C_5H_3[Si(CH_3)_3]_2$–1,3
Cp'''	$\eta^5\text{-}C_5H_2[Si(CH_3)_3]_3$–1,2,4
Cp^{tt}	$\eta^5\text{-}C_5H_3[Si^t\mathrm{Bu}(CH_3)_2]_2$–1,3
$\mathrm{CpCH_2Ph}$	$\eta^5\text{-}C_5H_4(CH_2C_6H_5)$
DABCO	1,4-diazabicyclo[2.2.2]octane
DMAP	dimethylaminopyridine
DMF	dimethylformamide
DMPE	$(Me)_2P(CH_2)_2P(Me)_2$
DMSO	dimethylsulfoxide
Et	ethyl = C_2H_5–
HTTA	thenoyl trifluoroacetone
mdt	1,3-dithiole-4,5-dithiolate
Me	methyl = CH_3–
$\mathrm{Me_2bpy}$	4,4′-dimethyl-2,2′-bipyridine
$\mathrm{Me_4COT}$	$\eta^8\text{-}C_8H_4(CH_3)_4$
MeCp	$\eta^5\text{-}C_5H_4(CH_3)$
$\mathrm{Me_4Cp}$	$\eta^5\text{-}C_5H(CH_3)_4$
$\mathrm{Me_4Fv}$	1,2,3,4-tetramethylfulvalene
Mes	2,4,6-$C_6H_2(CH_3)_3$
NAd	1-adamantyl
OAr	2,5-dimethylphenoxide
OTf	OSO_2CF_3
Ph	phenyl = C_6H_5–
$\mathrm{Ph_4COT}$	$\eta^8\text{-}C_8H_4(C_6H_5)_4$
PMDETA	pentamethyldiethylenediamine = $(Me_2NCH_2CH_2)_2NMe$
$^i\mathrm{Pr}$	*iso*-propyl = $(CH_3)_2CH$–
$^n\mathrm{Pr}$	*n*-propyl = C_3H_7–
pyr	pyridine = C_5H_5N; Hpyr = C_5H_5NH

$(SiMe_3)_2CHCp$	η^5-$C_5H_4[CH(SiMe_3)_2]$
THF	tetrahydrofuran = OC_4H_8
TMED	tetramethylethylenediamine

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REFERENCES

Ackermann, R. J. and Rauh, E. G. (1973) *J. Inorg. Nucl. Chem.*, **35**, 3787–94.

Adam, M., Yünlü, K., and Fischer, R. D. (1990) *J. Organomet. Chem.*, **387**, C13–16.

Adam, R., Villiers, C., Ephritikhine, M., Lance, M., Nierlich, M., and Vigner, J.-D. (1993) *J. Organomet. Chem.*, **445**, 99–106.

Akhtar, M. N. and Smith, A. J. (1969) *J. Chem. Soc., Chem. Commun.*, 705–6.

Akimoto, Y. (1960) Chemistry Division Semiannual Report, November 1959, UCRL-9093, p. 73.

Akimoto, Y. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2650–2.

Allen, F. H. (2002) *Acta Crystallogr.* B, **58**, 380–8.

Albering, J. H. and Jeitschko, W. (1995) *Z. Kristallogr.*, **210**, 878.

Alcock, N. W. (1973a) *J. Chem. Soc., Dalton Trans.*, 1614–16.

Alcock, N. W. (1973b) *J. Chem. Soc., Dalton Trans.*, 1610–13.

Alcock, N. W. (1973c) *J. Chem. Soc., Dalton Trans.*, 1616–20.

Alcock, N. W., Roberts, M. M., and Chakravorti, M. C. (1980a) *Acta Crystallogr. B*, **36**, 687–90.

Alcock, N. W., Kemp, T. J., Sostero, S., and Traverso, O. (1980b) *J. Chem. Soc., Dalton Trans.*, 1182–5.

Alcock, N. W., Flanders, D. J., Kemp, T. J., and Shand, M. A. (1985) *J. Chem. Soc., Dalton Trans.*, 517–21.

Alcock, N. W., Kemp, T. J., Leciejewicz, J., and Pennington, M. (1989) *Acta Crystallogr. C*, **45**, 719–21.

Alcock, N. W., Errington, W., Kemp, T. J., and Leciejewicz, J. (1996a) *Acta Crystallogr. C*, **52**, 615–17.

Alcock, N. W., Kemp, T. J., Roe, S. M., and Leciejewicz, J. (1996b) *Inorg. Chim. Acta*, **248**, 241–6.

Alenchikova, I. F., Zaitseva, L. L., Lipis, L. V., Nikolaev, N. S., Fomin, V. V., and Chebotarev, K. (1958) *Zh. Neorg. Khim.*, **3**, 951–5.

Amirthalingam, V. (1966) *J. Nucl. Mater.*, **20**, 193–4.

Ariyaratne, K. A. N. S., Cramer, R. E., and Gilje, J. W. (2002) *Organometallics*, **21**, 5799–802.

Arliguie, T., Baudry, D., Ephritikhine, M., Nierlich, M., Lance, M., and Vigner, J.-D. (1992) *J. Chem. Soc., Dalton Trans.*, 1019–24.

Arliguie, T., Ephritikhine, M., Lance, M., Vigner, J.-D., and Nierlich, M. (1994a) *J. Organomet. Chem.*, **484**, 195–201.

Arliguie, T., Lance, M., Nierlich, M., Vigner, J.-D., and Ephritikhine, M. (1994b) *J. Chem. Soc., Chem. Commun.*, 847–8.

Arliguie, T., Lance, M., Nierlich, M., Vigner, J.-D., and Ephritikhine, M. (1995) *J. Chem. Soc., Chem. Commun.*, 183–4.

Arliguie, T., Fourmigué, M., and Ephritikhine, M. (2000) *Organometallics*, **19**, 109–11.

Arliguie, T., Thuéry, P., Fourmigué, M., and Ephritikhine, M. (2003) *Organometallics*, **22**, 3000–3.

Armağan, N. (1977) *Acta Crystallogr. B*, **33**, 2281–4.

Arnaudet, L., Charpin, P., Folcher, G., Lance, M., Nierlich, M., and Vigner, J.-D. (1986) *Organometallics*, **5**, 270–4.

Arney, D. S. J., Burns, C. J., and Smith, D. C. (1992) *J. Am. Chem. Soc.*, **114**, 10068–9.

Arney, D. S. J. and Burns, C. J. (1995) *J. Am. Chem. Soc.*, **117**, 9448–60.

Arutyunyan, E. G., Porai-Koshits, M. A., and Molodkin, A. K. (1966a) *Zh. Strukt. Khim.*, **7**, 733–7.

Arutyunyan, E. G., Antsyshkina, A. S., and Balta, E. Ya. (1966b) *Zh. Strukt. Khim.*, **7**, 471–2.

Arutyunyan, E. G., Porai-Koshits, M. A., Molodkin, A. K., and Ivanova, O. M. (1966c) *Zh. Prikl. Khim.*, **7**, 813–14.

Asfari, Z., Bilyk, A., Dunlop, J. W. C., Hall, A. K., Harrowfield, J. M., Hosseini, M. W., Skelton, B. W., and White, A. H. (2001) *Angew. Chem. Int. Ed.Engl.*, **40**, 721–3.

Aslan, H., Yünlü, K., Fischer, R. D., Bombieri, G., and Benetollo, F. (1988) *J. Organomet. Chem.*, **354**, 63–76.

Asprey, L. B., Ellinger, F. H., Fried, S., and Zachariasen, W. H. (1955) *J. Am. Chem. Soc.*, **77**, 1707–8.

Asprey, L. B., Ellinger, F. H., Fried, S., and Zachariasen, W. H. (1957) *J. Am. Chem. Soc.*, **79**, 5825.

Asprey, L. B., Keenan, T. K., and Kruse, F. H. (1965) *Inorg. Chem.*, **4**, 985–6.

Asprey, L. B. and Haire, R. G. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 1121–8.

Atoji, M. and McDermott, M. J. (1970) *Acta Crystallogr. B*, **26**, 1540–4.

Atwood, J. L., Hains, C. F. Jr, Tsutsui, M., and Gebala, A. E. (1973) *J. Chem. Soc., Chem. Commun.*, 452–3.

Atwood, J. L., Tsutsui, M., Ely, N., and Gebala, A. E. (1976) *J. Coord. Chem.*, **5**, 209–15.

Avdeef, A., Raymond, K. N., Hodgson, K. O., and Zalkin, A. (1972) *Inorg. Chem.*, **11**, 1083–8.

Avens, L. R., Burns, C. J., Butcher, R. J., Clark, D. L., Gordon, J. C., Schake, A. R., Scott, B. L., Watkin, J. G., and Zwick, B. D. (2000) *Organometallics*, **19**, 451–7.

Avisimova, N. Yu., Gorbunova, Yu. E., Mikhailov, Yu. N., and Chumaevskii, N. A. (2001) *Zh. Neorg. Khim.*, **46**, 629–32.

Bagnall, K. W., Brown, D., and Jones, P. J. (1965) *J. Chem. Soc.*, 176–81.

Bagnall, K. W., Brown, D., and Easey, J. F. (1968a) *J. Chem. Soc. A*, 288–91.

Bagnall, K. W., Brown, D., and Easey, J. F. (1968b) *J. Chem. Soc. A*, 2223–7.

Bagnall, K. W., Benetollo, F., Bombieri, G., and De Paoli, G. (1984) *J. Chem. Soc., Dalton Trans.*, 67–73.

Bagnall, K. W., Payne, G. F., Alcock, N. W., Flanders, D. J., and Brown, D. (1986) *J. Chem. Soc., Dalton Trans.*, 783–7.

Baker, E. C., Raymond, K. N., Marks, T. J., and Wachter, W. A. (1974) *J. Am. Chem. Soc.*, **96**, 7586–8.

Baluka, M., Yeh, S., Banks, R., and Edelstein, N. (1980) *Inorg. Nucl. Chem. Lett.*, **16**, 75–7.

Bamberger, C. E., Haire, R. G., Begun, G. M., and Hellwege, H. E. (1984a) *J. Less Common Metals*, **102**, 179–86.

Bamberger, C. E., Haire, R. G., Hellwege, H. E., and Begun, G. M. (1984b) *J. Less Common Metals*, **97**, 349–56.

Bandoli, G., Graziani, R., and Zarli, B. (1968) *Acta Crystallogr. B*, **24**, 1129–30.

Banks, R. H., Edelstein, N. M., Rietz, R. R., Templeton, D. H., and Zalkin, A. (1978) *J. Am. Chem. Soc.*, **100**, 1957–8.

Baracco, L., Bombieri, G., Degetto, S., Forsellini, E., Graziani, R., and Marangoni, G. (1974) *Inorg. Nucl. Chem. Lett.*, **10**, 1045–50.

Barclay, G. A., Sabine, T. M., and Taylor, J. C. (1965) *Acta Crystallogr.*, **19**, 205–9.

Barnhart, D. M., Burns, C. J., Sauer, N. N., and Watkin, J. G. (1995a) *Inorg. Chem.*, **34**, 4079–84.

Barnhart, D. M., Butcher, R. J., Clark, D. L., Gordon, J. C., Watkin, J. G., and Zwick, B. D. (1995b) *New J. Chem.*, **19**, 503–8.

Baskin, Y. and Prasad, N. S. K. (1964) *J. Inorg. Nucl. Chem.*, **26**, 1385–90.

Baskin, Y. (1967) *J. Inorg. Nucl. Chem.*, **29**, 383–91.

Battiston, G. A., Sbrignadello, G., Bandoli, G., Clemente, D. A., and Tomat, G. (1979) *J. Chem. Soc., Dalton Trans.*, 1965–71.

Baudin, C., Charpin, P., Ephritikhine, M., Lance, M., Nierlich, M., and Vigner, J.-D. (1988) *J. Organomet. Chem.*, **345**, 263–74.

Baudry, D., Bulot, E., Charpin, P., Ephritikhine, M., Lance, M., Nierlich, M., and Vigner, J.-D. (1989a) *J. Organomet. Chem.*, **371**, 163–74.

Baudry, D., Bulot, E., Charpin, P., Ephritikhine, M., Lance, M., Nierlich, M., and Vigner, J.-D. (1989b) *J. Organomet. Chem.*, **371**, 155–62.

Baudry, D., Bulot, E., Ephritikhine, M., Nierlich, M., Lance, M., and Vigner, J.-D. (1990a) *J. Organomet. Chem.*, **388**, 279–87.

Baudry, D., Ephritikhine, M., Nief, F., Ricard, L., and Mathey, F. (1990b) *Angew. Chem.*, **102**, 1501–2.

Baybarz, R. D. (1968) *J. Inorg. Nucl. Chem.*, **30**, 1769–73.

Baybarz, R. D., Haire, R. G., and Fahey, J. A. (1972a) *J. Inorg. Nucl. Chem.*, **34**, 557–65.

Baybarz, R. D., Asprey, L. B., Strouse, C. E., and Fukushima, E. (1972b) *J. Inorg. Nucl. Chem.*, **34**, 3427–31.

Baybarz, R. D. (1973a) *J. Inorg. Nucl. Chem.*, **35**, 4149–58.

Baybarz, R. D. (1973b) *J. Inorg. Nucl. Chem.*, **35**, 483–7.

Becquerel, A. H. (1896) *Compt. Rend.*, **122**, 501–3.

Beeckman, W., Goffart, J., Rebizant, J., and Spirlet, M. R. (1986) *J. Organomet. Chem.*, **307**, 23–37.

Beer, P. D., Drew, M. G. B., Hesek, D., Kan, M., Nicholson, G., Schmitt, P., Sheen, P.D., and Williams, G. (1998) *J. Chem. Soc., Dalton Trans.*, 2783–5.

Belbeoch, P. B., Piekarski, C., and Pério, P. (1961) *Acta Crystallogr.*, **14**, 837–43.

Bénard, P., Louër, D., Dacheux, N., Brandel, V., and Genet, M. (1994) *Chem. Mater.*, **6**, 1049–58.

Bénard, P., Brandel, V., Dacheux, N., Jaulmes, S., Launay, S., Lindecker, C., Genet, M., Louër, D., and Quarton, M. (1996) *Chem. Mater.*, **8**, 181–8.

Bénard-Rocherullé, P., Louër, M., Louër, D., Dacheux, N., Brandel, V., and Genet, M. (1997) *J. Solid State Chem.*, **132**, 315–22.

Benetollo, F., Bombieri, G., Herrero, J. A., and Rojas, R. M. (1979) *J. Inorg. Nucl. Chem.*, **41**, 195–9.

Benetollo, F., Bombieri, G., Tomat, G., Castellani, C. B., Cassol, A., and Di Bernardo, P. (1984) *Inorg. Chim. Acta*, **95**, 251–61.

Benetollo, F., Bombieri, G., Herrero, P., and Rojas, R. M. (1995) *J. Alloys Compds*, **225**, 400–5.

Benz, R. and Zachariasen, W. H. (1966) *Acta Crystallogr.*, **21**, 838–40.

Bernstein, E. R., Keiderling, T. A., Lippard, S. J., and Mayerle, J. J. (1972a) *J. Am. Chem. Soc.*, **94**, 2552–3.

Bernstein, E. R., Hamilton, W. C., Keiderling, T. A., La Placa, S. J., Lippard, S. J., and Mayerle, J. J. (1972b) *Inorg. Chem.*, **11**, 3009–16.

Berthet, J.-C., Lance, M., Nierlich, M., Vigner, J.-D., and Ephritikhine, M. (1991a) *J. Organomet. Chem.*, **420**, C9–11.

Berthet, J.-C., Le Maréchal, J.-F., Nierlich, M., Lance, M., Vigner, J.-D., and Ephritikhine, M. (1991b) *J. Organomet. Chem.*, **408**, 335–41.

Berthet, J.-C., Ephritikhine, M., Nierlich, M., Lance, M., and Vigner, J.-D. (1993) *J. Organomet. Chem.*, **460**, 47–53.

Berthet, J.-C., Boisson, C., Lance, M., Vigner, J.-D., Nierlich, M., and Ephritikhine, M. (1995) *J. Chem. Soc., Dalton Trans.*, 3027–33.

