Table 31.4 Oxidation states and stereochemistries of compounds of the actinides

"An" is used as a general symbol for the actinide elements

Oxidation state	Coordination number	Stereochemistry	Examples
0	16	See Figs. 19.31 and 31.10	$[An(\eta^8\text{-}C_8H_8)_2]$ (An = Th $\rightarrow$ Pu), $[U(\eta^8\text{-}C_8H_4Ph_4)_2]$
3	6	Octahedral	$[AnCl_6]^{3-}$ (An = Np, Am, Bk)
	8	Bicapped trigonal prismatic	$AnCl_3$ (X = Br, An = Pu $\rightarrow$ Bk; X = I, An = Pa $\rightarrow$ Pu)
	9	Tricapped trigonal prismatic	$AnCl_3$ (An = U $\rightarrow$ Cm)
	15	See p. 1278	$[Th\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_3]$
4	4	Complex	$U(NPh_2)_4$
	5	Trigonal bipyramidal	$U_2(NEt_2)_8$
	6	Octahedral	$[AnX_6]^{2-}$ (An = U, Np, Pu; X = Cl, Br)
	7	Pentagonal bipyramidal	UBr_4
	8	Cubic	$[An(NCS)_8]^{4-}$ (An = Th $\rightarrow$ Pu)
		Dodecahedral	$[Th(C_2O_4)_4]^{4-}$, $[An(S_2CNEt_2)_4]$ (An = Th, U, Np, Pu)
		Square antiprismatic	$[An(acac)_4]$ (An = Th, U, Np, Pu)
	9	Tricapped trigonal prismatic	$(NH_4)_3[ThF_7]$
		Capped square antiprismatic	$[Th(tropolonate)_4(H_2O)]$
	10	Bicapped square antiprismatic	$K_4[Th(C_2O_4)_4].4H_2O$
		Complex	$[Th(NO_3)_4(OPPh_3)_2]^{(a)}$
	11	See Fig. 31.8a	$[Th(NO_3)_4(H_2O)_3].2H_2O$
	12	Icosahedral	$[Th(NO_3)_6]^{2-(a)}$
	14	Bicapped hexagonal antiprismatic	$[U(BH_4)_4]$
	20	See Fig. 31.9	$[An(\eta^5\text{-}C_5H_5)_4]$ (An = Th, U)
5	6	Octahedral	$Cs[AnF_6]$ (An = U, Np, Pu)
	7	Pentagonal bipyramidal	$PaCl_5$
	8	Cubic	$Na_3[AnF_8]$ (An = Pa, U, Np)
	9	Tricapped trigonal prismatic	$M_2[PaF_7]$ (M = NH_4, K, Rb, Cs)
6	6	Octahedral	AnF_6 (An = U, Np, Pu), UCl_6, $Cs_2[UO_2X_4]^{(b)}$ (X = Cl, Br)
	7	Pentagonal bipyramidal	$[UO_2(S_2CNEt_2)_2(ONMe_3)]^{(b)}$
	8	Hexagonal bipyramidal	$[UO_2(NO_3)_2(H_2O)_2]^{(b)}$
7	6	Octahedral	$Li_5[AnO_6]$ (An = Np, Pu)

$^{(a)}$These compounds are isostructural with the corresponding compounds of Ce (see Fig. 30.5, p. 1245) and can be visualized as octahedral if each NO_3^- is considered to occupy a single coordination site.

$^{(b)}$The polyhedra of these complexes are actually flattened because the two *trans* U–O bonds of the UO_2^{2+} group are shorter than the bonds to the remaining groups which form an equatorial plane.

now to be found in the +4 oxidation state rather than +3 as in the lanthanides.

31.3 Compounds of the Actinides[3,9,11,22-24]

Compounds with many non-metals are prepared, in principle simply, by heating the elements.

Hydrides of the types AnH_2 (An = Th, Np, Pu, Am, Cm) and AnH_3 (Pa $\rightarrow$ Am), as well as Th_4H_{15} (i.e. $ThH_{3.75}$) have been so obtained but are not very stable thermally and are decidedly unstable with respect to air and moisture. Borides, carbides, silicides and nitrides (q.v.) are mostly less sensitive chemically and, being refractory materials, those of Th, U and Pu in particular have been studied extensively as possible nuclear fuels.[15,25] Their stoichiometries are very varied but the more important ones are the semi-metallic monocarbides, AnC, and mononitrides, AnN, all of which have the rock-salt structure: they are predominantly ionic

[22] G. MEYER and L. R. MORSS (eds.) *Synthesis of Lanthanide and Actinide Compounds*, Kluwer, Dordrecht, 1991, 367 pp.

[23] K. W. BAGNALL, Chap. 40, pp. 1129–228, in *Comprehensive Coordination Chemistry*, Vol. 3, Pergamon Press, Oxford, 1987.

[24] I. SANTOS, A. P. de MATOS and A. G. MADDOCK, *Adv. Inorg. Chem.* **34**, 65–144 (1989).

[25] K. NAITO and N. KAGEGASHIRA, *Adv. Nucl. Sci. Tech.* **9**, 99–180 (1976).

Table 31.5   Oxides of the Actinide Elements[a]
The most stable oxide of each element is printed in **bold**.

Formal oxidation state of metal	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
+6	--	—	UO_3 o-y	—	--	—	—	--	—	—
	—	—	U_3O_8 dark g	--	—	—	--	—	—	--
+5	—	**Pa_2O_5** white	U_2O_5 black	Np_2O_5 dark br	—	--	—	—	--	--
+4	**ThO_2** white	PaO_2 black	UO_2 dark br	**NpO_2** br-g	**PuO_2** y-br	**AmO_2** black	CmO_2 black	**BkO_2** br	CfO_2 black	--
+3	—	—	--	--	Pu_2O_3 black	Am_2O_3 r-br	**Cm_2O_3** white	Bk_2O_3 y-g	**Cf_2O_3** pale g	**$Es_2O_3^{(b)}$** white

[a] br = brown; g = green; o = orange; r = red; y = yellow.

[b] This is the only known oxide of Es. It is expected to be the most stable for this actinide but investigation of the Es/O system is hampered not only by low availability but also by the high α-activity ($t_{\frac{1}{2}} = 20.5$ days) which causes crystals to disintegrate. Es_2O_3 was characterized by electron diffraction using microgram samples measuring only about 0.03 μm on edge.

but with supernumerary electrons in a delocalized conduction band.

31.3.1 Oxides and chalcogenides of the actinides[15,26]

Oxides of the actinides are refractory materials and, in fact, ThO_2 has the highest mp (3390°C) of any oxide. They have been extensively studied because of their importance as nuclear fuels.[25] However, they are exceedingly complicated because of the prevalence of polymorphism, nonstoichiometry and intermediate phases. The simple stoichiometries quoted in Table 31.5 should therefore be regarded as idealized compositions.

The only anhydrous trioxide is UO_3, a common form of which (γ-UO_3) is obtained by heating $UO_2(NO_3).6H_2O$ in air at 400°C; six other forms are also known.[27] Heating any of these, or indeed any other oxide of uranium, in air at 800–900°C yields U_3O_8 which contains pentagonal bipyramidal UO_7 units and can be used in gravimetric determinations of uranium. Reduction with H_2 or H_2S leads to a series of intermediate

nonstoichiometric phases (of which U_2O_5 may be mentioned) and ending with UO_2. Pentoxides are known also for Pa and Np. Pa_2O_5 is prepared by igniting Pa^V hydroxide in air, and the nonstoichiometric Np_2O_5 by treating Np^{IV} hydroxide with ozone and heating the resulting $NpO_3.H_2O$ at 300°C under vacuum.

Dioxides are known for all the actinides as far as Cf. They have the fcc fluorite structure (p. 118) in which each metal atom has CN = 8; the most common preparative method is ignition of the appropriate oxalate or hydroxide in air. Exceptions are CmO_2 and CfO_2, which require O_2 rather than air, and PaO_2 and UO_2, which are obtained by reduction of higher oxides.

From Pu onwards, sesquioxides become increasingly stable with structures analogous to those of Ln_2O_3 (p. 1238); BkO_2 is out-of-sequence but this is presumably due to the stability of the f^7 configuration in Bk^{IV}. For each actinide the C-type M_2O_3 structure (metal CN = 6) is the most common but A and B types (metal CN = 7) are often also obtainable.

Reports of monoxides formed as surface layers on the metals have not been substantiated although their existence in the vapour phase is not disputed (see pp. 237–8 of ref. 22). The oxides are basic in character but their reactivity is usually strongly influenced by their thermal history, being much more inert if they have

26 *J. Chem. Soc., Faraday Trans. II* **83**, 1065–285 (1987): a collection of papers on UO_2.

27 See for instance M. T. WELLER, P. G. DICKENS and D. J. PENNY, *Polyhedron* **7**, 243–4 (1988).

been ignited. Dioxides of Th, Np and Pu are best dissolved in conc HNO_3 with added F^-, but all oxides of U dissolve readily in conc HNO_3 or conc $HClO_4$ to yield salts of UO_2^{2+}.

Hydroxides are not well-characterized but gelantinous precipitates, which redissolve in acid, are produced by the addition of alkali to aqueous solutions of the actinides. Those of Th^{IV}, Pa^V, Np^V, Pu^{IV}, Am^{III} and Cm^{III} are stable to oxidation but lower oxidation states of these metals are rapidly oxidized. Aqueous solutions of hexavalent U, Np and Pu yield hydrous precipitates of $AnO_2(OH)_2$, which contain AnO_2^{2+} units linked by OH bridges, but they are often formulted as hydrated trioxides $AnO_3.xH_2O$.

Actinide chalcogenides can be obtained for instance by reaction of the elements, and thermal stability decreases S > Se > Te. Those of a given actinide differ from those of another in much the same way as do the oxides. Nonstoichiometry is again prevalent and, where the actinide appears to have an uncharacteristically low oxidation state, semimetallic behaviour is usually observed.

31.3.2 Mixed metal oxides

Alkali and alkaline earth metallates are obtained by heating the appropriate oxides, in the presence of oxygen where necessary. For instance, the reaction

$$\frac{5}{2} Li_2O + AnO_2 \xrightarrow[400-420°C]{O_2} Li_5AnO_6 \ [An = Np, Pu]$$
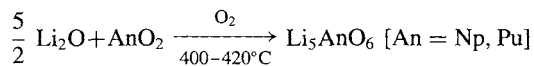
provides a means of stabilizing Np^{VII} and Pu^{VII} in the form of isolated $[AnO_6]^{5-}$ octahedra.

By suitable adjustment of the proportions of the reactants, An^{VI} species (An = U → Am) are obtained of which the "uranates" are the best known. These are of the types $M_2^I U_2O_7$, $M_2^I UO_4$, $M_4^I UO_5$ and $M_3^{II} UO_6$ in each of which the U atoms are coordinated by 6 O atoms disposed octahedrally but distorted by the presence of 2 short *trans* U–O bonds, characteristic of the uranyl UO_2^{2+} group. In view of the earlier inclusion of U in Group 6 it is interesting to note that, unlike Mo^{VI} and W^{VI}, U^{VI} apparently does

not show any tendency to form iso- or hetero-poly anions in aqueous solution.

$M^I An^V O_3$, $M_3^I An^V O_4$ and $M_7^I An^V O_6$ have been characterized for An = Pa → Am. Compounds of the first of these types have the perovskite structure (p. 963), those of the second a defect-rock-salt structure (p. 242), and those of the third have structures based on hexagonally close-packed O atoms. In all cases, therefore, the actinide atom is octahedrally coordinated. It is also notable that magnetic and spectroscopic evidence shows that, for uranium, these compounds contain the usually unstable U^V and not, as might have been supposed, a mixture of U^{IV} and U^{VI}.

$BaAn^{IV}O_3$ (An = Th → Am) all have the perovskite structure and are obtained from the actinide dioxide. In accord with normal redox behaviour, the Pa and U compounds are only obtainable if O_2 is rigorously excluded, and the Am compound if O_2 is present. Actinide dioxides also yield an extensive series of nonstoichiometric, mixed oxide phases in which a second oxide is incorporated into the fluorite lattice of the AnO_2. The UO_2/PuO_2 system, for example, is of great importance in the fuel of fast-breeder reactors.

31.3.3 Halides of the actinide elements [28]

The known actinide halides are listed in Table 31.6. They range from AnX_6 to AnX_2 and their distribution follows much the same trends as have been seen already in Tables 31.3 and 31.5. Thus the hexahalides are confined to the hexafluorides of U, Np and Pu (which are volatile solids obtained by fluorinating AnF_4) and the hexachloride of U, which is obtained by the reaction of $AlCl_3$ and UF_6. All are powerful oxidizing agents and are extremely sensitive to moisture:

$$AnX_6 + 2H_2O \longrightarrow AnO_2X_2 + 4HX$$

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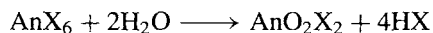
[28] J. C. TAYLOR, *Coord. Chem. Rev.* **20**, 197–273 (1976).

Table 31.6 Properties of actinide halides[a]

	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es
AnF_6			White 64° 6 o	Orange 54.7° 6 o	Brown 52° 6 o					
$AnCl_6$			Dark green 177° 6 o							
AnF_5		White na 7 pbp	Pale blue 348° 6 o	Pale blue na 7 pbp						
$AnCl_5$		Yellow 306° 7 pbp	Brown na 6 o							
$AnBr_5$		Dark red 6 o	Brown 6 o							
AnI_5		Black								
An_2F_9		Black (9)	Black (9)							
An_4F_{17}			Black		Red					
AnF_4	White 1068° 8 sa	Brown na 8 sa	Green 960° 8 sa	Green na 8 sa	Brown 1037° 8 sa	Tan na 8 sa	Brown na 8 sa	Yellow na 8 sa	Green na 8 sa	
$AnCl_4$	White 770° 8 d	Green-yellow na 8 d	Green 590° 8 d	Red-brown 517° 8 d						
$AnBr_4$	White 679° 8 d	Brown na 8 d	Brown 519° 7 pbp	Dark-red 464° 7 pbp						
AnI_4	Yellow 556° 8 sa	Black na na	Black 506° 6 ol							
AnF_3			Black decomp. 9 ttp	Purple na 9 ttp	Violet 1425° 9 ttp	Pink 1395° 9 ttp	White 1406° 9 ttp	Yellow na 9 ttp	Green na 8 btp	‡ na 8btp
$AnCl_3$			Green 837° 9 ttp	Green 800° 9 ttp	Green 767° 9 ttp	Pink 715° 9 ttp	White 695° 9 ttp	Green 603° 9 ttp	Green 575° 9 ttp	White na 9 ttp
$AnBr_3$			Red 727° 9 ttp	Green na 9 ttp	Green 681° 8 btp	White na 8 btp	White 625° 8 bpt	Yellow-green na 8 btp	Pale-green na 6 o	Light-brown na 6 o
AnI_3	Black na 8	Brown na 8 btp	Black 766° 8 btp	Purple 760° 8 btp	Green (777°) 8 btp	Yellow 950° 8 btp	White na 6 o	Yellow na 6 o	Yellow na 6 o	‡ na 6 ol
$AnCl_2$						Black 9 ttp			Amber	‡
$AnBr_2$						Black 8,7			Amber 8,7	‡
AnI_2	Gold complex					Black 7 co			Violet	‡

[a]Key: Colour (‡ indicates preparation but no report of colour); mp/°C (na indicates value not reported); coordination 9 ttp = tricapped trigonal prismatic; 8 d = dodecahedral; 8 sa = square antiprismatic; 8 btp = bicapped trigonal prismatic; 8,7 = mixed 8- and 7-coordination ($SrBr_2$ structure); 7 cc = capped octahedral; 7 pbp = pentagonal bipyramidal; 6 o = octahedral; 6 och = octahedral chain, 6 ol = octahedral layered.

UF_6 is important in the separation of uranium isotopes by gaseous diffusion (p. 1259).