Beshouri, S. M. and Zalkin, A. (1989) *Acta Crystallogr. C*, **45**, 1221–2.

Bismondo, A., Casellato, U., Sitran, S. and Graziani, R. (1985) *Inorg. Chim. Acta*, **110**, 205–10.

Bjorklund, C. W. (1957) *J. Am. Chem. Soc.*, **79**, 6347–50.

Blake, P. C., Lappert, M. F., Atwood, J. L., and Zhang, H. (1986a) *J. Chem. Soc., Chem. Commun.*, 1148–9.

Blake, P. C., Lappert, M. F., Taylor, R. G., Atwood, J. L., Hunter, W. E., and Zhang, H. (1986b) *J. Chem. Soc., Chem. Commun.*, 1394–5.

Blake, P. C., Lappert, M. F., Atwood, J. L., and Zhang, H. (1988a) *J. Chem. Soc., Chem. Commum.*, 1436–8.

Blake, P. C., Hey, E., Lappert, M. F., Atwood, J. L., and Zhang, H. (1988b) *J. Organomet. Chem.*, **353**, 307–14.

Blake, P. C., Lappert, M. F., Taylor, R. G., Atwood, J. L., Hunter, W. E., and Zhang, H. (1995) *J. Chem. Soc., Dalton Trans.*, 3335–41.

Blake, P. C., Edelman, M. A., Hitchcock, P. B., Hu, J., Lappert, M. F., Tian, S., Müller, G., Atwood, J. L., and Zhang, H. (1998) *J. Organomet. Chem.*, **551**, 261–70.

Blake, P. C., Edelstein, N. M., Hitchcock, P. B., Kot, W. K., Lappert, M. F., Shalimoff, G. V., and Tian, S. (2001) *J. Organomet. Chem.*, **636**, 124–9.

Blank, H. and Ronchi, C. (1968) *Acta Crystallogr. A*, **24**, 657–66.

Bohet, J. and Müller, W. (1978) *J. Less Common Metals*, **57**, 185–99.

Bombieri, G., Forsellini, E., Graziani, R., Tomat, G., and Magon, L. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 1003–7.

Bombieri, G., Graziani, R., and Forsellini, E. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 551–7.

Bombieri, G., Croatto, U., Graziani, R., Forsellini, E., and Magon, L. (1974a) *Acta Crystallogr. B*, **30**, 407–11.

Bombieri, G., Forsellini, E., Tomat, G., and Magon, L. (1974b) *Acta Crystallogr. B*, **30**, 2659–63.

Bombieri, G., Degetto, S., Forsellini, E., Marangoni, G., and Immirzi, A. (1977) *Cryst. Struct. Commun.*, **6**, 115–18.

Bombieri, G., De Paoli, G., and Immirzi, A. (1978a) *J. Inorg. Nucl. Chem.*, **40**, 1889–94.

Bombieri, G., De Paoli, G., and Immirzi, A. (1978b) *J. Inorg. Nucl. Chem.*, **40**, 799–802.

Bombieri, G., De Paoli, G., Del Pra, A., and Bagnall, K. W. (1978c) *Inorg. Nucl. Chem. Lett.*, **14**, 359–61.

Bombieri, G., Benetollo, F., Del Pra, A., and Rojas, R. (1979) *J. Inorg. Nucl. Chem.*, **41**, 201–3.

Bombieri, G., Benetollo, F., Forsellini, E., and Del Pra, A. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1423–30.

Bombieri, G., Benetollo, F., Rojas, R. M., and De Paz, M. L. (1981) *J. Inorg. Nucl. Chem.*, **43**, 3203–7.

Bombieri, G., Benetollo, F., Rojas, R. M., De Paz, M. L., and Del Pra, A. (1982) *Inorg. Chim. Acta*, **61**, 149–54.

Bombieri, G., Benetollo, F., Klähne, E., and Fischer, R. D. (1983a) *J. Chem. Soc., Dalton Trans.*, 1115–21.

Bombieri, G., Benetollo, F., Bagnall, K. W., Plews, M. J., and Brown, D. (1983b) *J. Chem. Soc., Dalton Trans.*, 45–9.

Bombieri, G. and Paolucci, G. (1998) in *Handbook on the Physics and Chemistry of Rare Earths*, vol. 25 (eds. K. A. Gschneidner Jr and L. Eyring), Elsevier, Amsterdam, pp. 265–413.

Borzone, G., Borsese, A., and Ferro, R. (1982) *J. Less Common Metals*, **84**, 165–72.

Boulet, P., Wastin, F., Colineau, E., Griveau, J. C., and Rebizant, J. (2003) *J. Phys., Condensed Matter*, **15**, S2305–8.

Boussie, T. R., Moore, R. M. Jr, Streitwieser, A., Zalkin, A., Brennan, J., and Smith, K. A. (1990) *Organometallics*, **9**, 2010–16.

Bowman, A. L., Arnold, G. P., Witteman, W. G., Wallace, T. C., and Nereson, N. G. (1966) *Acta Crystallogr.*, **21**, 670–1.

Bowman, A. L., Krikorian, N. H., Arnold, G. P., Wallace, T. C., and Nereson, N. G. (1968) *Acta Crystallogr. B*, **24**, 1121–3.

Bowman, A. L. and Arnold, G. P. (1971) *Acta Crystallogr. B*, **27**, 243–4.

Bradshaw, J. S., Izatt, R. M., Bordunov, A. V., Chu, C. Y., and Hathway, J. L. (1996) in *Comprehensive Supramolecular Chemistry: Molecular Recognition: Receptors for Cationic Guests,* vol. 1 (ed. G. W. Gokel), Pergamon, Oxford, pp. 35–95.

Brandenburg, N. P. and Loopstra, B. O. (1973) *Cryst. Struct. Commun.*, **2**, 243–6.

Brandenburg, N. P. and Loopstra, B. O. (1978) *Acta Crystallogr. B*, **34**, 3734–6.

Brauer, G. and Mitius, A. (1942) *Z. Anorg. Allg. Chem.*, **249**, 325–39.

Breeze, E. W. and Brett, N. H. (1972) *J. Nucl. Mater.*, **45**, 131–8.

Brennan, J. G. and Andersen, R. A. (1985) *J. Am. Chem. Soc.*, **107**, 514–16.

Brennan, J. G. and Zalkin, A. (1985) *Acta Crystallogr. C*, **41**, 1038–40.

Brennan, J. G., Andersen, R. A., and Zalkin, A. (1986a) *Inorg. Chem.*, **25**, 1756–60.

Brennan, J. G., Andersen, R. A., and Zalkin, A. (1986b) *Inorg. Chem.*, **25**, 1761–5.

Brennan, J. G., Stults, S. D., Andersen, R. A., and Zalkin, A. (1988a) *Organometallics*, **7**, 1329–34.

Brennan, J. G., Andersen, R. A., and Zalkin, A. (1988b) *J. Am. Chem. Soc.*, **110**, 4554–8.

Brewer, L., Sawyer, D. L., Templeton, D. H., and Dauben, C. H. (1951) *J. Am. Ceram. Soc.*, **34**, 173–9.

Brianese, N., Casellato, U., Ossola, F., Porchia, M., Rossetto, G., Zanella, P., and Graziani, R. (1989) *J. Organomet. Chem.*, **365**, 223–32.

Brixner, L. H. (1963) *J. Inorg. Nucl. Chem.*, **25**, 783–7.

Broach, R. W., Schultz, A. J., Williams, J. M., Brown, G. M., Manriquez, J. M., Fagan, P. J., and Marks, T. J. (1979) *Science*, **203**, 172–4.

Brown, A. and Norreys, J. J. (1959) Nature (*UK*), **183**, 673.

Brown, A. (1961) *Acta Crystallogr.*, **14**, 860–5.

Brown, D. and Jones, P. J. (1966) *J. Chem. Soc., Chem. Commun.*, 279–80.

Brown, D., Easey, J. F., and Jones, P. J. (1967) *J. Chem. Soc. A*, 1698–1702.

Brown, D. and Jones, P. J. (1967) *J. Chem. Soc. A*, 719–23.

Brown, D. (1968) *Halides of the Lanthanides and Actinides*, John Wiley, London.

Brown, D., Fletcher, S., and Holah, D. G. (1968a) *J. Chem. Soc. A*, 1889–94.

Brown, D., Petcher, T. J., and Smith, A. J. (1968b) *Nature* (*UK*), **217**, 737–8.

Brown, D., Petcher, T. J., and Smith, A. J. (1969) *Acta Crystallogr. B*, **25**, 178–82.

Brown, D. and Easey, J. F. (1970) *J. Chem. Soc. A*, 3378–81.

Brown, D., Hill, J., and Rickard, C. E. F. (1970) *J. Chem. Soc. A*, 476–80.

Brown, D. and Edwards, J. (1972) *J. Chem. Soc., Dalton Trans.*, 1757–62.

Brown, D. (1973) in *Comprehensive Inorganic Chemistry*, vol. 5 (eds. J. C. Bailar Jr, H. J. Emeléus, S. R. Nyholm, and A. F. Trotman-Dickenson), Pergamon, Oxford., pp. 151–217; 277–318.

Brown, D., Hall, T. L., and Moseley, P. T. (1973) *J. Chem. Soc., Dalton Trans.*, 686–91.

Brown, D., Petcher, D. J., and Smith, A. J. (1975) *Acta Crystallogr. B*, **31**, 1382–5.

Brown, D., Whittaker, B., and De Paoli, G. (1976) *The Thermal Stability and Other Physical Properties of Protactinium Penta- and Tetraiodide*, Report AERE-R 8367, Chem. Div., AERE, Harwell, UK.

Brown, D. (1979) *Inorg. Nucl. Chem. Lett.*, **15**, 219–23.

Brunelli, M., Perego, G., Lugli, G., and Mazzei, A. (1979) *J. Chem. Soc., Dalton Trans.*, 861–8.

Bruno, J. W., Kalina, D. G., Mintz, E. A., and Marks, T. J. (1982a) *J. Am. Chem. Soc.*, **104**, 1860–9.

Bruno, J. W., Marks, T. J., and Day, V. W. (1982b) *J. Am. Chem. Soc.*, **104**, 7357–60.

Bruno, J. W., Marks, T. J., and Day, V. W. (1983) *J. Organomet. Chem.*, **250**, 237–46.

Bruno, J. W., Smith, G. M., Marks, T. J., Fair, C. K., Schultz, A. J., and Williams, J. M. (1986) *J. Am. Chem. Soc.*, **108**, 40–56.

Budantseva, N. A., Fedoseev, A. M., Grigor'ev, M. S., Potemkina, T. I., Afonas'eva, T. V., and Krot, N. N. (1988) *Radiokhimiya*, **30**, 607–10.

Burdese, A. and Borlera, M. L. (1963) *Ann. Chim.*, **53**, 344–55.

Burkov, V. I., Mistryukov, V. E., Mikhailov, Yu. N., and Chuklanova, E. B. (1997) *Zh. Neorg. Khim.*, **42**, 391–5.

Burnaeva, A. A., Volkov, Yu. F., Kryukova, A. I., Korshunov, I. A., and Skiba, O. V. (1992) *Radiokhimiya*, **34**, 13–21.

Burns, J. H. and Laubereau, P. G. (1971) *Inorg. Chem.*, **10**, 2789–92.

Burns, J. H. and Peterson, J. R. (1971) *Inorg. Chem.*, **10**, 147–51.

Burns, J. H. and Baybarz, R. D. (1972) *Inorg. Chem.*, **11**, 2233–7.

Burns, J. H., Peterson, J. R., and Baybarz, R. D. (1973) *J. Inorg. Nucl. Chem.*, **35**, 1171–7.

Burns, J. H. (1974) *J. Organomet. Chem.*, **69**, 225–33.

Burns, J. H., Peterson, J. R., and Stevenson, J. N. (1975) *J. Inorg. Nucl. Chem.*, **37**, 743–9.

Burns, J. H. and Baldwin, W. H. (1977) *Inorg. Chem.*, **16**, 289–94.

Burns, J. H. and Musikas, C. (1977) *Inorg. Chem.*, **16**, 1619–22.

Burns, P. C. and Hayden, L. A. (2002) *Acta Crystallogr. C*, **58**, i121–3.

Burns, P. C., Alexopoulos, C. M., Hotchkiss, P. J., and Locock, A. J. (2004) *Inorg. Chem.*, **43**, 1816–18.

Burns, P. C., Kubatko, K.-A., Sigmon, G., Fryer, B. J., Gagnon, J. E., Antonio, M. R., and Soderholm, L. (2005) *Angew. Chem. Int. Ed.*, **44**, 2135.

Burns, R. C. and O'Donnell, T. A. (1977) *Inorg. Nucl. Chem. Lett.*, **13**, 657–60.

Burrell, A. K., Hemmi, G., Lynch, V., and Sessler, J. L. (1991a) *J. Am. Chem. Soc.*, **113**, 4690–2.

Burrell, A. K., Cyr, M. J., Lynch, V., and Sessler, J. L. (1991b) *J. Chem. Soc., Chem. Commun.*, 1710–13.

Butcher, R. J., Clark, D. L., Grumbine, S. K., and Watkin, J. G. (1995) *Organometallics*, **14**, 2799–805.

Calderazzo, F. (1973) *J. Organomet. Chem.*, **53**, 173–8.

Calderazzo, F. (1974) *J. Organomet. Chem.*, **79**, 175–80.

Calestani, G., Spirlet, J. C., Rebizant, J., and Müller, W. (1979) *J. Less Common Metals*, **68**, 207–12.

Campbell, G. C., Cotton, F. A., Haw, J. F., and Schwotzer, W. (1986) *Organometallics*, **5**, 274–9.

Cannon, J. F. and Farnsworth, P. B. (1983) *J. Less Common Metals*, **92**, 359–68.

Cariati, F., Erre, L., Micera, G., Clemente, D. A., and Cingi, M. B. (1983) *Inorg. Chim. Acta*, **79**, 205.

Casellato, U., Vigato, P. A., and Vidali, M. (1978) *Coord. Chem. Rev.*, **26**, 85–159.

Cendrowski-Guillaume, S. M., Lance, M., Nierlich, M., Vigner, J.-D., and Ephritikhine, M. (1994) *J. Chem. Soc., Chem. Commum.*, 1655–6.

Cendrowski-Guillaume, S. M., Nierlich, M., and Ephritikhine, M. (2002) *J. Organomet. Chem.*, **643–644**, 209–13.

Cesari, M., Pedretti, U., Zazzetta, A., Lugli, G., and Marconi, W. (1971) *Inorg. Chim. Acta*, **5**, 439–44.

Chackraburtty, D. M. (1963) *Acta Crystallogr.*, **16**, 834.

Chackraburtty, D. M. and Jayadevan, N. C. (1965) *Acta Crystallogr.*, **18**, 811–12.

Chadha, A., Sampath, S., and Chackraburtty, D. M. (1980) *Inorg. Chim. Acta*, **42**, 163–7.

Chakravorti, M. C., Bharadwaj, P. K., Pandit, S. C., and Mathur, B. K. (1978) *J. Inorg. Nucl. Chem.*, **40**, 1365–7.

Charpin, P., Costes, R. M., Folcher, G., Plurien, P., Navaza, A., and de Rango, C. (1977) *Inorg. Nucl. Chem. Lett.*, **13**, 341–7.

Charushnikova, I. A., Perminov, V. P., and Katser, S. B. (1995) *Radiokhimiya*, **37**, 493–8.

Charushnikova, I. A., Krot, N. N., and Katser, S. B. (1998) *Radiochemistry (Translation of Radiokhimiya)*, **40**, 558–64.

Charushnikova, I. A., Krot, N. N., and Starikova, Z. A. (2000a) *Radiochemistry (Translation of Radiokhimiya)*, **42**, 42–7.

Charushnikova, I. A., Krot, N. N., and Starikova, Z. A. (2000b) *Radiochemistry (Translation of Radiokhimiya)*, **42**, 37–41.

Charvillat, J. P. and Damien, D. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 559–63.