Pentahalides are, perhaps surprisingly, not found beyond Np (for which the pentafluoride alone is known) but all four are known for Pa. All the pentafluorides as well as $PaCl_5$ are polymeric and attain 7-coordination by means of double X-bridges between adjacent metal atoms (Fig. 31.6); by contrast UCl_5 and $PaBr_5$ consist of halogen-bridged dimeric An_2X_{10} units, e.g. $Cl_4U(\mu\text{-}Cl)_2UCl_4$. All are very sensitive to water, the hydrolysis of the U^V halides being complicated by simultaneous disproportionation. Fluorides of intermediate compositions An_2F_9 (An = Pa, U) and An_4F_{17} (An = U, Pu) have also been reported. U_2F_9 is the best known; its black colour probably results from charge transfer between U^{IV} and U^V
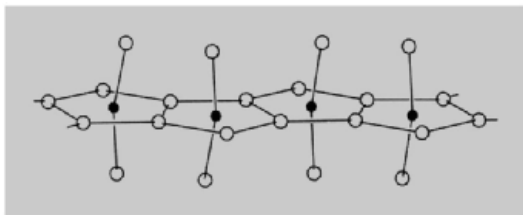
Figure 31.6   The polymeric structure of AnF_5 (An = Pa, U, Np) and $PaCl_5$, showing the distorted pentagonal bipyramidal coordination of the metal.

A much more extensive series is formed by the tetrahalides of which the tetrafluorides are known as far as Cf. The early tetrafluorides $ThF_4 \rightarrow PuF_4$ are produced by heating the dioxides in HF in the presence of H_2 for PaF_4 (in order to prevent oxidation) and in the presence of O_2 for NpF_4 and PuF_4 (in order to prevent reduction). The later tetrafluorides $AmF_4 \rightarrow CfF_4$ are obtained by heating the corresponding trifluoride with F_2. In all cases the metal is 8-coordinated, being surrounded by a slightly distorted square-antiprismatic array of F^- ions. The tetrachlorides (Th $\rightarrow$ Np) are prepared by heating the dioxides in CCl_4 or a similar chlorinated hydrocarbon, whereas the tetrabromides (Th $\rightarrow$ Np) and tetraiodides (Th $\rightarrow$ U) are obtained from the elements. Eight-coordination is again common (this time

dodecahedral) but a reduction to 7-coordination occurs with UBr_4 and $NpBr_4$, and to octahedral coordination for UI_4. AnF_4 are insoluble in water and, for Th, U and Pu at least, are precipitated as the hydrate $AnF_4.2\frac{1}{2}H_2O$ when F^- is added to any aqueous solution of An^{IV}. $AnCl_4$, $AnBr_4$ and AnI_4 are rather hygroscopic, and dissolve readily in water and other polar solvents. An extensive coordination chemistry is based on the actinide tetrahalides, and UCl_4 is one of the best-known compounds of uranium, providing the usual starting point for most studies of U^{IV} chemistry.

The trihalides are the most nearly complete series, all members having been obtained for the elements U $\rightarrow$ Es and the series could no doubt be extended. Preparative methods are varied and depend in particular on the actinide involved. For the heavier actinides (Am $\rightarrow$ Cf) heating the sesquioxide or dioxide in HX is generally applicable, but the lighter actinides require reducing conditions. For NpF_3 and PuF_3 the addition of H_2 to the reaction suffices, but UF_3 is best obtained by the reduction of UF_4 with metallic U or Al. Trichlorides and tribromides of these lighter actinides can be obtained by heating the actinide hydride with HX, and the triiodides by heating the metal with I_2 (U, Np) or HI (Pu). PaI_3 is said to be obtained by heating PaI_5 in a vacuum.

With the exception of their redox properties, the actinide trihalides form a homogeneous group showing strong similarities with the lanthanide trihalides. The ionic, high-melting trifluorides are insoluble in water, from which they can be precipitated as monohydrates; at Cf^{III} (ionic radius = 95 pm) they show the same structural change from CN 9 to CN 8 as the lanthanides do at Gd^{III} (ionic radius = 93.8 pm). The other trihalides are all hygroscopic, water-soluble solids, many of which crystallize as hexahydrates featuring 8-coordinate cations $[AnX_2(H_2O)_6]^+$. Reduction in coordination number as the cations get smaller, again parallels behaviour observed in the lanthanide trihalides but of course it occurs further along the series because of the larger size of the actinides.

Not surprisingly, in view of the stability of Th^{IV}, ThI_3 is quite different from the above

trihalides. It is rapidly oxidized by air, reduces water with vigorous evolution of H_2, and is probably best regarded as $[Th^{IV}, 3I^-, e^-]$. The air-sensitive ThI_2, which is obtained by heating ThI_4 with stoichiometric amounts of the metal, is similarly best formulated as $[Th^{IV}, 2I^-, 2e^-]$. It has a complicated layer structure and its lustre and high electrical conductivity indicate a close similarity with the diiodides of Ce, Pr and Gd.

Halides of truly divalent americium, however, can be prepared:

$$Am + HgX_2 \xrightarrow{400-500°C} AmX_2 + Hg \ (X = Cl, \ Br, \ I)$$
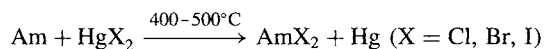
Like those of Eu with which they are structurally similar, these dihalides presumably owe their existence to their f^7 configuration. $CfBr_2$ and CfI_2 are also known and it seems probable that actinide dihalides would be increasingly stable as far as No if the problems of availability, etc., were overcome.

Several oxohalides[3,22,23] are also known, mostly of the types $An^{VI}O_2X_2$, $An^{V}O_2X$, $An^{IV}OX_2$ and $An^{III}OX$, but they have been less thoroughly studied than the halides. They are commonly prepared by oxygenation of the halide with O_2 or Sb_2O_3, or in case of AnOX by hydrolysis (sometimes accidental) of AnX_3. As is to be expected, the higher oxidation states are formed more readily by the lighter actinides; thus AnO_2X_2, apart from the fluoro compounds, are confined to $An = U$. Conversely the lower oxidation states are favoured by the heavier actinides (from Am onwards).

31.3.4 Magnetic and spectroscopic properties [3,11]

As the actinides are a second f series it is natural to expect similarities with the lanthanides in their magnetic and spectroscopic properties. However, while previous treatments of the lanthanides (p. 1242) provide a useful starting point in discussing the actinides, important differences are to be noted. Spin−orbit coupling is again strong (2000−4000 cm^{-1}) but, because of the greater exposure of the 5f

electrons, crystal-field splittings are now of comparable magnitude and J is no longer such a good quantum number. Furthermore, as already mentioned (p. 1266), the energy levels of the 5f and 6d orbitals are sufficiently close for the lighter actinides at least, to render the 6d orbitals accessible. As a result, rigorous treatments of electronic properties must consider each actinide compound individually. They must allow for the mixing of "J levels" obtained from Russell−Saunders coupling and for the population of thermally accessible excited levels. Accordingly, the expression $\mu_e = g\sqrt{J(J+1)}$ is less applicable than for the lanthanides: the values of magnetic moment obtained at room temperature roughly parallel those obtained for compounds of corresponding lanthanides (see Table 30.6), but they are usually appreciably lower and are much more temperature-dependent.

The electronic spectra of actinide compounds arise from three types of electronic transition:

(i) *f→f transitions* (see p. 1243). These are orbitally forbidden, but the selection rule is partially relaxed by the action of the crystal field in distorting the symmetry of the metal ion. Because the field is stronger than for the lanthanides, the bands are more intense by about a factor of 10 and, though still narrow, are about twice as broad and are more complex than those of the lanthanides. They are observed in the visible and ultraviolet regions and produce the colours of aqueous solutions of simple actinide salts as given in Table 31.3.

(ii) *5f→6d transitions.* These are orbitally allowed and give rise to bands which are therefore much more intense than those of type (i) and are usually rather broader. They occur at lower energies than do the 4f → 5d transitions of the lanthanides but are still normally confined to the ultraviolet region and do not affect the colour of the ion.

(iii) *Metal→ligand charge transfer.* These again are fully allowed transitions and

produce broad, intense absorptions usually found in the ultraviolet but sometimes trailing into the visible region. They produce the intense colours which characterize many actinide complexes, especially those involving the actinide in a high oxidation state with readily oxidizable ligands.