Charvillat, J. P., Benedict, U., Damien, D., and Muller, W. (1975) *Radiochem. Radioanal. Lett.*, **20**, 371–81.

Charvillat, J. P., Damien, D., and Wojakowski, A. (1977) *Rev. Chim. Miner.*, **14**, 178–88.

Charvillat, J. P. (1978) *Crystal Chemistry of Tranuranium Pnictides*, Report CEA-R-4933, CEA, Fontenay-aux-Roses, France.

Chevreton, M., Claudel, B., and Mentzen, B. (1968) *J. Chim. Phys. PCB*, **65**, 890–4.

Chikalla, T. D. and Eyring, L. (1968) *J. Inorg. Nucl. Chem.*, **30**, 133–45.

Chikalla, T. D. and Eyring, L. (1969) *J. Inorg. Nucl. Chem.*, **31**, 85–93.

Chiotti, P. (1954) *J. Electrochem. Soc.*, **101**, 567–70.

Choppin, G. R. and Stout, B. E. (1991) *Chemistry in Britain*, **27**, 1126–9.

Christ, C. L., Clark, J. R., and Evans, H. T. Jr (1955) *Science*, **121**, 472–3.

Chumaevskii, N. A., Minaeva, N. A., Mikhailov, Yu. N., Gorbunova, Yu. E., Beirakhov, A. G., and Shchelokov, R. N. (1998) *Zh. Neorg. Khim.*, **43**, 789–95.

Císařová, I., Skála, R., Ondruš, P., and Drábek, M. (2001) *Acta Crystallogr. E*, **57**, i32–4.

Clark, D. L., Conradson, S. D., Keogh, D. W., Palmer, P. D., Scott, B. L., and Tait, C. D. (1998a) *Inorg. Chem.* **37**, 2893–9.

Clark, D. L., Keogh, D. W., Palmer, P. D., Scott, B. L., and Tait, C. D. (1998b) *Angew. Chem. Int. Ed. Engl.*, **37**, 164–5.

Clark, R. J. and Corbett, J. D. (1963) *Inorg. Chem.*, **2**, 460–3.

Claudel, B., Mentzen, B., Navarro, A., and Sautereau, H. (1976) *J. Inorg. Nucl. Chem.*, **38**, 759–62.

Cloke, F. G. N., Hawkes, S. A., Hitchcock, P. B., and Scott, P. (1994) *Organometallics*, **13**, 2895–7.

Cohen, D. M. (1963) *Inorg. Chem.*, **2**, 866–7.

Cohen, D., Fried, S., Siegel, S., and Tani, B. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 257–60.

Copeland, J. C. and Cunningham, B. B. (1969) *J. Inorg. Nucl. Chem.*, **31**, 733–40.

Cotton, F. A. and Schwotzer, W. (1985) *Organometallics*, **4**, 942–3.

Cotton, F. A., Schwotzer, W., and Simpson, C. Q. (1986) *Angew. Chem.*, **98**, 652–4.

Cotton, F. A. and Schwotzer, W. (1987) *Organometallics*, **6**, 1275–80.

Cousson, A., Dabos, S., Abazli, H., Nectoux, F., Pages, M., and Choppin, G. (1984) *J. Less Common Metals*, **99**, 233–40.

Cousson, A. (1985) *Acta Crystallogr. C*, **41**, 1758–61.

Cousson, A., Stout, B., Nectoux, P., Pages, M., and Gasperin, M. (1986) *J. Less Common Metals*, **125**, 111–15.

Cousson, A., Proust, J., and Rizkalla, E. N. (1991) *Acta Crystallogr. C*, **47**, 2065–9.

Cousson, A., Nectoux, F., Pages, M., and Rizkalla, E. N. (1993) *Radiochim. Acta*, **61**, 177–80.

Cragg, P. J., Bott, S. G., and Atwood, J. L. (1988) *Lanthanide Actinide Res.*, **2**, 265–77.

Cramer, R. E., Maynard, R. B., and Gilje, J. W. (1978) *J. Am. Chem. Soc.*, **100**, 5562–4.

Cramer, R. E., Maynard, R. B., and Gilje, J. W. (1980) *Inorg. Chem.*, **19**, 2564–9.

Cramer, R. E., Maynard, R. B., Paw, J. C., and Gilje, J. W. (1981) *J. Am. Chem. Soc.*, **103**, 3589–90.

Cramer, R. E., Maynard, R. B., Paw, J. C., and Gilje, J. W. (1982) *Organometallics*, **1**, 869–71.

Cramer, R. E., Maynard, R. B., Paw, J. C., and Gilje, J. W. (1983) *Organometallics*, **2**, 1336–40.

Cramer, R. E., Panchanatheswaran, K., and Gilje, J. W. (1984a) *J. Am. Chem. Soc.*, **106**, 1853–4.

Cramer, R. E., Mori, A. L., Maynard, R. B., Gilje, J. W., Tatsumi, K., and Nakamura, A. (1984b) *J. Am. Chem. Soc.*, **106**, 5920–6.

Cramer, R. E., Engelhardt, U., Higa, K. T., and Gilje, J. W. (1987a) *Organometallics*, **6**, 41–5.

Cramer, R. E., Jeong, J. H., and Gilje, J. W. (1987b) *Organometallics*, **6**, 2010–12.

Cramer, R. E., Bruck, M. A., Edelmann, F., Afzal, D., Gilje, J. W., and Schmidbaur, H. (1988a) *Chem. Berichte*, **121**, 417–20.

Cramer, R. E., Edelmann, F., Mori, A. L., Roth, S., Gilje, J. W., Tatsumi, K., and Nakamura, A. (1988b) *Organometallics*, **7**, 841–9.

Cramer, R. E., Roth, S., and Gilje, J. W. (1989) *Organometallics*, **8**, 2327–30.

Cramer, R. E., Hitt, J., Chung, T., and Gilje, J. W. (1995a) *New J. Chem.*, **19**, 509–14.

Cramer, R. E., Ariyaratne, K. A. N. S., and Gilje, J. W. (1995b) *Z. Anorg. Allg. Chem.*, **621**, 1856–64.

Cromer, D. T. and Harper, P. E. (1955) *Acta Crystallogr.*, **8**, 847–8.

Cromer, D. T., Larson, A. C., and Roof, R. B. (1964) *Acta Crystallogr.*, **17**, 947–50.

Cunningham, B. B. and Wallmann, J. C. (1964) *J. Inorg. Nucl. Chem.*, **26**, 271–5.

Cymbaluk, T. H., Ernst, R. D., and Day, V. W. (1983) *Organometallics*, **2**, 963–9.

D'Eye, R. W. M., Sellman, P. G., and Murray, J. R. (1952) *J. Chem. Soc.*, 2555–62.

D'Eye, R. W. M. (1953) *J. Chem. Soc.*, 1670–2.

D'Eye, R. W. M. and Sellman, P. G. (1954) *J. Chem. Soc.*, 3760–6.

D'Eye, R. W. M. (1958) *J. Chem. Soc., Abstr.*, 196–9.

Dalley, N. K., Mueller, M. H., and Simonsen, S. H. (1971) *Inorg. Chem.*, **10**, 323–8.

Damien, D. (1971) *Inorg. Nucl. Chem. Lett.*, **7**, 291–7.

Damien, D. and Jové, J. (1971) *Inorg. Nucl. Chem. Lett.*, **7**, 685–8.

Damien, D. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 501–4.

Damien, D. and Charvillat, J. P. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 705–8.

Damien, D., Marcon, J. P., and Jové, J. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 317–20.

Damien, D. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 453–6.

Damien, D., Damien, N., Jové, J., and Charvillat, J. P. (1973) *Inorg. Nucl. Chem. Lett.*, **9**, 649–55.

Damien, D. (1974) *J. Inorg. Nucl. Chem.*, **36**, 307–8.

Damien, D. and Wojakowski, A. (1975) *Radiochem. Radioanal. Lett.*, **23**, 145–54.

Damien, D., Charvillat, J. P., and Müller, W. (1975) *Inorg. Nucl. Chem. Lett.*, **11**, 451–7.

Damien, D., Wojakowski, A., and Müller, W. (1976a) *Inorg. Nucl. Chem. Lett.*, **12**, 533–8.

Damien, D., Wojakowski, A., and Müller, W. (1976b) *Inorg. Nucl. Chem. Lett.*, **12**, 441–9.

Damien, D., Haire, R. G., and Peterson, J. R. (1979a) *J. Less Common Metals*, **68**, 159–65.

Damien, D. A., Haire, R. G., and Peterson, J. R. (1979b) *J. Phys., Colloq.*, **40** (C4), 95–100.

Damien, D., Haire, R. G., and Peterson, J. R. (1980a) *J. Inorg. Nucl. Chem.*, **42**, 995–8.

Damien, D., Haire, R. G., and Peterson, J. R. (1980b) *Inorg. Nucl. Chem. Lett.*, **16**, 537–41.

Damien, D. and de Novion, C. H. (1981) *J. Nucl. Mater.*, **100**, 167–77.

Damien, D., de Novion, C. H., and Thévenin, T. (1986) in *Handbook on the Physics and Chemistry of the Actinides,* vol. 4 (eds. A. J. Freeman and C. Keller), North-Holland, Amsterdam, pp. 39–96.

Dancausse, J.-P., Gering, E., Heathman, S., Benedict, U., Gerward, L., Olsen, S. S., and Hulliger, F. (1992) *J. Alloys Compds*, **189**, 205–8.

Danis, J. A., Hawkins, H. T., Scott, B. L., Runde, W. H., Scheetz, B. E., and Eichhorn, B. W. (2000) *Polyhedron*, **19**, 1551–7.

Danis, J. A., Lin, M. R., Scott, B. L., Eichhorn, B. W., and Runde, W. H. (2001) *Inorg. Chem.*, **40**, 3389–94.

Dao, N. Q., Bkouche-Waksman, I., Walewski, M., and Caceres, D. (1984) *Bull. Soc. Chim. Fr.*, 129–32.

Day, V. W., Marks, T. J., and Wachter, W. A. (1975) *J. Am. Chem. Soc.*, **97**, 4519–27.

De Ridder, D. J. A., Apostolidis, C., Rebizant, J., Kanellakopulos, B., and Maier, R. (1996a) *Acta Crystallogr. C*, **52**, 1436–8.

De Ridder, D. J. A., Rebizant, J., Apostolidis, C., Kanellakopulos, B., and Dornberger, E. (1996b) *Acta Crystallogr. C*, **52**, 597–600.

de Villardi, G. C., Charpin, P., Costes, R.-M., Folcher, G., Plurien, P., Rigny, P., and De Rango, C. (1978) *J. Chem. Soc., Chem. Commun.*, 90–2.

Debets, P. C. (1966) *Acta Crystallogr.*, **21**, 589–93.

Debets, P. C. (1968) *Acta Crystallogr. B*, **24**, 400–2.

Degetto, S., Baracco, L., Graziani, R., and Celon, E. (1978) *Transit. Met. Chem.*, **3**, 351–4.

Dejean, A., Charpin, P., Folcher, G., Rigny, P., Navaza, A., and Tsoucaris, G. (1987) *Polyhedron*, **6**, 189–95.

Delapalme, A., Schweiss, P., Spirlet, M. R., Rebizant, J., and Kanellakopulos, B. (1988) *MS Forum*, **27/28**, 211–16.

Deschamps, J. R. and Flippen-Anderson, J. L. (2002) in *Encyclopedia of Physical Science and Technology,* 3rd edn, vol. 4 (ed. R. A. Meyers), Academic Press, San Diego, CA, pp. 121–53.

Deshayes, L., Keller, N., Lance, M., Nierlich, M., and Vigner, J.-D. (1993) *Acta Crystallogr. C*, **49**, 16–19.

Deshayes, L., Keller, N., Lance, M., Navaza, A., Nierlich, M., and Vigner, J.-D. (1994a) *Polyhedron*, **13**, 1725–33.

Deshayes, L., Keller, N., Lance, M., Nierlich, M., Vigner, J.-D. (1994b) *Acta Crystallogr. C*, **50**, 1541–4.

Diaconescu, P. L. and Cummins, C. C. (2002) *J. Am. Chem. Soc.*, **124**, 7660–1.

Dodge, R. P., Smith, G. S., Johnson, Q., and Elson, R. E. (1967) *Acta Crystallogr.*, **22**, 85–9.

Dodge, R. P., Smith, G. S., Johnson, Q., and Elson, R. E. (1968) *Acta Crystallogr. B*, **24**, 304–11.

Dormond, A., Belkalem, B., Charpin, P., Lance, M., Vigner, J.-D., Folcher, G., and Guilard, R. (1986) *Inorg. Chem.*, **25**, 4785–90.

Douglass, R. M. and Staritzky, E. (1956) *Anal. Chem.*, **28**, 1211.

Douglass, R. M. (1962) *Acta Crystallogr.*, **15**, 505–6.

Drobyshevskii, I. V., Prusakov, V. N., Serik, V. F., and Sokolov, V. B. (1980) *Radiokhimiya*, **22**, 591–4.

Dusausoy, Y., Ghermani, N. E., Podor, R., and Cuney, M. (1996) *Eur. J. Miner.*, **8**, 667–73.

Duttera, M. R., Fagan, P. J., Marks, T. J., and Day, V. W. (1982) *J. Am. Chem. Soc.*, **104**, 865–7.

Duttera, M. R., Day, V. W., and Marks, T. J. (1984) *J. Am. Chem. Soc.*, **106**, 2907–12.

Edelman, M. A., Lappert, M. F., Atwood, J. L., and Zhang, H. (1987) *Inorg. Chim. Acta*, **139**, 185–6.

Edelman, M. A., Hitchcock, P. B., Hu, J., and Lappert, M. F. (1995) *New J. Chem.*, **19**, 481–9.

Edelmann, F. T. and Gun'ko, Y. K. (1997) *Coord. Chem. Rev.*, **165**, 163–237.

Edelmann, F. T. and Lorenz, V. (2000) *Coord. Chem. Rev.*, **209**, 99–160.

Eick, H. A. (1965) *Inorg. Chem.*, **4**, 1237–9.

Eick, H. A. and Mulford, R. N. R. (1969) *J. Inorg. Nucl. Chem.*, **31**, 371–5.

Eigenbrot, C. W. Jr and Raymond, K. N. (1981) *Inorg. Chem.*, **20**, 1553–6.

Eigenbrot, C. W. Jr and Raymond, K. N. (1982) *Inorg. Chem.*, **21**, 2653–60.

Eliseev, A. A., Molodkin, A. K., and Ivanova, O. M. (1967) *Zh. Neorg. Khim.*, **12**, 2854–5.

Eller, P. G. and Penneman, R. A. (1976) *Inorg. Chem.*, **15**, 2439–42.

Eller, P. G., Larson, A. C., Peterson, J. R., Ensor, D. D., and Young, J. P. (1979) *Inorg. Chim. Acta*, **37**, 129–33.

Ellinger, F. H. and Zachariasen, W. H. (1954) *J. Phys Chem.*, **58**, 405–8.

Ellinger, F. H. (1956) *J. Met.*, **8**, 1256–9.

Ernst, R. D., Kennelly, W. J., Day, C. S., Day, V. W., and Marks, T. J. (1979) *J. Am. Chem. Soc.*, **101**, 2656–64.

Ernst, R. D. and Marks, T. J. (1987) *J. Organomet. Chem.*, **318**, 29–82.

Ernst, R. D. (1990) *J. Organomet. Chem.*, **392**, 51–92.

Evans, W. J., Nyce, G. W., Johnston, M. A., and Ziller, J. W. (2000) *J. Am. Chem. Soc.*, **122**, 12019–20.

Evans, W. J., Nyce, G. W., and Ziller, J. W. (2001) *Organometallics*, **20**, 5489–91.

Evans, W. J., Kozimor, S. A., Nyce, G. W., and Ziller, J. W. (2003a) *J. Am. Chem. Soc.*, **125**, 13831–5.

Evans, W. J., Kozimor, S. A., and Ziller, J. W. (2003b) *J. Am. Chem. Soc.*, **125**, 14264–5.

Fagan, P. J., Manriquez, J. M., Marks, T. J., Day, V. W., Vollmer, S. H., and Day, C. S. (1980) *J. Am. Chem. Soc.*, **102**, 5393–6.

Fahey, J. A., Peterson, J. R., and Baybarz, R. D. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 101–7.

Fahey, J. A., Turcotte, R. P., and Chikalla, T. D. (1974) *Inorg. Nucl. Chem. Lett.*, **10**, 459–65.

Fahey, J. A., Turcotte, R. P., and Chikalla, T. D. (1976) *J. Inorg. Nucl. Chem.*, **38**, 495–500.

Fankuchen, I. (1935) *Z. Kristallogr.*, **91**, 473–9.

Farr, J. D., Giorgi, A. L., Bowman, M. G., and Money, R. K. (1961) *J. Inorg. Nucl. Chem.*, **18**, 42–7.

Favas, M. C., Kepert, D. L., Patrick, J. M., and White, A. H. (1983) *J. Chem. Soc., Dalton Trans.*, 571–81.

Fedoseev, A. M. and Perminov, V. P. (1983) *Radiokhimiya*, **25**, 555–7.

Fedosseev, A. M., Budantseva, N. A., Grigoriev, M. S., Bessonov, A. A., Astafurova, L. N., Lapitskaya, T. S., and Krupa, J.-C. (1999) *Radiochim. Acta*, **86**, 17–22.

Fellows, R. L., Peterson, J. R., Noé, M., Young, J. P., and Haire, R. G. (1975) *Inorg. Nucl. Chem. Lett.*, **11**, 737–42.

Ferro, R. (1952a) *Atti. Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat.*, **13**, 151–7.

Ferro, R. (1952b) *Atti. Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat.*, **13**, 401–5.

Ferro, R. (1953) *Atti. Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat.*, **14**, 89–94.

Ferro, R. (1954) *Z. Anorg. Allg. Chem.*, **275**, 320–6.

Ferro, R. (1955) *Acta Crystallogr.*, **8**, 360.

Ferro, R. (1956) *Acta Crystallogr.*, **9**, 817–18.

Finch, R. J., Cooper, M. A., Hawthorne, F. C., Ewing, R. C. (1999) *Can. Miner.*, **37**, 929–38.

Fischer, R. D., Klähne, E., and Kopf, J. (1978) *Z. Naturforsch. B*, **33**, 1393–7.

Fischer, R. D., Werner, G.-D., Lehmann, T., Hoffmann, G., and Weigel, F. (1981) *J. Less Common Metals*, **80**, 121–32.

Florin, A. E., Tannenbaum, I. R., and Lemons, J. F. (1956) *J. Inorg. Nucl. Chem.*, **2**, 368–79.

Folcher, G., Charpin, P., Costes, R. M., Keller, N., and de Villardi, G. C. (1979) *Inorg. Chim. Acta.*, **34**, 87–90.

Fried, S., Hagemann, F., and Zachariasen, W. H. (1950) *J. Am. Chem. Soc.*, **72**, 771–5.

Fried, S., Cohen, D., Siegel, S., and Tani, B. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 495–8.

Fronczek, F. R., Halstead, G. W., and Raymond, K. N. (1977) *J. Am. Chem. Soc.*, **99**, 1769–75.

Fujita, D. K., Cunningham, B. B., and Parsons, T. C. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 307–13.

Galešić, N., Matković, B., Topić, M., Coffou, E., and Śljukić, M. (1984) *Croat. Chem. Acta*, **57**, 597–608.

Gantzel, P. K. and Baldwin, N. L. (1964) *Acta Crystallogr.*, **17**, 772–3.

Gardner, E. R., Markin, T. L., and Street, R. S. (1965) *J. Inorg. Nucl. Chem.*, **27**, 541–51.

Gibson, J. K. and Haire, R. G. (1985a) *J. Solid State Chem.*, **59**, 317–23.

Gibson, J. K. and Haire, R. G. (1985b) *J. Less Common Metals*, **109**, 251–9.

Gibson, J. K. and Haire, R. G. (1987) *J. Less Common Metals*, **127**, 267.

Gieren, A. and Hoppe, W. (1971) *J. Chem. Soc., Chem. Commun.*, 413–14.

Gilbert, T. M., Ryan, R. R., and Sattelberger, A. P. (1988) *Organometallics*, **7**, 2514–18.

Gilbert, T. M., Ryan, R. R., and Sattelberger, A. P. (1989) *Organometallics*, **8**, 857–9.

Gingerich, K. A. and Wilson, D. W. (1965) *Inorg. Chem.*, **4**, 987–93.

Girolami, G. S., Milam, S. N., and Suslick, K. S. (1987) *Inorg. Chem.*, **26**, 343–4.

Girolami, G. S., Milam, S. N., and Suslick, K. S. (1988) *J. Am. Chem. Soc.*, **110**, 2011–12.

Girolami, G. S., Gorlin, P. A., Milam, S. N., Suslick, K. S., and Wilson, S. R. (1994) *J. Coord. Chem.*, **32**, 173–212.

Goldschmidt, V. M. and Thomassen, L. (1923) Videnskapsselskapets Skrifter I, *Mat.-Naturv. Klasse*, 48 pp.

Gottfriedsen, J. and Edelmann, F. T. (2005) *Coord. Chem. Rev.*, **249**, 919–69.

Govindarajan, S., Patil, K. C., Poojary, M. D., and Manohar, H. (1986) *Inorg. Chim. Acta*, **120**, 103–7.

Gradoz, P., Ephritikhine, M., Lance, M., Vigner, J.-D., and Nierlich, M. (1994) *J. Organomet. Chem.*, **481**, 69–73.

Graf, P., Cunningham, B. B., Dauben, C. H., Wallmann, J. C., Templeton, D. H., and Ruben, H. (1956) *J. Am. Chem. Soc.*, **78**, 2340.

Graham, J. and McTaggart, F. K. (1960) *Aust. J. Chem.*, **13**, 67–73.

Graziani, R., Zarli, B., and Bandoli, G. (1967) *Ric. Sci.*, **37**, 984–5.

Graziani, R., Bombieri, G., and Forsellini, E. (1972) *J. Chem. Soc., Dalton Trans.*, 2059–61.

Graziani, R., Battiston, G. A., Casellato, U., and Sbrignadello, G. (1983) *J. Chem. Soc., Dalton Trans.*, 1–7.

Greaves, C. and Fender, B. E. F. (1972) *Acta Crystallogr. B*, **28**, 3609–14.

Green, J. L. and Cunningham, B. B. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 343–9.

Greenwood, N. N. and Earnshaw, A. (2001) *Chemistry of the Elements*, 2nd edn, Butterworth-Heinemann, Oxford., pp. 1227–84.

Grigor'ev, M. S., Yanovskii, A. I., Fedoseev, A. M., Budantseva, N. A., Struchkov, Y. T., and Krot, N. N. (1991a) *Radiokhimiya*, **33**, 17–19.

Grigor'ev, M. S., Bessonov, A. A., Yanovskii, A. I., Struchkov, Yu. T., and Krot, N. N. (1991b) *Radiokhimiya*, **33**, 46–53.

Grigor'ev, M. S., Baturin, N. A., Regel, L. L., and Krot, N. N. (1991c) *Radiokhimiya*, **33**, 19–25.

Grigor'ev, M. S., Baturin, N. A., Budantseva, N. A., and Fedoseev, A. M. (1993a) *Radiokhimiya*, **35**, 29–38.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Yu. T. (1993b) *Radiokhimiya*, **35**, 24–30.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Yu. T. (1993c) *Radiokhimiya*, **35**, 31–7.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Yu. T. (1994) *Zh. Neorg. Khim.*, **39**, 1328–31.

Grigor'ev, M. S., Charushnikova, I. A., Baturin, N. A., and Krot, N. N. (1995) *Zh. Neorg. Khim.*, **40**, 732–5.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Yu. T. (1996) *Zh. Neorg. Khim.*, **41**, 539–42.

Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., and Struchkov, Yu. T. (1997) *Radiochemistry* (*Translation of Radiokhimiya*), **39**, 420–3.

Grønvold, F. (1955) *J. Inorg. Nucl. Chem.*, **1**, 357–70.

Guang-Di, Y., Yu-Guo, F., and Yan-De, H. (1990) *Science in China* (*Series B*), **33**, 1418–24.

Guesdon, A., Provost, J., and Raveau, B. (1999) *J. Mater. Chem.*, **9**, 2583–7.

Guesdon, A., Chardon, J., Provost, J., and Raveau, B. (2002) *J. Solid State Chem.*, **165**, 89–93.

Guggenberger, L. J. and Jacobson, R. A. (1968) *Inorg. Chem.*, **7**, 2257–60.

Gun'ko, Y. K. and Edelmann, F. T. (1996) *Coord. Chem. Rev.*, **156**, 1–89.

Gutberlet, T., Dreissig, W., Luger, P., Bechthold, H.-C., Maung, R., and Knöchel, A. (1989) *Acta Crystallogr. C*, **45**, 1146–9.

Habash, J. and Smith, A. J. (1983) *Acta Crystallogr. C*, **39**, 413–15.

Haddad, S. F., Al-Far, R. H., and Ahmed, F. R. (1987) *Acta Crystallogr. C*, **43**, 453–6.

Haire, R. G. and Baybarz, R. D. (1973) *J. Inorg. Nucl. Chem.*, **35**, 489–96.

Haire, R. G. and Baybarz, R. D. (1974) *J. Inorg. Nucl. Chem.*, **36**, 1295–302.

Haire, R. G. and Asprey, L. B. (1976) *Inorg. Nucl. Chem. Lett.*, **12**, 73–84.

Haire, R. G. and Baybarz, R. D. (1979) *J. Phys., Colloq.*, 101–2.

Haire, R. G., Young, J. P., and Peterson, J. R. (1983) *J. Less Common Metals*, **93**, 339–45.

Haire, R. G. and Eyring, L. (1994) in *Handbook on the Physics and Chemistry of Rare Earths,* vol. 18 (eds. K. A. Gschneidner Jr, L. Eyring, G. R. Choppin, and G. H. Lander), Elsevier, Amsterdam, pp. 413–505.

Hale, W. H. Jr and Mosley, W. C. (1973) *J. Inorg. Nucl. Chem.*, **35**, 165–71.

Hall, D., Rae, A. D., and Waters, T. N. (1965) *Acta Crystallogr.*, **19**, 389–95.

Halstead, G. W., Baker, E. C., and Raymond, K. N. (1975) *J. Am. Chem. Soc.*, **97**, 3049–52.

Harper, E. A., Hedger, H. J., and Dalton, J. T. (1968) *Nature* (*UK*), **219**, 151.

Harrowfield, J. M., Ogden, M. I., and White, A. H. (1991a) *J. Chem. Soc., Dalton Trans.*, 979–85.

Harrowfield, J. M., Ogden, M. I., and White, A. H. (1991b) *J. Chem. Soc., Dalton Trans.*, 2625–32.

Haschke, J. M., Hodges, A. E. III, and Lucas, R. L. (1987) *J. Less Common Metals*, **133**, 155–66.

Hassaballa, H., Steed, J. W., and Junk, P. C. (1988) *J. Chem. Soc., Chem. Commun.*, 577–8.

Hassaballa, H., Steed, J. W., Junk, P. C., and Elsegood, M. R. J. (1998) *Inorg. Chem.*, **37**, 4666–71.

Hauck, J. (1976) *Inorg. Nucl. Chem. Lett.*, **12**, 617–22.

Haug, H. O. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2753–8.

Haug, H. O. and Baybarz, R. D. (1975) *Inorg. Nucl. Chem. Lett.*, **11**, 847–55.

Hayes, R. G. and Thomas, J. L. (1971) *Organomet. Chem. Rev. A*, **7**, 1–50.

Henkie, Z., Wiśniewski, P., and Gukasov, A. (1997) *J. Crystal Growth*, **172**, 459–65.

Herak, R. and Jovanovic, B. (1969) *Inorg. Nucl. Chem. Lett.*, **5**, 693–7.

Herrero, J. A., Bermudez, J., and Rios, E. G. (1977) *An. Quim.*, **73**, 1271–9.

Hery, Y. (1979) *Synthesis, Crystallographic, and Magnetic Properties of Protactinium Pnictides*, Report CEA-R-4971, CEA, Fontenay-aux-Roses, France.

Hery, Y., Damien, D., and Charvillat, J. P. (1979) *Radiochem. Radioanal. Lett.*, **37**, 17–26.

Hillebrand, W. F. (1893) *Z. Anorg. Allg. Chem.*, **3**, 249–51.

Hitchcock, P. B., Lappert, M. F., and Taylor, R. G. (1984) *J. Chem. Soc., Chem. Commun.*, 1082–4.

Hoard, J. L. and Stroupe, J. D. (1958) *Structure of Crystalline Uranium Hexafluoride*, TID-5290 (Book 1), U.S. Atomic Energy Commun., pp. 325–49.

Hodgson, K. O. and Raymond, K. N. (1973) *Inorg. Chem.*, **12**, 458–66.

Hoekstra, H. R. and Siegel, S. (1961) *J. Inorg. Nucl. Chem.*, **18**, 154–65.

Hoekstra, H. R., Siegel, S., and Galloy, J. J. (1970) *J. Inorg. Nucl. Chem.*, **32**, 3237–48.

Hoekstra, H. R. (1982) in *Gmelin Handbook of Inorganic Chemistry, Uranium*, 8th edn, Suppl. vol. A5 (eds. K.-C. Buschbeck and C. Keller), Springer-Verlag, Berlin., pp. 211–40.

Horyn, R., Henry, J. Y., and Rossat-Mignod, J. (1983) *J. Crystal Growth*, **63**, 407–9.

Howatson, J., Grev, D. M., and Morosin, B. (1975) *J. Inorg. Nucl. Chem.*, **37**, 1933–5.

Hughes, K.-A. and Burns, P. C. (2003) *Acta. Crystallogr.* C, **59**, i7–8.

Hulet, E. K., Wild, J. F., Lougheed, R. W., and Hayes, W. N. (1976) in *Proc. Moscow Symp. Chem. Transuranium Elements*, 1972 (eds. V. I. Spitsyn and J. J. Katz), Pergamon, Oxford, pp. 33–5.

Hulliger, F. (1966) Nature (*UK*), **209**, 499–500.

Hunt, E. B. and Rundle, R. E. (1951) *J. Am. Chem. Soc.*, **73**, 4777–81.

Hunter, W. E. and Atwood, J. L. (1984) *Inorg. Chim. Acta*, **94**, 80.

Hurtgen, C. and Fuger, J. (1977) *Inorg. Nucl. Chem. Lett.*, **13**, 179–88.

Hutchings, M. T. (1987) *J. Chem. Soc., Faraday Trans. 2*, **83**, 1083–103.

Hyeon, J.-Y. and Edelmann, F. T. (2003a) *Coord. Chem. Rev.*, **241**, 249–72.

Hyeon, J.-Y. and Edelmann, F. T. (2003b) *Coord. Chem. Rev.*, **247**, 21–78.

Hyeon, J.-Y., Gottgriedsen, J., and Edelmann, F. T. (2005) *Coord. Chem. Rev.*, **249**, 2787–844.

Iandelli, A. (1952a) *Atti. Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat.*, **13**, 144–51.

Iandelli, A. (1952b) *Atti. Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. e Nat.*, **13**, 138–43.

Immirzi, A., Bombieri, G., Degetto, S., and Marangoni, G. (1975) *Acta Crystallogr. B*, **31**, 1023–8.

Irish, D. E., Pursel, R., Taylor, N. J., and Toogood, G. E. (1985) *Acta Crystallogr. C*, **41**, 1012–3.

Iyer, P. N. and Natarajan, P. R. (1989) *J. Less Common Metals*, **146**, 161–6.

Iyer, P. N. and Natarajan, P. R. (1990) *J. Less Common Metals*, **159**, 1–11.

Jacob, C. W. and Warren, B. E. (1937) *J. Am. Chem. Soc.*, **59**, 2588–91.

Jacobson, E. L., Freeman, R. D., Tharp, A. G., and Searcy, A. W. (1956) *J. Am. Chem. Soc.*, **78**, 4850–2.