In view of the magnitude of crystal-field effects it is not surprising that the spectra of actinide ions are sensitive to the latter's environment and, in contrast to the lanthanides, may change drastically from one compound to another. Unfortunately, because of the complexity of the spectra and the low symmetry of many of the complexes, spectra are not easily used as a means of deducing stereochemistry except when used as "fingerprints" for comparison with spectra of previously characterized compounds. However, the dependence on ligand concentration of the positions and intensities, especially of the charge-transfer bands, can profitably be used to estimate stability constants.

31.3.5 Complexes of the actinide elements [3,11,23,29]

Because of the technical importance of solvent extraction, ion-exchange and precipitation processes for the actinides, a major part of their coordination chemistry has been concerned with aqueous solutions, particularly that involving uranium. It is, however, evident that the actinides as a whole have a much stronger tendency to form complexes than the lanthanides and, as a result of the wider range of available oxidation states, their coordination chemistry is more varied.

Oxidation state VII

This has been established only for Np and Pu, alkaline An^{VI} solutions of which can be electrolytically oxidized to give dark-green solutions probably containing species such as $[AnO_4(OH)_2]^{3-}$. Similar strongly oxidizing solutions (the more so if made acidic) are obtained when the mixed oxides Li_5AnO_6 are dissolved in water.

Oxidation state VI

Fluorocomplexes of U^{VI} are known of which $(NH_4)_4UF_{10}$ with a probable coordination number of ten is notable.[30] Otherwise, apart from UO_3 and the An^{VI} halides already discussed, this oxidation state is dominated by the dioxo, or "actinyl" AnO_2^{2+} ions which are found both in aqueous solutions and in solid compounds of U, Np, Pu and Am. These dioxo ions retain their identity throughout a wide variety of reactions and are present, for instance, in the oxohalides AnO_2X_2. The An–O bond strength and the resistance of the group to reduction decreases in the order U > Np > Pu > Am. Thus yellow uranyl salts are the most common salts of uranium and are the final products when other compounds of the element are exposed to air and moisture. The nitrate is the most familiar and has the remarkable property, utilized in the extraction of U, of being soluble in nonaqueous solvents such as tributyl phosphate. On the other hand, the formation of AmO_2^{2+} requires the use of such strong oxidizing agents as peroxodisulfate, $S_2O_8^{2-}$. Similarly, whereas the oxofluorides AnO_2F_2 are known for U, Np, Pu and Am, only U forms the corresponding oxochloride and oxobromide, Cl^- and Br^- reducing AmO_2^{2+} to Am^V species.

In aqueous solutions hydrolysis of the actinyl ions is important and such solutions are distinctly acidic. The reactions are complicated but, at least in the case of UO_2^{2+}, it appears that loss of H^+ from coordinated H_2O is followed by polymerization involving $-OH-$ bridges and yielding species such as $[(UO_2)(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$.

[29] N. B. MIKHEEV and A. N. KAMENSKAYA, *Coord. Chem. Revs.* **109**, 1–59 (1991).

[30] S. MILICEV and B. DRUZINA, *Polyhedron* **9**, 47–51 (1990).

(a)   (b)   (c)

○ Uranium   ◉ Nitrogen   ○ Oxygen   ⊂⊃ Acetate   ◎ Chlorine
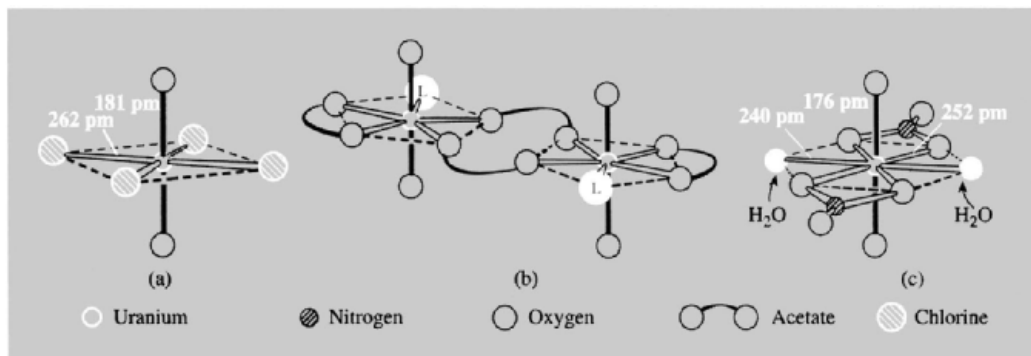
Figure 31.7   (a) The octahedral anion in $Cs_2[UO_2Cl_4]$. (b) Pentagonal bipyramidal coordination of U in dinuclear $[UO_2(O_2CMe)_2L]_2$ (L = $OPPh_3$, $OAsPh_3$). (c) Hexagonal bipyramidal coordination of U in uranyl nitrate, $UO_2(NO_3)_2.6H_2O$.

Actinyl ions seem to behave rather like divalent, class-a, metal ions of smaller size (or metal ions of the same size but higher charge) and, accordingly, they readily form complexes with F^- and O-donor ligands such as OH^-, SO_4^{2-}, NO_3^- and carboxylates.[31] The $O{=\!\!=}An{=\!\!=}O$ groups are in all cases linear, and coordination of a further 4, 5 or 6 ligands is possible in the equatorial plane. Octahedral, pentagonal bipyramidal, and hexagonal bipyramidal geometries result;[32] some examples are shown in Fig. 31.7. These ligands lying in the plane may be neutral molecules such as H_2O, OPR_3, $OAsR_3$, py or the anions mentioned above, many of which are bidentate.

The axial O–An bonds are clearly very strong. They cannot be protonated and are nearly always shorter than the equatorial bonds. In the case of UO_2^{2+}, for instance, it is likely that the U–O bond order is even greater than 2, since the U–O distance is only about 180 pm; in spite of the difference in the ionic radii of the metal ions (U^{VI} = 73 pm, Os^{VI} = 54.5 pm), this is close to that of the $Os{=}O$ double bond found in the isostructural, osmyl group (175 pm, see p. 1085). It is usually assumed that combinations

of appropriate metal 6d and 5f orbitals overlap with the three p orbitals (or two p and one sp hybrid) of each oxygen to produce one σ and two π bonds, i.e. $O{\rightleftharpoons}U{\unlhd}O$. This interpretation implies that the change from bent to linear geometries in comparing MoO_2^{2+} (p. 1024) and UO_2^{2+} is due to the involvement of empty f orbitals in the latter case. More pertinently, the unstable ThO_2 which is isoelectronic with UO_2^{2+}, is bent (angle O–Th–O 122°) and the difference has been convincingly explained in a relativistic extended Hückel treatment, on the basis that d-orbitals favour bent and f-orbitals linear geometries; in UO_2^{2+} the 6d orbitals are lower in energy than the 5f whereas in ThO_2 the order is reversed.[33]

Oxidation state V

In aqueous solution the AnO_2^+ ions (An = Pa → Am) may be formed, at least in the absence of strongly coordinating ligands. They are linear cations like AnO_2^{2+} but are less persistent and, indeed, it is probable that PaO_2^+ should be formulated as $[PaO(OH)_2]^+$ and $[PaO(OH)]^{2+}$. Hydrolysis is extensive in aqueous solutions of Pa^V and colloidal hydroxo species are formed which readily lead to precipitation of
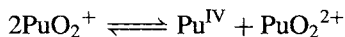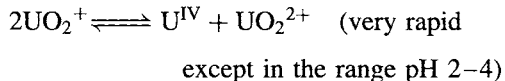
[31] J. LECIEJEWICZ, N. W. ALCOCK and T. J. KEMP, *Structure and Bonding* **82**, 43–84 (1995).
[32] See pp. 1424–31 of ref. 3.

[33] P. PYYKKÖ, L. S. LAAKKONEN and K. TATSUMI, *Inorg. Chem.* **28**, 1801–5 (1989).