Janczak, J. and Kubiak, R. (1999) *Polyhedron*, **18**, 1621–7.

Janczak, J., Kubiak, R., Svoboda, I., Jezierski, A., and Fuess, H. (2000) *Inorg. Chim. Acta*, **304**, 150–5.

Jayadevan, N. C. and Chackraburtty, D. M. (1972) *Acta Crystallogr. B*, **28**, 3178–82.

Jayadevan, N. C., Dias, R. M. A., and Chakraburtty, D. M. (1973) *J. Inorg. Nucl. Chem.*, **35**, 1037–40.

Jayadevan, N. C., Mudher, K. D. S., and Chackraburtty, D. M. (1975) *Acta Crystallogr. B*, **31**, 2277–80.

Jayadevan, N. C., Mudher, K. D. S., and Chackraburtty, D. M. (1982) *Z. Kristallogr.*, **161**, 7–13.

Jelenić, I., Grdenić, D., and Bezjak, A. (1964) *Acta Crystallogr.*, **17**, 758–9.

Jette, E. R. (1955) *J. Chem. Phys.*, **23**, 365–8.

Jiang, J., Sarsfield, M. J., Renshaw, J. C., Livens, F. R., Collison, D., Charnock, J. M., Helliwell, M., and Eccles, H. (2002) *Inorg. Chem.*, **41**, 2799–806.

Kadish, K. M., Liu, Y. H., Anderson, J. E., Charpin, P., Chevrier, G., Lance, M., Nierlich, M., Vigner, J.-D., Dormond, A., Belkalem, B., and Guilard, R. (1988) *J. Am. Chem. Soc.*, **110**, 6455–62.

Kanellakopulos, B. and Bagnall, K. W. (1972) in *MTP International Review of Science, Inorganic Chemistry,* vol. 7 (ed. K. W. Bagnall), Butterworths, London., pp. 299–322.

Kanellakopulos, B. and Aderhold, C. (1973) *XXIVth IUPAC Congress*, Hamburg, Abstracts, p. 632.

Kanellakopulos, B., Dornberger, E., and Baumgärtner, F. (1974) *Inorg. Nucl. Chem. Lett.*, **10**, 155–60.

Kannan, S., Raj, S. S., and Fun, H.-K. (2001) *Polyhedron*, **20**, 2145–50.

Karmazin, L., Mazzanti, M., and Pécaut, J. (2002) *J. Chem. Soc., Chem. Commun.,* 654–5.

Karraker, D. G., Stone, J. A., Jones, E. R. Jr, and Edelstein, N. (1970) *J. Am. Chem. Soc.*, **92**, 4841–5.

Karraker, D. G. and Stone, J. A. (1974) *J. Am. Chem. Soc.*, **96**, 6885–8.

Kato, Y., Kimura, T., Yoshida, Z., and Nitani, N. (1998) *Radiochim. Acta*, **82**, 63–8.

Keenan, T. K. and Kruse, F. H. (1964) *Inorg. Chem.*, **3**, 1231–2.

Keenan, T. K. (1965) *Inorg. Chem.*, **4**, 1500–1.

Keenan, T. K. (1968) *Inorg. Nucl. Chem. Lett.*, **4**, 381–4.

Keenan, T. K. and Asprey, L. B. (1969) *Inorg. Chem.*, **8**, 235–8.

Keller, C. and Walter, K. H. (1965) *J. Inorg. Nucl. Chem.*, **27**, 1253–60.

Keller, C. (1973) in *Comprehensive Inorganic Chemistry,* vol. 5, (eds. J. C. Bailar Jr, H. J. Emeléus, S. R. Nyholm, and A. F. Trotman-Dickenson), Pergamon, Oxford, pp. 219–76.

Kemmler-Sack, S. (1969) *Z. Anorg. Allg. Chem.*, **364**, 88–99.

Kempter, C. P. and Krikorian, N. H. (1962) *J. Less Common Metals*, **4**, 244–51.

Khodadad, P. (1959) *Compt. Rend.*, **249**, 694–6.

Kierkegaard, P. (1956) *Acta Chem. Scand.*, **10**, 599–616.

Kilimann, U. and Edelmann, F. T. (1995) *Coord. Chem. Rev.*, **141**, 1–61.

Kimmel, G. (1978) *J. Less Common Metals*, **59**, P83–6.

Kiplinger, J. L., Morris, D. E., Scott, B. L., and Burns, C. J. (2002a) *Organometallics*, **21**, 5978–82.

Kiplinger, J. L., John, K. D., Morris, D. E., Scott, B. L., and Burns, C. J. (2002b) *Organometallics*, **21**, 4306–8.

Kiplinger, J. L., Morris, D. E., Scott, B. L., and Burns, C. J. (2002c) *Organometallics*, **21**, 3073–5.

Kirchner, H. P., Merz, K. M., and Brown, W. R. (1963) *J. Am. Ceram. Soc.*, **46**, 137–41.

Knösel, F., Roesky, H. W., and Edelmann, F. (1987) *Inorg. Chim. Acta*, **139**, 187–8.

Knowles, K. J., Rahakrishna, P., and Willis, B. T. M. (1981) *Room-Temperature Study of Uranium Dioxides by Pulse Neutron Powder Diffraction*, AERE-MPD/NBS-169, Sci. Res. Counc., Rutherford Laboratory, Chilton, UK.

Kobayashi, T. (1978) *Bull. Inst. Chem. Res. Kyoto. Univ.*, **56**, 204–212.

Kohlmann, H. and Beck, H. P. (1997) *Z. Anorg. Allg. Chem.*, **623**, 785–90.

Kohlmann, H. and Beck, H. P. (1999) *Z. Kristallogr.*, **214**, 341–5.

Konrad, T., Jeitschko, W., Danebrock, M. E., and Evers, C. B. H. (1996) *J. Alloys Compds*, **234**, 56–61.

Korst, W. L. (1962) *Acta Crystallogr.* **15**, 287–8.

Kovba, L. M., Trunov, V. K., and Grigor'ev, A. I. (1965) *Zh. Strukt. Khim.*, **6**, 919–21.

Krivovichev, S. V. and Burns, P. C. (2004) *Radoichemistry*, **46**, 16–9.

Kruger, O. L. and Moser, J. B. (1967) *J. Phys. Chem. Solids*, **28**, 2321–5.

Krupka, M. C. (1970) *J. Less Common Metals*, **20**, 135–40.

Kunitomi, N., Hamaguchi, Y., Sakamoto, M., Doi, K., and Komura, S. (1964) *J. Phys.* (*Paris*), **25**, 462–8.

La Ginestra, A., Variali, G., and Valigi, M. (1965) *Gazz. Chim. Ital.*, **95**, 1096–9.

Laidler, J. B. (1966) *J. Chem. Soc. A*, 780–4.

Land, C. C., Johnson, K. A., and Ellinger, F. H. (1965) *J. Nucl. Mater.*, **15**, 23–32.

Lander, G. H., Heaton, L., Mueller, M. H., and Anderson, K. D. (1969) *J. Phys. Chem. Solids*, **30**, 733–7.

Larson, D. T. and Haschke, J. M. (1981) *Inorg. Chem.*, **20**, 1945–50.

Laubereau, P. G. and Burns, J. H. (1970a) *Inorg. Chem.*, **9**, 1091–5.

Laubereau, P. G. and Burns, J. H. (1970b) *Inorg. Nucl. Chem. Lett.*, **6**, 59–63.

Laugt, M. (1973) *J. Appl. Crystallogr.*, **6**, 299–301.

Lawaldt, D., Marquart, R., Werner, G.-D., and Weigel, F. (1982) *J. Less Common Metals*, **85**, 37–41.

Le Bihan, T., Noël, H., and Rogl, P. (1996) *J. Alloys Compds*, **240**, 128–33.

Le Borgne, T., Lance, M., Nierlich, M., and Ephritikhine, M. (2000) *J. Organomet. Chem.*, **598**, 313–17.

Le Cloarec, M. F., Dartyge, J. M., Kovacevic, S., and Muxart, R. (1976) *J. Inorg. Nucl. Chem.*, **38**, 737–9.

Le Cloarec, M. F. and Cazaussus, A. (1978) *J. Inorg. Nucl. Chem.*, **40**, 1680–1.

Le Maréchal, J. F., Villiers, C., Charpin, P., Lance, M., Nierlich, M., Vigner, J.-D., and Ephritikhine, M. (1989a) *J. Chem. Soc., Chem. Commun.*, 308–10.

Le Maréchal, J. F., Villiers, C., Charpin, P., Nierlich, M., Lance, M., Vigner, J.-D., and Ephritikhine, M. (1989b) *J. Organomet. Chem.*, **379**, 259–69.

Le Roux, S. D., Van Tets, A., and Adrian, H. W. W. (1979) *Acta Crystallogr. B*, **35**, 3056–7.

Leger, J. M., Yacoubi, N., and Loriers, J. (1981) *J. Solid State Chem.*, **36**, 261–70.

Legros, J.-P. and Jeannin, Y. (1976) *Acta Crystallogr. B*, **32**, 2497–503.

Leigh, H. D. and McCartney, E. R. (1974) *J. Am. Ceram. Soc.*, **57**, 192.

Leong, J., Hodgson, K. O., and Raymond, K. N. (1973) *Inorg. Chem.*, **12**, 1329–35.

Lescop, C., Arliguie, T., Lance, M., Nierlich, M. and Ephritikhine, M. (1999) *J. Organomet. Chem.*, **580**, 137–44.

Leverd, P. C., Arliguie, T., Lance, M., Nierlich, M., Vigner, J.-D., and Ephritikhine, M. (1994) *J. Chem. Soc., Dalton Trans.*, 501–4.

Leverd, P. C., Ephritikhine, M., Lance, M., Vigner, J.-D., and Nierlich, M. (1996) *J. Organomet. Chem.*, **507**, 229–37.

Leverd, P. C., Berthault, P., Lance, M., and Nierlich, M. (1998) *Eur. J. Inorg. Chem.*, 1859–62.

Leverd, P. C., Dumazet-Bonnamour, I., Lamartine, R., and Nierlich, M. (2000) *J. Chem. Soc., Chem. Commun.*, 493–4.

Leverd, P. C. and Nierlich, M. (2000) *Eur. J. Inorg. Chem.*, 1733–8.

Leverd, P. C., Rinaldo, D., and Nierlich, M. (2002) *J. Chem. Soc., Dalton Trans.*, 829–31.

Levet, J. C., Potel, M., and Le Marouille, J.-Y. (1977) *Acta Crystallogr. B*, **33**, 2542–6.

Levet, J. C. and Noël, H. (1979) *J. Solid State Chem.*, **28**, 67–73.

Levet, J. C. and Noël, H. (1981) *J. Inorg. Nucl. Chem.*, **43**, 1841–3.

Levy, J. H., Taylor, J. C., and Wilson, P. W. (1975) *Acta Crystallogr. B*, **31**, 880–2.

Levy, J. H., Taylor, J. C., and Wilson, P. W. (1976) *J. Chem. Soc., Dalton Trans.*, 219–24.

Levy, J. H., Taylor, J. C., and Wilson, P. W. (1977) *J. Inorg. Nucl. Chem.*, **39**, 1989–91.

Levy, J. H., Taylor, J. C., and Wilson, P. W. (1978) *J. Inorg. Nucl. Chem.*, **40**, 1055–7.

Levy, J. H., Taylor, J. C., and Waugh, A. B. (1980) *Inorg. Chem.*, **19**, 672–4.

Lin, Z., Le Maréchal, J.-F., Sabat, M., and Marks, T. J. (1987) *J. Am. Chem. Soc.*, **109**, 4127–9.

Lin, Z., Brock, C. P., and Marks, T. J. (1988) *Inorg. Chim. Acta*, **141**, 145–9.

Locock, A. J. and Burns, P. C. (2002) *J. Solid State Chem.*, **163**, 275–80.

Loopstra, B. O. (1964) *Acta Crystallogr.*, **17**, 651–4.

Loopstra, B. O. (1970) *Acta Crystallogr. B*, **26**, 656–7.

Loopstra, B. O., Taylor, J. C., and Waugh, A. B. (1977) *J. Solid State Chem.*, **20**, 9–19.

Lorenz, R., Scherff, H. L., and Toussaint, N. (1969) *J. Inorg. Nucl. Chem.*, **31**, 2381–90.

Lorenzelli, R. (1968) *Compt. Rend. Acad. Sci. C*, **226**, 900–2.

Louër, M., Brochu, R., Louër, D., Arsalane, S., and Ziyad, M. (1995) *Acta Crystallogr. B*, **51**, 908–13.

Lukens, W. W. Jr, Beshouri, S. M., Blosch, L. L., Stuart, A. L., and Andersen, R. A. (1999) *Organometallics*, **18**, 1235–46.

Lundgren, G. (1950) *Arkiv. Kemi*, **2**, 535–49.

Lundgren, G. (1952) *Arkiv. Kemi*, **2**, 421–8.

Lundgren, G. (1953) *Arkiv. Kemi*, **5**, 349–63.

Maier, R., Kanellakopulos, B., Apostolidis, C., Meyer, D., and Rebizant, J. (1993) *J. Alloys Compds*, **190**, 269–71.

Malcic, S. S. (1958a) *Bull. Inst. Nucl. Sci. Boris Kidrich*, **8**, 99–104.

Malcic, S. S. (1958b) *Bull. Inst. Nucl. Sci. Boris Kidrich*, **8**, 95–7.

Mallett, M. W., Gerds, A. F., and Vaughan, D. A. (1951) *J. Electrochem. Soc.*, **98**, 505–9.

Malm, J. G., Weinstock, B., and Weaver, E. E. (1958) *J. Phys. Chem.*, **62**, 1506–8.

Malm, J. G., Williams, C. W., Soderholm, L., and Morss, L. R. (1993) *J. Alloys Compds*, **194**, 133–7.

Manriquez, J. M., Fagan, P. J., Marks, T. J., Day, C. S., and Day, V. W. (1978) *J. Am. Chem. Soc.*, **100**, 7112–14.

Manriquez, J. M., Fagan, P. J., Marks, T. J., Vollmer, S. H., Day, C. S., and Day, V. W. (1979) *J. Am. Chem. Soc.*, **101**, 5075–8.

Marangoni, G., Degetto, S., Graziani, R., Bombieri, G., and Forsellini, E. (1974) *J. Inorg. Nucl. Chem.*, **36**, 1787–94.

Marcon, J. P. and Pascard, R. (1966) *J. Inorg. Nucl. Chem.*, **28**, 2551–60.

Marcon, J. P. (1969) *Contribution à l'Etude des Sulfures Actinides*, CEA-R-3919, Sous. Dir. Met., CEA, Fontenay-aux-Roses, France.

Marks, T. J. (1974) *J. Organomet. Chem.*, **79**, 181–99.

Marks, T. J. (1975) *J. Organomet. Chem.*, **95**, 301–15.

Marks, T. J. (1976) *J. Organomet. Chem.*, **119**, 229–41.

Marks, T. J. (1977) *J. Organomet. Chem.*, **138**, 157–83.

Marks, T. J. (1978) *J. Organomet. Chem.*, **158**, 325–43.

Marks, T. J. (1979a) *J. Organomet. Chem.*, **180**, 153–75.

Marks, T. J. (1979b) *Prog. Inorg. Chem.*, **25**, 223–333.

Marks, T. J. (1980) *J. Organomet. Chem.*, **203**, 415–48.

Marks, T. J. (1982a) *Science*, **217**, 989–97.

Marks, T. J. (1982b) *J. Organomet. Chem.*, **227**, 317–40.

Marples, J. A. C. (1965) *Acta Crystallogr.*, **18**, 815–17.

Marples, J. A. C. (1970) *J. Phys. Chem. Solids*, **31**, 2431–9.

Marquart, R., Hoffmann, G., and Weigel, F. (1983) *J. Less Common Metals*, **91**, 119–27.

Masaki, N. and Doi, K. (1972) *Acta Crystallogr. B*, **28**, 785–91.