$Pa_2O_5.nH_2O$. NpO_2^+ in aqueous $HClO_4$ is stable but UO_2^+, PuO_2^+ and AmO_2^+ are unstable to disproportionation:

$$2UO_2^+ \rightleftharpoons U^{IV} + UO_2^{2+} \quad \text{(very rapid}$$

$$\text{except in the range pH 2–4)}$$

$$2PuO_2^+ \rightleftharpoons Pu^{IV} + PuO_2^{2+}$$

and then $PuO_2^+ + Pu^{IV} \rightleftharpoons Pu^{III} + PuO_2^{2+}$.[†] Likewise:

$$3AmO_2^+ \rightleftharpoons Am^{III} + 2AmO_2^{2+}$$

Though the low charge on AnO_2^+ ions precludes the formation of very stable complexes, and disproportionation into An^{IV} and An^{VI} species is common, a number of complexes of NpO_2^+ have been prepared,[34] several containing the pentagonal bipyramidal $\{NpO_2(SO_4)_2L\}$ unit. In other cases, strongly coordinating ligands are able to replace the oxygen atoms of the AnO_2^+ ions and so inhibit disproportionation where this might otherwise occur. F^- is notable in this respect and complex ions, AnF_6^- ($An = Pa, U, Np, Pu$), PaF_7^{2-} and PaF_8^{3-} can be precipitated from aqueous HF solutions. However, in nonaqueous solvents, preparations such as the oxidation of M^IF and AnF_2 by F_2 are more common for U, Np and Pu and extend the range of complex ions to include AnF_7^{2-} ($An = U, Np, Pu$) and AnF_8^{3-} ($An = U, Np$). The stereochemistries of these anions are dependent on the particular counter cation as well as on An, and involve 6-, 7-, 8- and 9-coordination. The most remarkable of these complexes are the compounds Na_3AnF_8 ($An = Pa, U, Np$) in which the actinide ion is surrounded by 8 F^- at the corners of a nearly perfect cube in spite of the large inter-ligand repulsions which this entails.

[†] In the diagram of volt-equivalent versus oxidation state of Pu (Fig. 31.5) the oxidation states III to VI inclusive lie virtually on a straight line. It follows that if either Pu^{IV} or Pu^V is dissolved in water, disproportionations are thermodynamically feasible, and within a matter of hours mixtures of Pu in all four oxidation states are obtained.

[34] M. S. GRIGOR'EV, I. A. CHARUSHNIKOV, N. N. KROT, A. I. YANOVSKII and Y. T. STRUCHNOV, *Russ. J. Inorg. Chem. (Engl. Trans.)* **39**, 1267–70 (1994).

Finally, the alkoxides $U(OR)_5$ must be mentioned.[35] Although easily hydrolysed, they are thermally stable and unusually resistant to disproportionation. They are usually dimeric, $[(RO)_4U(\mu\text{-}OR)_2U(OR)_4]$, and are best obtained by the reactions:

$$2[U(OEt)_4] \xrightarrow[(-2NaBr)]{Br_2 + 2NaOEt} [\{U(OEt)_5\}_2] \xrightarrow{10ROH}$$

$$[\{U(OR)_5\}_2]$$
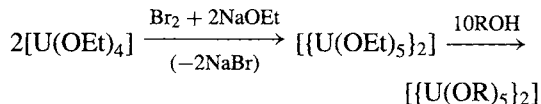
Oxidation state IV

This is the only important oxidation state for Th, and is one of the two for which U is stable in aqueous solution; it is moderately stable for Pa and Np also. In water Pu^{IV}, like Pu^V, disproportionates into a mixture of oxidation states III, IV, V and VI, while Am^{IV} not only disproportionates into $Am^{III} + Am^VO_2^+$ but also (like the strongly oxidizing Cm^{IV}) undergoes rapid self-reduction due to its α-radioactivity. As a result, aqueous Am^{IV} and Cm^{IV} require stabilization with high concentrations of F^- ion. Berkelium(IV), though easily reduced, clearly has an enhanced stability, presumably due to its f^7 configuration, and the only other +4 ion is Cf^{IV}, found in the solids CfF_4 and CfO_2.

In aqueous solutions the hydrated cations are probably 8- or even 9-coordinated and, because they are the most highly charged ions in the actinide series, they have the greatest tendency to split-off protons and so function as quite strong acids (slightly stronger in most cases than H_2SO_3). This hydrolysis is followed by polymerization which has been most extensively studied in the case of Th. The aquated, dimeric ion, $[Th_2(OH)_2]^{6+}$, which probably involves two OH bridges, seems to predominate even in quite acidic solutions, but in solutions more alkaline than pH 3 polymerization increases considerably and eventually yields an amorphous precipitate of the hydroxide. Just before precipitation it is noticeable that the polymerization process slows down and equilibrium may take weeks to attain.

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[35] W. G. VAN DER SLUYS and A. P. SATTELBERGER, *Chem. Revs.* **96**, 1027–40 (1990).
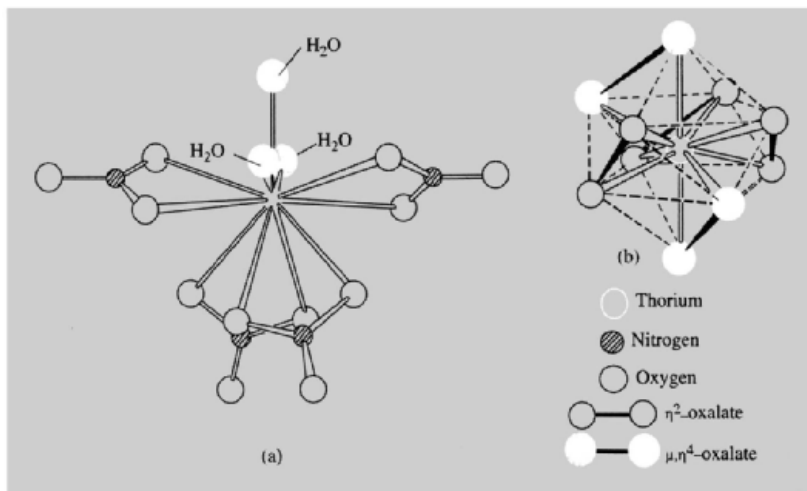
Figure 31.8   (a) Eleven-coordinate Th in $Th(NO_3)_4.5H_2O$: av. Th–O (of NO_3) = 257 pm; av. Th–O (of H_2O) = 246 pm. (b) The 10-coord. bicapped square antiprismatic anion in $K_4[Th(C_2O_4)_4].4H_2O$. Note that two pyramidal (267 pm) and three equatorial edges (276 pm) are spanned by oxalate groups, but none of the longer edges of the squares (311 pm). The oxalate groups on the pyramidal edges are actually quadridentate, being coordinated also to adjacent Th atoms.

The same effect is found also with Pu^{IV} where the persistence of polymers, even at acidities which would prevent their formation, can cause serious problems in the reprocessing of nuclear fuels.

The isolation of An^{IV} salts with oxoanions is limited by hydrolysis and redox compatibility. Thus, with the possible exception of $Pu(CO_3)_2$, carbonate ions furnish only basic carbonates or carbonato complexes such as $[An(CO_3)_5]^{6-}$ (An = Th, U, Pu). Stable tetranitrates are isolable only for Th and Pu, but $Th(NO_3)_4.5H_2O$ is the most common salt of Th and is notable as the first confirmed example of 11-coordination (Fig. 31.8(a). $Pu(NO_3)_4.5H_2O$ is isomorphous, and stabilization of Pu^{IV} by strong nitric acid solutions is crucial in the recovery of Pu by solvent extraction. O-donor ligands such as dmso, Ph_3PO and C_5H_5NO form adducts, of which $[Th(NO_3)_4(OPPh_3)_2]$ is known to have a 10-coordinate structure like its Ce^{IV} analogue (Fig. 30.5b, p. 1245) and $[Th(C_5H_5NO)_6(NO_3)_2]^{2+}$ has a 10-coordinate distorted bicapped antiprismatic structure.[36]

Anionic complexes $[An(NO_3)_6]^{2-}$ (An = Th, U, Np, Pu) are also obtained, that of Th, and probably the others, having bidentate NO_3^- ions forming a slightly distorted icosahedron similar to that of the Ce^{IV} analogue (see Fig. 30.5a). $Th(ClO_4)_4.4H_2O$ is readily obtained from aqueous solutions but attempts to prepare the U^{IV} salt have produced a green explosive solid of uncertain composition. Hydrated sulfates are known for Th, U, Np and Pu. That of Np is of uncertain hydration but the others can be prepared with both $4H_2O$ and $8H_2O$, $PuSO_4.4H_2O$ having possible use as an analytical standard.

The actinides provide a wider range of complexes in their +4 oxidation state than in any other, and these display the usual characteristics of actinide complexes, namely high coordination numbers and varied geometry. Complexes with halides and with O-donor chelating ligands are particularly numerous. The main fluoro-complexes are of the types $[AnF_5]^-$, $[AnF_6]^{2-}$, $[AnF_7]^{3-}$, $[AnF_8]^{4-}$ and $[An_6F_{31}]^{7-}$ which are nearly all known for An = Th → Bk. Their stoichiometries have not all been determined but, in some cases at least, are known

[36] D. M. L. GOODGAME, S. NEWNHAM, C. A. O'MAHONEY and D. J. WILLIAMS, *Polyhedron* **9**, 491–4 (1992).

to depend on the counter cation. For instance, $[UF_6]^{2-}$ has a distorted cubic structure in its K^+ salt and a distorted dodecahedral structure in its Rb^+ salt.

Several carboxylates, both simple salts and complex anions, have been prepared often as a means of precipitating the An^{IV} ion from solution or, as in the case of simple oxalates, in order to prepare the dioxides by thermal decomposition. In $K_4[Th(C_2O_4)_4].4H_2O$ the anion is known to have a 10-coordinate, bicapped square antiprismatic structure (Fig. 31.8b). β-diketonates are precipitated from aqueous solutions of An^{IV} and the ligand by addition of alkali, and nearly all are sublimable under vacuum. $[An(acac)_4]$, $(An = Th, U, Np, Pu)$ are apparently dimorphic but both structures are based on an 8-coordinate, distorted square antiprism.

Complexes with *S*-donor ligands are generally less stable and more liable to hydrolysis than those with *O*-donors but can be obtained if the ligand is anionic and chelating. Diethyldithiocarbamates $[An(S_2CNEt_2)_4]$ $(An = Th, U, Np, Pu)$ are the best known and possess an almost ideal dodecahedral structure.

Finally, the borohydrides $An(BH_4)_4$ must be mentioned.[37] Those of Th and U were originally prepared as part of the Manhattan Project and those of Pa, Np and Pu have been prepared more recently, all by the general reaction

$$AnF_4 + 2Al(BH_4)_3 \longrightarrow An(BH_4)_4 + 2AlF_2BH_4$$
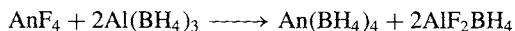
The compounds are isolated by sublimation from the reaction mixture. Perhaps surprisingly the compounds fall into two quite distinct classes. Those of Np and Pu are unstable, volatile, monomeric liquids which at low temperatures crystallize with the 12-coordinate structure of $Zr(BH_4)_4$ (Fig. 21.7, p. 969). The borohydrides of Th, Pa and U, on the other hand, are thermally more stable and less reactive solids. They possess a curious helical polymeric structure in which each An is surrounded by 6 BH_4^- ions, 4 being bridging groups attached by 2 H atoms and

2 being *cis* terminal groups attached by 3 H atoms. The coordination number of the actinide is therefore 14 and the stereochemistry may be described as bicapped hexagonal antiprismatic.

Oxidation state III

This is the only oxidation state which, with the possible exception of Pa, is displayed by all actinides. From U onwards, its resistance to oxidation in aqueous solution increases progressively with increase in atomic number and it becomes the most stable oxidation state for Am and subsequent actinides (except No for which the f^{14} configuration confers greater stability on the +2 state).

Amber $Th^{3+}(aq)$ has recently been prepared from aqueous solutions of $ThCl_4$ and HN_3, and is stable for over 1 h before being oxidized by water.[37a] U^{III} can be obtained by reduction of UO_2^{2+} or U^{IV}, either electrolytically or with Zn amalgam, but is thermodynamically unstable to oxidation not only by O_2 and aqueous acids but by pure water also.[†] It is nevertheless possible to crystallize double sulfates or double chlorides from aqueous solution and these can then be used to prepare other U^{III} complexes in nonaqueous solvents. Crystallographic data are not plentiful but it has been shown that in $(NH_4)U^{III}(SO_4)_2(H_2O)_4$ each SO_4^{2-} is bidentate to one U and monodentate to a second. Three H_2O complete a coordination sphere of 9 oxygens for each uranium with a geometry intermediate between tricapped trigonal prismatic and monocapped square antiprismatic.[38] A number of cationic amide complexes are also known for which infrared evidence suggests[39]

[†] In pure water the activity of H^+ is only 10^{-7} mol dm^{-3}, and E for the $2H^+/H_2$ couple consequently falls to -0.414 V compared to $E° = 0$. However, $E°$ for U^{4+}/U^{3+} is even more negative (-0.607 V) and U^{III} will accordingly reduce water.

[37a] T. M. KLAPÖTKE and A. SCHULZ, *Polyhedron* **16**, 989–91 (1997).

[38] J. I. BULLOCK,   M. F. C. LADD,   D. C. POVEY   and A. E. STOREY, *Inorg. Chim. Acta.* **43**, 101–8 (1980).

[39] J. I. BULLOCK, A. E. STOREY and P. THOMPSON, *J. Chem. Soc., Dalton Trans.*, 1040–4 (1979).

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[37] R. H. BANKS and N. M. EDELSTEIN, *Lanthanide and Actinide Chemistry and Spectroscopy*, ACS Symposium, Series 131, Am. Chem. Soc., Washington, 1980, pp. 331–48.

the low symmetry coordination of 8 oxygen atoms to each uranium atom.

Instability also limits the number of complexes of Np^{III} and Pu^{III} but for Am^{III} the number so far prepared is apparently limited mainly by unavailability of the element. As has already been pointed out, the problem becomes still more acute as the series is traversed. While it is clear that lanthanide-like dominance by the tervalent state occurs with the actinides after Pu, the experimental evidence though compelling, is understandably sparse, being largely restricted to solvent extraction and ion-exchange behaviour.[40]

Oxidation state II

This state is found for the six elements Am and Cf → No, though in aqueous solution only for Fm, Md and No. However, for No, alone amongst all the f-series elements, it is the normal oxidation state in aqueous solution. The greater stabilization of the +2 state at the end of the actinides as compared to that at the end of the lanthanides which this implies, has been taken[40] to indicate a greater separation between the 5f and 6d than between the 4f and 5d orbitals at the ends of the two series. This is the reverse of the situation found at the beginnings of the series (p. 1266).

Reports of the observation of the +1 oxidation state in aqueous solutions of Md have not been substantiated despite attempts in several major laboratories, and it has been concluded that Md^I does not exist in either aqueous or ethanolic solutions.[41]

31.3.6 Organometallic compounds of the actinides[42]

The growth of organoactinide chemistry, like that of organolanthanide chemistry, is comparatively

recent. Attempts in the 1940s to prepare volatile carbonyls and alkyls of uranium for isotopic separations were unsuccessful though, as with the lanthanides, simple carbonyls of uranium have since been obtained in argon matrices quenched to 4 K. Subsequent work has mainly centred on cyclopentadienyls and, to a lesser extent, cyclooctatetraenyls; σ-bonded alkyl and aryl derivatives of the cyclopentadienyls have also been obtained. In general, these compounds are thermally stable, sublimable, but extremely air-sensitive solids which are sometimes water-sensitive also. Their bonding is evidently more covalent than that in organolanthanides, presumably because of the involvement of 5f orbitals, and relativistic effects.

The cyclopentadienyls are of the three main types: (a) $[An^{III}(C_5H_5)_3]$, (b) $[An^{IV}(\eta^5-C_5H_5)_4]$ and (c) derivatives of the type $[An^{IV}(\eta^5-C_5H_5)_3X]$ where X is a halogen atom, an alkyl or alkoxy group, or BH_4.