Masaki, N. and Tagawa, H. (1975) *J. Nucl. Mater.*, **58**, 241–3.

Masci, B., Nierlich, M., and Thuéry, P. (2002a) *New J. Chem.*, **26**, 120–8.

Masci, B., Gabrielli, M., Mortera, S. L., Nierlich, M., and Thuéry, P. (2002b) *Polyhedron*, **21**, 1125–31.

Matson, L. K., Moody, J. W., and Himes, R. C. (1963) *J. Inorg. Nucl. Chem.*, **25**, 795–800.

Matković, B. and Šljukić, M. (1965) *Croat. Chem. Acta*, **37**, 115–16.

Matković, B., Prodić, B., and Šljukić, M. (1968a) *Bull. Soc. Chim. Fr.*, **4**, 1777–9.

Matković, B., Prodić, B., Šljukić, M., and Peterson, S. W. (1968b) *Croat. Chem. Acta*, **40**, 147–61.

McWhan, D. B., Wallmann, J. C., Cunningham, B. B., Asprey, L. B., Ellinger, F. H., and Zachariasen, W. H. (1960) *J. Inorg. Nucl. Chem.*, **15**, 185–7.

McWhan, D. B., Cunningham, B. B., and Wallmann, J. C. (1962) *J. Inorg. Nucl. Chem.*, **24**, 1025–38.

Mefod'eva, M. P., Grigor'ev, M. S., Afonos'eva, T. V., and Kryukov, E. B. (1981) *Radiokhimiya*, **23**, 697–703.

Menovsky, A., Franse, J. J. M., and Klaasse, J. C. P. (1984) *J. Crystal Growth*, **70**, 519–22.

Mentzen, B. F. (1977) *Acta Crystallogr. B*, **33**, 2546–9.

Mentzen, B. F., Puaux, J.-P., and Loiseleur, H. (1977) *Acta Crystallogr. B*, **33**, 1848–51.

Mentzen, B. F., Puaux, J.-P., and Sautereau, H. (1978a) *Acta Crystallogr. B*, **34**, 1846–9.

Mentzen, B. F., Puaux, J.-P., and Sautereau, H. (1978b) *Acta Crystallogr. B*, **34**, 2707–11.

Mentzen, B. F. and Sautereau, H. (1980) *Acta Crystallogr. B*, **36**, 2051–3.

Mereiter, K. (1986a) *Acta Crystallogr. C*, **42**, 1678–81.

Mereiter, K. (1986b) *Acta Crystallogr. C*, **42**, 1682–4.

Meunier-Piret, J., Declercq, G., Germain, G., and Van Meerssche, M. (1980a) *Bull. Soc. Chim. Belg.*, **89**, 121–4.

Meunier-Piret, J., Germain, G., Declercq, J. P., and Van Meerssche, M. (1980b) *Bull. Soc. Chim. Belg.*, **89**, 241–5.

Meunier-Piret, J. and Van Meerssche, M. (1984) *Bull. Soc. Chim. Belg.*, **93**, 299–305.

Mikhailov, Yu. N., Gorbunova, Yu. E., Serezhkina, L. B., Losev, V. Yu., and Serezhkin, V. N. (1996) *Zh. Neorg. Khim.*, **41**, 2058–62.

Mikhailov, Yu. N., Kanishcheva, A. S., Gorbunova, Yu. E., Belomestnykh, V. I., and Sveshnikova, L. B. (1997) *Zh. Neorg. Khim.*, **42**, 1980–5.

Mikhailov, Yu. N., Gorbunova, Yu. E., Shishkina, O. V., Serezhkina, L. B., and Serezhkin, V. N. (2000a) *Zh. Neorg. Khim.*, **45**, 1999–2002.

Mikhailov, Yu. N., Gorbunova, Yu. E., Shishkina, O. V., Serezhkina, L. B., and Serezhkin, V. N. (2000b) *Zh. Neorg. Khim.*, **45**, 1825–9.

Ming, W., Pei-Ju, Z., Jing-Zhi, Z., Zhong, C., Jin-Ming, S., and Yong-Hui, Y. (1987a) *Acta Crystallogr. C*, **43**, 873–5.

Ming, W., Pei-Ju, Z., Jing-Zhi, Z., Zhong, C., Jin-Ming, S., and Yong-Hui, Y. (1987b) *Acta Crystallogr. C*, **43**, 1544–6.

Ming, W., Boyi, W., Pei-Ju, Z., Wenji, W., and Jie, L. (1988) *Acta Crystallogr. C*, **44**, 1913–16.

Mitchell, A. W. and Lam., D. J. (1970a) *J. Nucl. Mater.*, **36**, 110–12.

Mitchell, A. W. and Lam, D. J. (1970b) *J. Nucl. Mater.*, **37**, 349–52.

Mitchell, A. W. and Lam, D. J. (1971) *J. Nucl. Mater.*, **39**, 219–23.

Mitchell, A. W. and Lam, D. J. (1974) *J. Nucl. Mater.*, **52**, 125–7.

Moloy, K. G., Marks, T. J., and Day, V. W. (1983) *J. Am. Chem. Soc.*, **105**, 5696–8.

Moody, D. C. and Ryan, R. R. (1979) *Crystal Struct. Commun.*, **8**, 933–6.

Moody, D. C., Penneman, R. A., and Salazar, K. V. (1979) *Inorg. Chem.*, **18**, 208–9.

Mooney, R. C. L. (1949) *Acta Crystallogr.*, **2**, 189–91.

Morse, J. W., Shanbhag, P. M., Saito, A., and Choppin, G. R. (1984) *Chem. Geol.*, **42**, 85–99.

Morss, L. R., Fuger, J., Goffart, J., and Haire, G. (1983) *Inorg. Chem.*, **22**, 1993–6.

Morss, L. R., Richardson, J. W., Williams, C. W., Lander, G. H., Lawson, A. C., Edelstein, N. M., and Shalimoff, G. V. (1989) *J. Less Common Metals*, **156**, 273–89.

Moseley, P. T., Brown, D., and Whittaker, B. (1972) *Acta Crystallogr. B*, **28**, 1816–21.

Mosley, W C. (1972) *J. Inorg. Nucl. Chem.*, **34**, 539–55.

Mudher, K. D. S., Krishnan, K., Chackraburtty, D. M., and Jayadevan, N. C. (1988) *J. Less Common Metals*, **143**, 173–82.

Mudher, K. D. S., Keskar, M., and Venugopal, V. (1999) *J. Nucl. Mater.*, **265**, 146–53.

Mudher, K. D. S. and Krishnan, K. (2000) *J. Alloys Compds*, **313**, 65–8.

Mueller, U. and Kolitsch, W. (1974) *Z. Anorg. Allg. Chem.*, **410**, 32–8.

Müller, U. (1979) *Acta Crystallogr. B*, **35**, 2502–9.

Mulford, R. N. R., Ellinger, F. H., and Zachariasen, W. H. (1954) *J. Am. Chem. Soc.*, **76**, 297–8.

Mulford, R. N. R. and Wiewandt, T. A. (1965) *J. Phys. Chem.*, **69**, 1641–4.

Musikas, C. and Burns, J. H. (1976) in *Transplutonium Elements, Proc. 4th Int. Transplutonium Elements Symp., 1975* (eds. W. Muller and R. Lindner), North-Holland, Amsterdam, pp. 237–45.

Naito, K. and Kamegashira, N. (1976) *Adv. Nucl. Sci. Technol.*, **9**, 99–180.

Nassimbeni, L. R., Rodgers, A. L., and Haigh, J. M. (1976) *Inorg. Chim. Acta*, **20**, 149–53.

Navaza, A., Villain, F., and Charpin, P. (1984) *Polyhedron*, **3**, 143–9.

Navaza, A., Charpin, P., and Vigner, J.-D. (1991) *Acta Crystallogr. C*, **47**, 1842–5.

Navratil, J. D. and Bramlet, H. L. (1973) *J. Inorg. Nucl. Chem.*, **35**, 157–63.

Nectoux, F. and Tabuteau, A. (1981) *Radiochem. Radioanal. Lett.*, **49**, 43–8.

Nectoux, F., Abazli, H., Jové, J., Cousson, A., Pages, M., Gasperin, M., and Choppin, G. (1984) *J. Less Common Metals*, **97**, 1–10.

Nierlich, M., Sabattie, J.-M., Keller, N., Lance, M., and Vigner, J.-D. (1994) *Acta Crystallogr. C*, **50**, 52–4.

Nigon, J. P., Penneman, R. A., Staritzky, E., Keenan, T. K., and Asprey, L. B. (1954) *J. Phys. Chem.*, **58**, 403–4.

Niinisto, L., Toivonen, J., and Valkonen, J. (1978) *Acta Chem. Scand. A*, **32**, 647–51.

Noé, M., Fuger, J., and Duyckaerts, G. (1970) *Inorg. Nucl. Chem. Lett.*, **6**, 111–19.

Noël, H. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1715–17.

Noël, H. and Potel, M. (1982) *Acta Crystallogr. B*, **38**, 2444–5.

Noël, H. and Le Marouille, J. Y. (1984) *J. Solid State Chem.*, **52**, 197–202.

Noël, H. (1985) *Physica B+C*, **130**, 499–500.

Noël, H. and Levet, J. C. (1989) *J. Solid State Chem.*, **79**, 28–33.

Noël, H., Potel, M., Troc, R., and Shlyk, L. (1996) *J. Solid State Chem.*, **126**, 22–6.

Okamoto, H. (1999) *J. Phase Equil.*, **20**, 351.

Olsen, J. S., Gerward, L., Benedict, U., Itié, J.-P., and Richter, K. (1986) *J. Less Common Metals*, **121**, 445–53.

Olson, W. M. and Mulford, R. N. R. (1964) *J. Phys. Chem.*, **68**, 1048–51.

Olson, W. M. and Mulford, R. N. R. (1966) *J. Phys. Chem.*, **70**, 2934–7.

Paine, R. T., Ryan, R. R., and Asprey, L. B. (1975) *Inorg. Chem.*, **14**, 1113–17.

Panattoni, C., Graziani, R., Bandoli, G., Zarli, B., and Bombieri, G. (1969) *Inorg. Chem.*, **8**, 320–5.

Paolucci, G., Fischer, R. D., Benetollo, F., Seraglia, R., and Bombieri, G. (1991) *J. Organomet. Chem.*, **412**, 327–42.

Parry, J., Carmona, E., Coles, S., and Hursthouse, M. (1995) *J. Am. Chem. Soc.*, **117**, 2649–50.

Pasilis, S. P. and Pemberton, J. E. (2003) *Inorg. Chem.*, **42**, 6793–800.

Peacock, R. D. and Edelstein, N. (1976) *J. Inorg. Nucl. Chem.*, **38**, 771–3.

Penneman, R. A., Ryan, R. R., and Rosenzweig, A. (1973) *Struct. Bonding*, **13**, 1–52.

Pepper, M. and Bursten, B. E. (1991) *Chem. Rev.*, **91**, 719–41.

Perego, G., Cesari, M., Farina, F., and Lugli, G. (1976) *Acta Crystallogr. B*, **32**, 3034–9.

Peters, R. G., Warner, B. P., Scott, B. L., and Burns, C. J. (1999) *Organometallics*, **18**, 2587–9.

Peterson, J. R. and Cunningham, B. B. (1967a) *Inorg. Nucl. Chem. Lett.*, **3**, 327–36.

Peterson, J. R. and Cunningham, B. B. (1967b) *Inorg. Nucl. Chem. Lett.*, **3**, 579–83.

Peterson, J. R. and Burns, J. H. (1968) *J. Inorg. Nucl. Chem.*, **30**, 2955–8.

Peterson, J. R. and Cunningham, B. B. (1968a) *J. Inorg. Nucl. Chem.*, **30**, 1775–84.

Peterson, J. R. and Cunningham, B. B. (1968b) *J. Inorg. Nucl. Chem.*, **30**, 823–8.

Peterson, J. R., Fahey, J. A., and Baybarz, R. D. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3345–51.

Peterson, J. R., and Fuger, J. (1971) *J. Inorg. Nucl. Chem.*, **33**, 4111–17.

Peterson, J. R. (1972) *J. Inorg. Nucl. Chem.*, **34**, 1603–7.

Peterson, J. R. and Baybarz, R. D. (1972) *Inorg. Nucl. Chem. Lett.*, **8**, 423–31.

Peterson, J. R. and Burns, J. H. (1973) *J. Inorg. Nucl. Chem.*, **35**, 1525–30.

Phipps, K. D. and Sullenger, D. B. (1964) *Science*, **145**, 1048–9.

Pietraszko, D. and Lukaszewicz, K. (1971) *Roczniki Chemii*, **46**, 1105–17.

Picon, M. and Flahaut, J. (1958) *Bull. Soc. Chim. Fr.*, **25**, 772–80.

Podor, R., Francois, M., and Dacheux, N. (2003) *J. Solid State Chem.*, **172**, 66–72.

Poojary, M. D. and Patil, K. C. (1987) *Proc. Indian. Acad. Sci., Chem. Sci.*, **99**, 311–15.

Porchia, M., Brianese, N., Casellato, U., Ossola, F., Rossetto, G., Zanella, P., and Graziani, R. (1989) *J. Chem. Soc., Dalton Trans.*, 677–81.

Post, B., Glaser, F. W., and Moskowitz, D. (1954) *Acta Met.*, **2**, 20–5.

Potel, M., Brochu, R., Padiou, J., and Grandjean, D. (1972) *Compt. Rend. Acad. Sci. C*, **275**, 1421.

Pyykkö, P., Laakkonen, L. J., and Tatsumi, K. (1989) *Inorg. Chem.*, **28**, 1801–5.

Quarton, M., Zouiri, M., and Freundlich, W. (1984) *Compt. Rend. Acad. Sci. II*, **299**, 785–8.

Rannou, J. P. and Lucas, J. (1969) *Mat. Res. Bull.*, **4**, 443–50.

Rebizant, J., Spirlet, M. R., and Goffart, J. (1983) *Acta Crystallogr. C*, **39**, 1041–3.

Rebizant, J., Spirlet, M. R., and Goffart, J. (1985) *Acta Crystallogr. C*, **41**, 334–6.

Rebizant, J., Spirlet, M. R., Kanellakopulos, B., and Dornberger, E. (1986a) *Acta Crystallogr. C*, **42**, 1497–500.

Rebizant, J., Spirlet, M. R., Kanellakopulos, B., and Dornberger, E. (1986b) *J. Less Common Metals*, **122**, 211–14.

Rebizant, J., Apostolidis, C., Spirlet, M. R., and Kanellakopulos, B. (1987) *Inorg. Chim. Acta*, **139**, 209–10.

Rebizant, J., Spirlet, M. R., Van den Bossche, G., and Goffart, J. (1988) *Acta Crystallogr. C*, **44**, 1710–12.

Rebizant, J., Spirlet, M. R., Bettonville, S., and Goffart, J. (1989) *Acta Crystallogr. C*, **45**, 1509–11.

Rebizant, J., Spirlet, M. R., Apostolidis, C., and Kanellakopulos, B. (1991) *Acta Crystallogr. C*, **47**, 854–6.

Rebizant, J., Spirlet, M. R., Apostolidis, C., and Kanellakopulos, B. (1992) *Acta Crystallogr. C*, **48**, 452–4.

Richter, J. and Edelmann, F. T. (1996) *Coord. Chem. Rev.*, **147**, 373–442.

Rietveld, H. M. (1967) *Acta Crystallogr.*, **22**, 151–2.

Rietz, R. R., Zalkin, A., Templeton, D. H., Edelstein, N. M., and Templeton, L. K. (1978a) *Inorg. Chem.*, **17**, 653–8.

Rietz, R. R., Edelstein, N. M., Ruben, H. W., Templeton, D. H., and Zalkin, A. (1978b) *Inorg. Chem.*, **17**, 658–60.

Ritger, P. L., Burns, J. H., and Bombieri, G. (1983) *Inorg. Chim. Acta*, **77**, L217–19.

Roberts, L. E. J. and Walter, A. J. (1966) in *Physico-Chimie du Protactinium* (eds. G. Bouissières and R. Muxart), Orsay, 2–8 July 1965, Centre National de la Recherche Scientifique, Paris, pp. 51–9.

Roddy, J. W. (1973) *J. Inorg. Nucl. Chem.*, **35**, 4141–8.

Roddy, J. W. (1974) *J. Inorg. Nucl. Chem.*, **36**, 2531–3.

Rogers, R. D., Kurihara, L. K., and Benning, M. M. (1987a) *Inorg. Chem.*, **26**, 4346–52.

Rogers, R. D., Kurihara, L. K., and Benning, M. M. (1987b) *J. Inclusion Phenom.*, **5**, 645–58.

Rogers, R. D., Kurihara, L. K., and Benning, M. M. (1987c) *Acta Crystallogr. C*, **43**, 1056–8.

Rogers, R. D. (1988) *Acta Crystallogr. C*, **44**, 638–41.

Rogers, R. D. and Benning, M. M. (1988a) *Acta Crystallogr. C*, **44**, 641–4.

Rogers, R. D. and Benning, M. M. (1988b) *Acta Crystallogr. C*, **44**, 1397–9.

Rogers, R. D., Kurihara, L. K., and Benning, M. M. (1988) *J. Chem. Soc., Dalton Trans.*, 13–16.

Rogers, R. D. (1989) *Lanthanide Actinide Res.*, **3**, 71–81.

Rogers, R. D., Benning, M. M., Etzenhouser, R. D., and Rollins, A. N. (1989) *J. Chem. Soc., Chem. Commun.*, 1586–8.

Rogers, R. D. and Rogers, L. M. (1990) *J. Organomet. Chem.*, **380**, 51–76.

Rogers, R. D. and Benning, M. M. (1991) *J. Inclusion Phenom. Mol. Recog. Chem.*, **11**, 121–35.

Rogers, R. D., Bond, A. H., Hipple, W. G., Rollins, A. N., and Henry, R. F. (1991) *Inorg. Chem.*, **30**, 2671–9.

Rogers, R. D. and Rogers, L. M. (1991) *J. Organomet. Chem.*, **416**, 201–90.

Rogers, R. D. and Bond, A. H. (1992) *Acta Crystallogr. C*, **48**, 1199–201.

Rogers, R. D. and Rogers, L. M. (1992a) *J. Organomet. Chem.*, **442**, 83–224.

Rogers, R. D. and Rogers, L. M. (1992b) *J. Organomet. Chem.*, **442**, 225–69.

Rogers, R. D. and Rogers, L. M. (1993) *J. Organomet. Chem.*, **457**, 41–62.

Rogers, R. D., Zhang, J., and Campbell, D. T. (1998) *J. Alloys Compds*, **271–273**, 133–8.

Rojas, R., Del Pra, A., Bombieri, G., and Benetollo, F. (1979) *J. Inorg. Nucl. Chem.*, **41**, 541–5.

Ronchi, C. and Heirnaut, J. P. (1996) *J. Alloys Compds*, **240**, 179–85.

Rosen, R. K. and Zalkin, A. (1989) *Acta Crystallogr. C*, **45**, 1139–41.

Ross, M. and Evans, H. T. Jr (1960) *J. Inorg. Nucl. Chem.*, **15**, 338–51.

Rouse. K. D., Wills, B. T. M., and Pryor, A. W. (1968) *Acta Crystallogr. B,* **24**, 117–22.

Rundle, R. E. (1947) *J. Am. Chem. Soc.*, **69**, 1719–23.

Rundle, R. E. (1948) *Acta Crystallogr.*, **1**, 180–7.

Rundle, R. E. (1951) *J. Am. Chem. Soc.*, **73**, 4172–4.

Rundle, R. E., Shull, C. G., and Wollan, E. O. (1952) *Acta Crystallogr.*, **5**, 22–6.

Runnalls, O. J. C. and Boucher, R. R. (1955) *Acta Crystallogr.*, **8**, 592.

Ryan, R. R., Penneman, R. A., and Kanellakopulos, B. (1975) *J. Am. Chem. Soc.*, **97**, 4258–60.

Ryan, R. R., Penneman, R. A., Asprey, L. B., and Paine, R. T. (1976) *Acta Crystallogr. B*, **32**, 3311–13.

Ryan, R. R., Salazar, K. V., Sauer, N. N., and Ritchey, J. M. (1989) *Inorg. Chim. Acta*, **162**, 221–5.

Sari, C., Müller, W., and Benedict, U. (1972/73) *J. Nucl. Mater.*, **45**, 73–5.

Sarsfield, M. J. and Helliwell, M. (2004) *J. Am. Chem. Soc.*, **126**, 1036–7.

Sarsfield, M. J., Helliwell, M., and Raftery, J. (2004) *Inorg. Chem.*, **43**, 3170–9.

Scaife, D. E., Turnbull, A. G., and Wylie, A. W. (1965) *J. Chem. Soc., Abstr.*, 1432–7.

Scaife, D. E. (1966) *Inorg. Chem.*, **5**, 162–4.

Šćavničar, S. and Prodić, B. (1965) *Acta Crystallogr.*, **18**, 698–702.

Schake, A. R., Avens, L. R., Burns, C. J., Clark, D. L., Sattelberger, A. P., and Smith, W. H. (1993) *Organometallics*, **12**, 1497–8.

Scherer, O. J., Werner, B., Heckmann, G., and Wolmershäuser, G. (1991) *Angew. Chem. Int. Ed. Engl.*, **30**, 553–5.

Scherer, O. J., Schulze, J., and Wolmershäuser, G. (1994) *J. Organomet. Chem.*, **484**, C5–7.

Scherer, V., Weigel, F., and Van Ghemen, M. E. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 589–95.

Schlechter, M. (1970) *J. Nucl. Mater.*, **37**, 82–8.

Schnabel, R. C., Scott, B. L., Smith, W. H., and Burns, C. J. (1999) *J. Organomet. Chem.*, **591**, 14–23.

Schock, L. E., Seyam, A. M., Sabat, M., and Marks, T. J. (1988) *Polyhedron*, **7**, 1517–29.

Scott, P. and Hitchcock, P. B. (1995) *J. Organomet. Chem.*, **497**, C1–3.

Secaur, C. A., Day, V. W., Ernst, R. D., Kennelly, W. J., and Marks, T. J. (1976) *J. Am. Chem. Soc.*, **98**, 3713–15.

Sellers, P. A., Fried, S., Elson, R. E., and Zachariasen, W. H. (1954) *J. Am. Chem. Soc.*, **76**, 5935–8.

Serizawa, H., Fukuda, K., Ishii, Y., Morii, Y., and Katsura, M. (1994) *J. Nucl. Mater.*, **208**, 128–34.

Sessler, J. L., Mody, T. D., and Lynch, V. (1992) *Inorg. Chem.*, **31**, 529–31.

Sessler, J. L. and Weghorn, S. J. (1997) *Tetrahedron Organic Chemistry Series: Expanded, Contracted, and Isomeric Porphyrins,* vol. 15, Pergamon, Oxford.

Sessler, J. L., Gebauer, A., Hoehner, M. C., and Lynch, V. (1998) *J. Chem. Soc., Chem. Commun.*, 1835–6.

Sessler, J. L., Vivian, A. E., Seidel, D., Burrell, A. K., Hoehner, M., Mody, T. D., Gebauer, A., Weghorn, S. J., and Lynch, V. (2001a) *Coord. Chem. Rev.*, **216–217**, 411–34.

Sessler, J. L., Seidel, D., Vivian, A. E., Lynch, V., Scott, B. L., and Keogh, D. W. (2001b) *Angew. Chem. Int. Ed. Engl.*, **40**, 591–4.

Sessler, J. L., Gorden, A. E. V., Seidel, D., Hannah, S., Lynch, V., Gordon, P. L., Donohoe, R. J., Tait, C. D., and Keogh, D. W. (2002) *Inorg. Chim. Acta*, **341**, 54–70.

Shankar, J. and Khubchandani, P. G. (1957) *Anal. Chem.*, **29**, 1375.

Shchelokov, R. N., Orlova, I. M., Beirakhov, A. G., Mikhailov, Yu. N., and Kanishcheva, A. S. (1984) *Koord. Khim.*, **10**, 1644–50.

Shchelokov, R. N., Mikhailov, Yu. N., Orlova, I. M., Sergeev, A. V., Ashurov, Z. K., Tashev, M. T., and Parpiev, N. A. (1985) *Koord. Khim.*, **11**, 1010–14.

Sheft, I. and Fried, S. (1953) *J. Am. Chem. Soc.*, **75**, 1236–7.

Siegel, S., Hoekstra, H. R., and Sherry, E. (1966) *Acta Crystallogr.*, **20**, 292–5.

Silva, M. R., Beja, A. M., Paixão, J. A., da Veiga, L. A., and Martin-Gil, J. (1999) *Acta Crystallogr. C*, **55**, 2039–41.

Silverwood, P. R., Collison, D., Livens, F. R., Beddoes, R. L., and Taylor, R. J. (1998) *J. Alloys Compds*, **271–273**, 180–3.

Smetana, Z., Sechovský, V., and Meňovský, A. (1975) *Phys. Status Solidi A*, **27**, K73–5.

Smith, G. M., Suzuki, H., Sonnenberger, D. C., Day, V. W., and Marks, T. J. (1986) *Organometallics*, **5**, 549–61.

Smith, G. S., Johnson, Q., and Elson, R. E. (1967) *Acta Crystallogr.*, **22**, 300–3.

Smith, J. L. and Kmetko, E. A. (1983) *J. Less Common Metals*, **90**, 83–8.

Smith, P. K., Hale, W. H., and Thompson, M. C. (1969) *J. Chem. Phys.*, **50**, 5066–76.

Spirlet, J. C., Kalbusch, J., Moens, A., Rijkeboer, C., and Rebizant, J. (1991) *Lanthanide Actinide Res.*, **3**, 277–83.

Spirlet, M. R., Rebizant, J., and Goffart, J. (1982) *Acta Crystallogr. B*, **38**, 2400–4.

Spirlet, M. R., Rebizant, J., Kanellakopulos, B., and Dornberger, E. (1986) *J. Less Common Metals*, **122**, 205–10.

Spirlet, M. R., Rebizant, J., Kanellakopulos, B., and Dornberger, E. (1987a) *Acta Crystallogr. C*, **43**, 19–21.

Spirlet, M. R., Rebizant, J., and Goffart, J. (1987b) *Acta Crystallogr. C*, **43**, 354–5.

Spirlet, M. R., Rebizant, J., Apostolidis, C., Andreetti, G. D., and Kanellakopulos, B. (1989) *Acta Crystallogr. C*, **45**, 739–41.

Spirlet, M. R., Rebizant, J., Apostolidis, C., Van den Bossche, G., and Kanellakopulos, B. (1990a) *Acta Crystallogr. C*, **46**, 2318–20.

Spirlet, M. R., Rebizant, J., Bettonville, S., and Goffart, J. (1990b) *Acta Crystallogr. C*, **46**, 1234–6.

Spirlet, M. R., Rebizant, J., Apostolidis, C., and Kanellakopulos, B. (1992a) *Acta Crystallogr. C*, **48**, 2135–7.

Spirlet, M. R., Rebizant, J., Bettonville, S., and Goffart, J. (1992b) *Acta Crystallogr. C*, **48**, 1221–3.

Spirlet, M. R., Rebizant, J., Apostolidis, C., and Kanellakopulos, B. (1993a) *Acta Crystallogr. C*, **49**, 929–31.

Spirlet, M. R., Rebizant, J., Bettonville, S., and Goffart, J. (1993b) *Acta Crystallogr. C*, **49**, 1138–40.

Spirlet, M. R., Rebizant, J., Bettonville, S., and Goffart, J. (1993c) *J. Organomet. Chem.*, **460**, 177–80.

Spirlet, M. R., Jemine, X., and Goffart, J. (1994) *J. Alloys Compds*, **216**, 269–71.

Staritzky, E. (1956) *Anal. Chem.*, **28**, 2021–2.

Staritzky, E. and Cromer, D. T. (1956) *Anal. Chem.*, **28**, 1354–5.

Staritzky, E., Cromer, D. T., and Walker, D. I. (1956) *Anal. Chem.*, **28**, 1634–5.

Starks, D. F., Parsons, T. C., Streitweiser, A. Jr, and Edelstein, N. (1974) *Inorg. Chem.*, **13**, 1307–8.

Steeb, S. and Mitsch, P. (1965) *J. Nucl. Mater.*, **15**, 81–7.

Steeb, S. and Brucklacher, D. (1966) *J. Less Common Metals*, **11**, 263–72.

Stein, L. (1964) *Inorg. Chem.*, **3**, 995–8.

Sternal, R. S., Sabat, M., and Marks, T. J. (1987) *J. Am. Chem. Soc.*, **109**, 7920–1.

Stevenson, J. N. and Peterson, J. R. (1973) *J. Inorg. Nucl. Chem.*, **35**, 3481–6.

Stöwe, K. (1996) *Z. Anorg. Allg. Chem.*, **622**, 1423–7.

Stöwe, K. (1997) *J. Alloys Compds*, **246**, 111–23.

Straub, T., Frank, W., Reiss, G. J., and Eisen, M. S. (1996) *J. Chem. Soc., Dalton Trans.*, 2541–6.

Streitweiser, A. Jr and Müller-Westerhoff, U. (1968) *J. Am. Chem. Soc.*, **90**, 7364.

Suortti, P. (2002) in *Encyclopedia of Physical Science and Technology*, 3rd edn, vol. 17 (ed. R. A. Meyers), Academic Press, San Diego, CA, pp. 989–1023.

Suski, W., Gibinski, T., Wojakowski, A., and Czopnik, A. (1972) *Phys. Status Solidi A*, **9**, 653–8.

Tatsumi, K. and Hoffmann, R. (1980) *Inorg. Chem.*, **19**, 2656–8.

Taylor, J. C., Mueller, M. H., and Hitterman, R. L. (1966) *Acta Crystallogr.*, **20**, 842–51.

Taylor, J. C. and Wilson, P. W. (1973a) *Acta Crystallogr. B*, **29**, 1942–4.

Taylor, J. C. and Wilson, P. W. (1973b) *Acta Crystallogr. B*, **29**, 1073–6.

Taylor, J. C., Wilson, P. W., and Kelly, J. W. (1973) *Acta Crystallogr. B*, **29**, 7–12.

Taylor, J. C. and Wilson, P. W. (1974a) *Acta Crystallogr. B*, **30**, 2803–5.

Taylor, J. C. and Wilson, P. W. (1974b) *Acta Crystallogr. B*, **30**, 2664–7.

Taylor, J. C. and Wilson, P. W. (1974c) *Acta Crystallogr. B*, **30**, 1481–4.

Taylor, J. C. and Wilson, P. W. (1974d) *Acta Crystallogr. B*, **30**, 175–7.

Taylor, J. C. and Wilson, P. W. (1974e) *J. Chem. Soc., Chem. Commun.*, 232–3.

Taylor, J. C. (1976) *Coord. Chem. Rev.*, **20**, 197–273.

Templeton, D. H. and Dauben, C. H. (1953) *J. Am. Chem. Soc.*, **75**, 4560–2.

Templeton, L. K., Templeton, D. H., and Walker, R. (1977) *Inorg. Chem.*, **15**, 3000–3.

Thévenin, T., Pages, M., and Wojakowski, A. (1982) *J. Less Common Metals*, **84**, 133–7.

Thévenin, T., Jové, J., and Pages, M. (1984) *Hyperfine Interact.*, **20**, 173–86.

Thévenin, T., Jové, J., and Madic, C. (1986) *J. Less Common Metals*, **121**, 477–81.

Thewlis, J. (1951) *Nature* (*UK*), **168**, 198–9.

Thoma, R. E. and Brunton, G. D. (1966) *Inorg. Chem.*, **5**, 1937–9.

Thuéry, P., Keller, N., Lance, M., Sabattié, J.-M., Vigner, J.-D., and Nierlich, M. (1995a) *Acta Crystallogr. C*, **51**, 801–5.

Thuéry, P., Nierlich, M., Keller, N., Lance, M., and Vigner, J.-D. (1995b) *Acta Crystallogr. C*, **51**, 1300–2.