(a) $[An^{III}(C_5H_5)_3]$ (An = Th → Cf): the uranium compound is prepared directly from UCl_3 and $K(C_5H_5)$ but those of the heavier actinides are best made by the reaction:

$$2AnCl_3 + 3Be(C_5H_5)_2 \xrightarrow{65°C} 2An(C_5H_5)_3 + 3BeCl_2$$
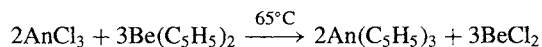
Complete structural data are sparse but X-ray diffraction patterns suggest that both η^5 and η^1 bonding modes are involved (cf. $Sm(C_5H_5)_3$ p. 1248). In $[Th^{III}\{\eta^5-C_5H_3(SiMe_3)_2\}_3]$ the centres of three rings form a trigonal plane around the Th atom.[43] The spectroscopic properties of this blue paramagnetic compound imply a $6d^1$ rather than $5f^1$ configuration.[44]

(b) $[An^{IV}(C_5H_5)_4]$ (An = Th → Np): the Pa compound is prepared by treating $PaCl_4$ with $Be(C_5H_5)_2$ but the general method of preparation is:

$$AnCl_4 + 4K(C_5H_5) \xrightarrow[\text{in } C_6H_6]{\text{reflux}} [An(C_5H_5)_4] + 4KCl$$
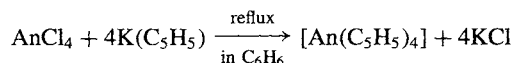
[40] See, for instance, E. K. HULET, ref. 37, pp. 239–63.

[41] K. HULET, P. A. BAISEN, R. DOUGAN, J. H. LANDRUM, R. W. LOUGHEED and J. F. WILD, *J. Inorg. Nucl. Chem.* **43**, 2941–5 (1981).

[42] T. J. MARKS and R. D. ERNST, pp. 211–70 of Chap. 21 in *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, Oxford, 1982. See also Vol. 4 of *COMC II*, 1995.

[43] P. C. BLAKE, M. F. LAPPERT, J. L. ATWOOD and H. ZHANG, *J. Chem. Soc., Chem. Commun.*, 1148–9 (1986).

[44] W. K. KOT, G. V. SHALIMOFF and N. M. EDELSTEIN, *J. Am. Chem. Soc.* **110**, 986–7 (1988).

$[M(C_5H_5)_4]$ (M = Th, U) contain four identical η^5 rings arranged tetrahedrally around the metal atom (Fig. 31.9). The corresponding compounds of Pa and Np are probably the same since all four compounds have very similar nmr and ir spectra.
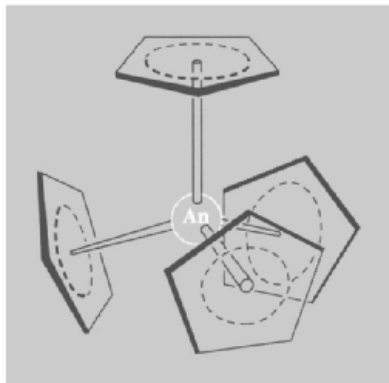
Figure 31.9 Structure of $[An(\eta^5\text{-}C_5H_5)_4]$ showing the tetrahedral arrangement of the four rings around the metal atom.

(c) Halide derivatives: the most plentiful are of the type $[An^{IV}(C_5H_5)_3X]$ (An = Th, Pa, U, Np); they can be prepared by the general reaction:

$$AnX_4 + 3M^I(C_5H_5) \longrightarrow [An(C_5H_5)_3X] + 3M^IX$$
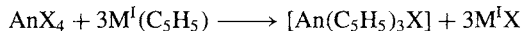
Indeed, the first report of an organoactinide was that of the pale brown $[U(C_5H_5)_3Cl]$ by L. T. Reynolds and G. Wilkinson in 1956. They showed that, unlike $Ln(C_6H_5)_3$, this compound does not yield ferrocene on reaction with $FeCl_2$, suggesting greater covalency in the bonding of $C_5H_5^-$ to U^{IV} than to Ln^{III}.

Replacement of Cl in $[U(C_5H_5)_3Cl]$ and $[Th(C_5H_5)_3Cl]$, by other halogens or by alkoxy, alkyl, aryl or BH_4 groups, provides the most extensive synthetic route in this field. An essentially tetrahedral disposition of three $(\eta^5\text{-}C_5H_5)$ rings and the fourth group around the metal appears to be general. The alkyl and aryl derivatives $[An(\eta^5\text{-}C_5H_5)_3R]$ (An = Th, U), are of interest as they provide a means of investigating the An–C σ bond, and mechanistic studies of their thermal decomposition (thermolysis) have been prominent. The precise mechanism is not yet certain but it is clearly not β-elimination

(of an olefin, see p. 926) since the eliminated molecule is RH, the H of which originates from a cyclopentadienyl ring. The decomposition of the Th compounds are cleaner than those of U and a crystalline product can be isolated from the thermolysis at 170°C of a solution of $[Th(\eta^5\text{-}C_5H_5)_3Bu^n]$. This product is a dimer with the 2 Th atoms bridged by a pair of $(\eta^5,\eta^1\text{-}C_5H_5)$ rings, i.e. $[Th(\eta^5\text{-}C_5H_5)_2\text{-}\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_5)]_2$. This remarkable bridge system is like that in niobocene (Fig. 22.12a, p. 1001) but each Th has two additional $(\eta^5\text{-}C_5H_5)$ rings instead of one $(\eta^5\text{-}C_5H_5)$ and an H atom.

It has not so far been possible to obtain either An^{III} or An^{IV} compounds with three C_5Me_5 rings around a single metal atom. However, $[M(\eta^5\text{-}C_5Me_4H)_3Cl]^{(45)}$ (M = Th, U) and $[U(\eta^5\text{-}C_4Me_4P)_3Cl]^{(46)}$ have been prepared.

The complexes $[An(\eta^8\text{-}C_8H_8)_2]$ of cyclooctatetraene (cot) have been prepared for An = Th → Pu by the reactions:

$$AnCl_4 + 2K_2C_8H_8 \xrightarrow{\text{thf}} [An(C_8H_8)_2] + 4KCl$$

$$(An = Th \to Np)$$

and

$$[NEt_4]_2[PuCl_6] + 2K_2C_8H_8 \xrightarrow{\text{thf}} [Pu(C_8H_8)_2]$$
$$+ 4KCl + 2[NEt_4]Cl$$
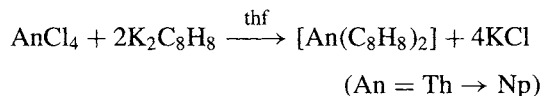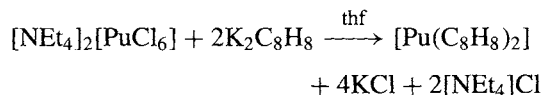
followed by sublimation under vacuum. They are "sandwich" molecules with parallel and eclipsed rings (see Fig. 19.31, p. 942). This structure is strikingly similar to that of ferrocene (Fig. 19.27, p. 937), and extensive discussions on the nature of the metal-ring bonding suggests that this too is very similar.[3] In order to emphasise these resemblances with the d-series cyclopentadienyls, the names "uranocene", etc., have been coined. Although thermally stable, these compounds are extremely sensitive to air and, except for uranocene, are also decomposed by water.

[45] F. G. N. CLOKE, S. A. HAWKES, P. B. HITCHCOCK and P. SCOTT, *Organometallics* **13**, 2895–7 (1994).

[46] P. GRADOZ, C. BOISSON, D. BAUDRY, M. LANCE, M. NIERLICH, J. VIGNER and M. EPHRITIKHINE, *J. Chem. Soc., Chem. Commun.*, 1720–1 (1992).