Thuéry, P., Keller, N., Lance, M., Vigner, J.-D., and Nierlich, M. (1995c) *Acta Crystallogr. C*, **51**, 1570–4.

Thuéry, P., Keller, N., Lance, M., Vigner, J.-D., and Nierlich, M. (1995d) *New J. Chem.*, **19**, 619–25.

Thuéry, P., Lance, M., and Nierlich, M. (1996) *Supramol. Chem.*, **7**, 183–5.

Thuéry, P. and Nierlich, M. (1997) *J. Inclusion Phenom. Mol. Recog. Chem.*, **27**, 13–20.

Thuéry, P., Nierlich, M., Ogden, M. I., and Harrowfield, J. M. (1998) *Supramol. Chem.*, **9**, 297–303.

Thuéry, P., Nierlich, M., Masci, B., Asfari, Z., and Vicens, J. (1999a) *J. Chem. Soc., Dalton Trans.*, 3151–2.

Thuéry, P., Nierlich, M., Souley, B., Asfari, Z., and Vicens, J. (1999b) *J. Chem. Soc., Dalton Trans.*, 2589–94.

Thuéry, P., Nierlich, M., Vicens, J., Masci, B., and Takemura, H. (2001a) *Eur. J. Inorg. Chem.*, 637–43.

Thuéry, P., Nierlich, M., Vicens, J., and Masci, B. (2001b) *J. Chem. Soc., Dalton Trans.*, 867–74.

Thuéry, P., Nierlich, M., Vicens, J., and Takemura, H. (2001c) *Polyhedron*, **20**, 3183–7.

Thuéry, P., Nierlich, M., Harrowfield, J. M., and Ogden, M. I. (2001d) in *Calixarenes 2001* (eds. Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens), Kluwer Academic, Dordrecht, pp. 561–82.

Thuéry, P. and Masci, B. (2003) *Polyhedron*, **22**, 3499–505.

Thuéry, P. and Masci, B. (2004) *Polyhedron*, **23**, 649–54.

Tomilin, S. V., Volkov, Yu. F., Visyashcheva, G. I., and Kapshukov, I. I. (1984) *Radiokhimiya*, **26**, 734–9.

Tougait, O., Potel, M., and Noël, H. (1998a) *Inorg. Chem.*, **37**, 5088–91.

Tougait, O., Potel, M., Jevet, J. C., and Noël, H. (1998b) *Eur. J. Solid State Inorg. Chem.*, **35**, 67–76.

Tougait, O., Potel, M., and Noël, H. (1998c) *J. Solid State Chem.*, **139**, 356–61.

Traill, R. J. (1952) *Am. Mineral.*, **37**, 394–406.

Troost, L. (1893) *Compt. Rend. Acad. Sci. Paris*, **116**, 1229.

Tucker, C. W. Jr (1950) *Trans. Am. Soc. Met.*, **42**, 762–70.

Tucker, C. W. Jr (1951) *Acta Crystallogr.*, **4**, 425–31.

Turcotte, R. P., Chikalla, T. D., and Eyring, L. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3749–63.

Turcotte, R. P., Chikalla, T. D., Haire, R. G., and Fahey, J. A. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1729–33.

Ueki, T., Zalkin, A., and Templeton, D. H. (1966) *Acta Crystallogr.*, **20**, 836–41.

Van Der Sluys, W. G., Burns, C. J., Huffman, J. C., and Sattelberger, A. P. (1988) *J. Am. Chem. Soc.*, **110**, 5924–5.

Vegas, A., Martinez-Cruz, L. A., Ramos-Gallardo, A., and Romero, A. (1995) *Z. Kristallogr.*, **210**, 574–80.

Ventelon, L., Lescop, C., Arliguie, T., Leverd, P. C., Lance, M., Nierlich, M., and Ephritikhine, M. (1999) *J. Chem. Soc., Chem. Comm.*, 659–60.

Voinova, L. M. (1998) *Radiokhimiya*, **40**, 299–301.

Voliotis, S. and Rimsky, A. (1975a) *Acta Crystallogr. B*, **31**, 2612–15.

Voliotis, S. and Rimsky, A. (1975b) *Acta Crystallogr. B*, **31**, 2615–20.

Volkov, Yu. F., Visyashcheva, G. I., Tomilin, S. V., Kapshukov, I. I., and Rykov, A. G. (1981) *Radiokhimiya*, **23**, 237–42.

Volkov, Yu. F., Tomilin, S. V., Orlova, A. I., Lizin, A. A., Spiryakov, V. I., and Lukinykh, A. N. (2003) *Radiokhimiya*, **45**, 289–97.

Vollath, D. (1984) in *Gmelin Handbook of Inorganic Chemistry, Uranium*, 8th edn, Suppl. vol. C4 (eds. R. Keim and C. Keller), Springer-Verlag, Berlin, pp. 97–138.

Wadt, W. R. (1981) *J. Am. Chem. Soc.*, **103**, 6053–7.

Wait, E. (1955) *J. Inorg. Nucl. Chem.*, **1**, 309–12.

Wallmann, J. C. (1964) *J. Inorg. Nucl. Chem.*, **26**, 2053–7.

Ward, J. W., Haschke, J. M., Rebizant, J., and Bartscher, W. (1984) *J. Less Common Metals*, **100**, 195–214.

Ward, J. W., Bartscher, W., and Rebizant, J. (1987) *J. Less Common Metals*, **130**, 431–9.

Wasserman, H. J., Zozulin, A. J., Moody, D. C., Ryan, R. R., and Salazar, K. V. (1983) *J. Organomet. Chem.*, **254**, 305–11.

Weigel, F. and Haug, H. (1965) *Radiochim. Acta*, **4**, 227–8.

Weigel, F. and ter Meer, N. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 403–8.

Weigel, F. and Hoffmann, G. (1976a) *J. Less Common Metals*, **44**, 99–123.

Weigel, F. and Hoffmann, G. (1976b) *J. Less Common Metals*, **44**, 125–32.

Weigel, F. and Hoffmann, G. (1976c) *J. Less Common Metals*, **44**, 133–6.

Weigel, F. and Hauske, H. (1977) *J. Less Common Metals*, **55**, 243–7.

Weigel, F., Wittmann, F. D., and Marquart, R. (1977) *J. Less Common Metals*, **56**, 47–53.

Weigel, F., Wishnevsky, V., and Wolf, M. (1979) *J. Less Common Metals*, **63**, 81–6.

Weigel, F. and Marquart, R. (1983) *J. Less Common Metals*, **90**, 283–90.

Weigel, F., Wittmann, F. D., Schuster, W., and Marquart, R. (1984) *J. Less Common Metals*, **102**, 227–38.

Weigel, F. and Kohl, R. (1985) in *Americium Curium Chem. Technol., Pap. Symp.*, 1984 (eds. N. M. Edelstein, J. D. Navratil, and W. W. Schulz), Reidel, Dordrecht, Netherlands, pp. 159–91.

Weigel, F. (1986) in *Chemistry of the Actinide Elements*, 2nd edn, vol. 1 (eds. J. J. Katz, G. T. Seaborg, and L. R. Morss), Chapman and Hall, New York., p. 267.

Weigel, F. and Hellmann, H. (1986) *J. Less Common Metals*, **121**, 415–23.

Weller, M. T., Dickens, P. G., and Penny, D. J. (1988) *Polyhedron*, **7**, 243–4.

Wilkerson, M. P., Burns, C. J., Dewey, H. J., Martin, J. M., Morris, D. E., Paine, R. T., and Scott, B. L. (2000) *Inorg. Chem.*, **39**, 5277–85.

Willis, B. T. M. (1963) *Nature* (*UK*), **197**, 755–6.

Willis, B. T. M. (1964) *J. Phys.* (*Paris*), **25**, 431–9.

Willis, B. T. M. (1978) *Acta Crystallogr. A,* **34**, 88–90.

Willis, B. T. M. (1987) *J. Chem. Soc., Faraday Trans. 2*, **83**, 1073–81.

Wills, J. M. and Eriksson, O. (1992) *Phys. Rev. B*, **45**, 13879–90.

Wilson, T. A. (1933) *Physica*, **4**, 148–52.

Wojakowski, A. and Damien, D. (1982) *J. Less Common Metals*, **83**, 263–7.

Wojakowski, A., Damien, D., and Hery, Y. (1982) *J. Less Common Metals*, **83**, 169–74.

Wong, C.-H., Yen, T.-M., and Lee, T.-Y. (1965) *Acta Crystallogr.*, **18**, 340–5.

Wrobleski, D. A., Ryan, R. R., Wasserman, H. J., Salazar, K. V., Paine, R. T., and Moody, D. C. (1986a) *Organometallics*, **5**, 90–4.

Wrobleski, D. A., Cromer, D. T., Ortiz, J. V., Rauschfuss, T. B., Ryan, R. R., and Sattelberger, A. P. (1986b) *J. Am. Chem. Soc.*, **108**, 174–5.

Yang, X., Stern, C. L., and Marks, T. J. (1991) *Organometallics*, **10**, 840–2.

Zachariasen, W. H. (1948a) *Phys. Rev.*, **73**, 1104–5.

Zachariasen, W. H. (1948b) *Acta Crystallogr.*, **1**, 265–8.

Zachariasen, W. H. (1948c) *Acta Crystallogr.*, **1**, 285–7.

Zachariasen, W. H. (1949a) *Nat. Nucl. Ener. Ser.*, Manhattan Proj. Tech. Sect., Div. 4, Plutonium Proj. 14B, 1489–91.

Zachariasen, W. H. (1949b) *Acta Crystallogr.*, **2**, 388–90.

Zachariasen, W. H. (1949c) *Nat. Nucl. Ener. Ser.*, Manhattan Proj. Tech. Sect., Div. 4, Plutonium Proj. 14B, 1448–50.

Zachariasen, W. H. (1949d) *Acta Crystallogr.*, **2**, 94–9.

Zachariasen, W. H. (1949e) *Acta Crystallogr.*, **2**, 291–6.

Zachariasen, W. H. (1949f) *Acta Crystallogr.*, **2**, 288–91.

Zachariasen, W. H. (1949g) *Acta Crystallogr.*, **2**, 296–8.

Zachariasen, W. H. (1951) *Acta Crystallogr.*, **4**, 231–6.

Zachariasen, W. H. (1952a) *Acta Crystallogr.*, **5**, 660–4.

Zachariasen, W. H. (1952b) *Acta Crystallogr.*, **5**, 664–7.

Zachariasen, W. H. (1952c) *Acta Crystallogr.*, **5**, 17–19.

Zachariasen, W. H. (1953) *Acta Crystallogr.*, **6**, 393–5.

Zachariasen, W. H. (1954) *Acta Crystallogr.*, **7**, 795–9.

Zachariasen, W. H. and Ellinger, F. H. (1955) *Acta Crystallogr.*, **8**, 431–3.

Zachariasen, W. H. and Ellinger, F. H. (1957) *J. Chem. Phys.,* **27**, 811–12.

Zachariasen, W. H. and Ellinger, F. H. (1959) *Acta Crystallogr.*, **12**, 175–6.

Zachariasen, W. H. and Plettinger, H. A. (1959) *Acta Crystallogr.*, **12**, 526–30.

Zachariasen, W. H. and Ellinger, F. H. (1963a) *Acta Crystallogr.*, **16**, 777–83.

Zachariasen, W. H. and Ellinger, F. H. (1963b) *Acta Crystallogr.*, **16**, 369–75.

Zachariasen, W. H. (1975) *J. Inorg. Nucl. Chem.*, **37**, 1441–2.

Zalkin, A., Forrester, J. D., and Templeton, D. H. (1964) *Inorg. Chem.*, **3**, 639–44.

Zalkin, A. and Raymond, K. N. (1969) *J. Am. Chem. Soc.*, **91**, 5667–8.

Zalkin, A., Rietz, R. R., Templeton, D. H., and Edelstein, N. M. (1978a) *Inorg. Chem.*, **17**, 661–3.

Zalkin, A., Ruben, H., and Templeton, D. H. (1978b) *Inorg. Chem.*, **17**, 3701–2.

Zalkin, A., Templeton, D. H., Berryhill, S. R., and Luke, W. D. (1979) *Inorg. Chem.*, **18**, 2287–9.

Zalkin, A., Templeton, D. H., Le Vanda, C., and Streitweiser, A. Jr (1980) *Inorg. Chem.*, **19**, 2560–3.

Zalkin, A., Templeton, D. H., Luke, W. D., and Streitwieser, A. Jr (1982) *Organometallics*, **1**, 618–22.

Zalkin, A. and Brennan, J. G. (1985) *Acta Crystallogr. C*, **41**, 1295–7.

Zalkin, A., Templeton, D. H., Kluttz, R., and Streitwieser, A. Jr (1985) *Acta Crystallogr. C*, **41**, 327–9.

Zalkin, A. and Brennan, J. G. (1987) *Acta Crystallogr. C*, **43**, 1919–22.

Zalkin, A., Brennan, J. G., and Andersen, R. A. (1987a) *Acta Crystallogr. C*, **43**, 1706–8.

Zalkin, A., Brennan, J. G., and Andersen, R. A. (1987b) *Acta Crystallogr. C*, **43**, 418–20.

Zalkin, A., Brennan, J. G., and Andersen, R. A. (1987c) *Acta Crystallogr. C*, **43**, 421–3.

Zalkin, A. and Beshouri, S. M. (1988) *Acta Crystallogr. C*, **44**, 1826–7.

Zalkin, A., Brennan, J. G., and Andersen, R. A. (1988a) *Acta Crystallogr. C*, **44**, 2104–6.

Zalkin, A., Stuart, A. L., and Andersen, R. A. (1988b) *Acta Crystallogr. C*, **44**, 2106–8.

Zalkin, A. and Beshouri, S. M. (1989a) *Acta Crystallogr. C*, **45**, 1080–2.

Zalkin, A. and Beshouri, S. M. (1989b) *Acta Crystallogr. C*, **45**, 1219–21.

Zanella, P., De Paoli, G., Bombieri, G., Zanotti, G., and Rossi, R. (1977) *J. Organomet. Chem.*, **142**, C21–4.

Zanella, P., Paolucci, G., Rossetto, G., Benetollo, F., Polo, A., Fischer, R. D., and Bombieri, G. (1985) *J. Chem. Soc., Chem. Commun.*, 96–8.

Zanella, P., Brianese, N., Casellato, U., Ossola, F., Porchia, M., Rossetto, G., and Graziani, R. (1987a) *J. Chem. Soc., Dalton Trans.*, 2039–43.

Zanella, P., Ossola, F., Porchia, M., Rossetto, G., Villa, A. C., and Guastini, C. (1987b) *J. Organomet. Chem.*, **323**, 295–303.

Zanella, P., Brianese, N., Casellato, U., Ossola, F., Porchia, M., and Rossetto, G. (1988) *Inorg. Chim. Acta*, **144**, 129–34.

Zhang, Y.-J., Collison, D., Livens, F. R., Helliwell, M., Eccles, H., and Tinker, N. (1998) *J. Alloys Compds*, **271–273**, 139–43.

Zhang, Y.-J., Collison, D., Livens, F. R., Powell, A. K., Wocadlo, S., and Eccles, H. (2000) *Polyhedron*, **19**, 1757–67.

Zhang, Y.-J., Collison, D., Livens, F. R., Helliwell, M., Heatley, F., Powell, A. K., Wocadlo, S., and Eccles, H. (2002a) *Polyhedron*, **21**, 81–96.

Zhang, Y.-J., Livens, F. R., Collison, D., Helliwell, M., Heatley, F., Powell, A. K., Wocadlo, S., and Eccles, H. (2002b) *Polyhedron*, **21**, 69–79.

Zhang, Z. and Pitzer, R. M. (1999) *J. Phys. Chem. A*, **103**, 6880–6.

Zivadinovich, M. S. (1967) *Bull. Boris Kidric Inst. Nucl. Sci.*, **18**, 1–8.

Zumbusch, M. (1941) *Z. Anorg. Allg. Chem.*, **245**, 402–8.