However, uranocene can be made more air-stable by use of sufficiently bulky substituents, and 1,3,5,7-tetraphenylcyclo-octatetraene yields the completely air-stable $[U(\eta^8\text{-}C_8H_4Ph_4)_2]$, in which the parallel ligands are virtually eclipsed but the phenyl substituents staggered and rotated on average 42° out of the C_8 ring plane (Fig. 31.10).
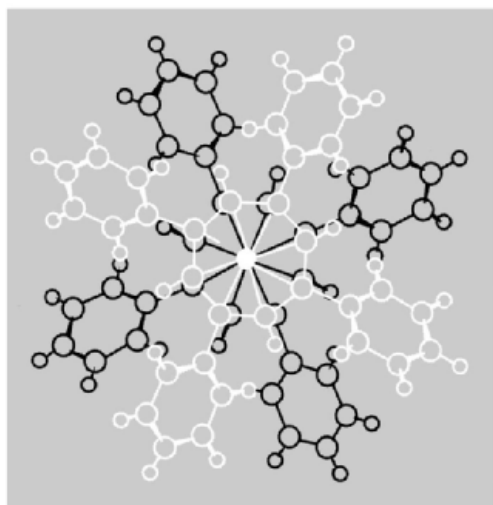
Figure 31.10   The structure of $[U(\eta^8\text{-}C_8H_4Ph_4)_2]$.

31.4 The Transactinide Elements (Z = 104−112)

31.4.1 Introduction

The addition of nine further elements ($Z = 104-112$) to the Periodic Table during the past three decades has involved outstanding feats of intellectual and experimental virtuosity. Some of the discoveries have been widely accepted but others have been hotly contested and this has led to distressingly persistent disagreements concerning priority. For this reason IUPAC and IUPAP set up a neutral international group in 1987 to establish "the criteria that must be satisfied for the discovery of a new element to be recognised" and to apply these criteria to questions of priority in the discovery of the transfermium elements. Some of the conclusions of this group have already been briefly mentioned (see Table 31.1). Their detailed Reports[5] were accepted by both IUPAC and IUPAP and the group's final recommendations, which form the basis of this Section, have been very widely though not universally accepted by the scientific community. Many subtle and difficult points are involved and the full reports repay careful reading. It is also worth noting that the word *discovery* is something of a misnomer in this context: *synthesis and characterization* of new elements would perhaps be a better discription.

The separate question of names and symbols for the new elements has, unfortunately, taken even longer to resolve, but definitive recommendations were ratified by IUPAC in August 1997 and have been generally accepted. It is clearly both unsatisfactory and confusing to have more than one name in current use for a given element and to have the same name being applied to two different elements. For this reason the present treatment refers to the individual elements by means of their atomic numbers. However, to help readers with the nomenclature used in the references cited, a list of the various names that are in use or that have been suggested from time to time is summarised in Table 31.7.

Two general types of nuclear reaction have been used to produce transfermium elements. The first type, hot fusion reactions, uses accelerated light particles with Z in the range 5–10 (typically $_5B$, $_6C$, $_7N$, $_8O$ or $_{10}Ne$) to bombard targets with $Z = 92-98$ (typically $_{92}U$, $_{94}Pu$, $_{95}Am$, $_{96}Cm$ or $_{98}Cf$). This method can be used effectively up to about element 106 but, increasingly, the compound nucleus is formed with such high excitation energy that many particles, including charged ones, evaporate off before the desired product nucleus is reached. To solve this problem the group at Dubna suggested an ingenious alternative route, cold fusion, which exploits the fact that nuclei such as $_{82}Pb$ or $_{83}Bi$ have high binding energies due to closed nuclear shells. If these nuclei are bombarded with moderately heavy ions which are preferably also near closed nuclear shells (e.g. $_{24}Cr$, $_{26}Fe$ or $_{28}Ni$) at energies just above the Coulomb

Table 31.7   Names and symbols in current use (or proposed) for elements 104–112

Z	Systematic (1977)[a]	IUPAC (1997)	Other names suggested from time to time
104	Un-nil-quadium (Unq)	**Rutherfordium (Rf)**	Kurchatovium (Ku), Dubnium (Db)
105	Un-nil-pentium (Unp)	**Dubnium (Db)**	Nielsbohrium (Ns), Hahnium (Ha), Joliotium (Jl)
106	Un-nil-hexium (Unh)	**Seaborgium (Sg)**	Rutherfordium (Rf)
107	Un-nil-septium (Uns)	**Bohrium (Bh)**	Nielsbohrium (Ns)
108	Un-nil-octium (Uno)	**Hassium (Hs)**	Hahnium (Hn)
109	Un-nil-ennium (Une)	**Meitnerium (Mt)**	—
110	Un-un-nilium (Uun)	—	—
111	Un-un-unium (Uuu)	—	—
112	Un-un-bium (Uub)	—	—

[a]The hyphens in the systematic names have been inserted here to assist comprehension and pronunciation; they are not part of the names. The roots nil, un, bi, etc. were chosen to allow a unique set of three-letter symbols to be generated for any (atomic) number.

barrier, they produce compound product nuclei with much lower resultant excitation energies. As a result, the probability of (unwanted) fission is very much reduced and, under sufficiently fine-tuned conditions, neutron-only emission will dominate over all other light-particle emissions. This method has been outstandingly successful in producing elements with $Z > 106$.

31.4.2 Element 104

The first (inconclusive) work bearing on the synthesis of element 104 was published by the Dubna group in 1964. However, the crucial Dubna evidence (1969–70) for the production of element 104 by bombardment of $_{94}Pu$ with $_{10}Ne$ came after the development of a sophisticated method for rapid *in situ* chlorination of the product atoms followed by their gas-chromatographic separation on an atom-by-atom basis. This was a heroic enterprise which combined cyclotron nuclear physics and chemical separations. As we have seen, the actinide series of elements ends with $_{103}Lr$. The next element should be in Group 4 of the transition elements, i.e. a heavier congener of Ti, Zr and Hf.* As such it would be expected to have a chloride

*A happy consequence of nuclear systematics is that element 104 is in Group 4, element 105 is in Group 5, etc. This mnemonic holds to the end of the transition series at element 112 and presumably beyond; it can be compared with the similar relation between the group numbers of the post-transition main-group elements (13–18) and the group numbers of the preceding transition elements (3–8).

which is significantly more volatile than those of the actinide elements. After extensive preliminary work to develop and prove the method, the recoil products emitted from the target were chlorinated with a stream of gaseous $NbCl_5$ or $ZrCl_4$ within a fraction of a second from the instant of formation of the new atom, and then separated gas-chromatographically in a 4-metre-long quartz tube at either 250° or 300°C before being detected by spontaneous fission. When part of the tube was replaced by a KCl capillary the activity in the detection zone ceased, because of the formation of an involatile complex, presumably $K_2[104]Cl_6$. As no nucleus with $Z > 104$ can be formed by bombarding $_{94}Pu$ with $_{10}Ne$, and no spontaneously fissioning atom with $Z < 104$ forms a volatile chloride, the new activity must be due to element 104. During the later stages of this work, and essentially contemporaneously with it, the Berkeley group established the reactions $^{249}Cf(^{12}C,4n)^{257}104$, $^{249}Cf(^{13}C,3n)^{259}104$ and $^{248}Cm(^{16}O,6n)^{258}104$ by elegant work which included the obsevation of generic parent–daughter α-decays to the known isotopes $^{253}102$ and $^{255}102$. It was concluded that credit for the discovery of element 104 should be shared between the groups at Dubna and Berkeley. Detailed references to the original papers, and an assessment of the many scientific points involved are in ref. 5. The name rutherfordium now recommended and adopted by IUPAC for element 104 was first suggested by the Berkeley group in 1969.

Nine isotopes of element 104 are now known with certainty in the mass range 255–264 and a tenth, ^{254}Rf, is possible. They have half-lives in the range 7 ms–65 s and can only be produced slowly one atom at a time. This clearly restricts chemical studies, though ingenious techniques have been developed to overcome some of the problems.[47] It has been found that element 104 is indeed a Group 4 homologue and tends to resemble Zr and Hf rather than Th in its aqueous solution chemistry and extractability. The predominant oxidation state is +4 and complexes such as $RfCl_6^{2-}$ have been confirmed. Distribution coefficients obtained for its extraction into thenoyltrifluoroacetone (TTA) lead to an ionic radius of 102 pm for 8-coordinated Rf, between those of Th and Pu. Gas-phase studies of element 104 by isothermal chromatography indicate that its bromides are more volatile than those of Hf, and that the chlorides of both Hf and Rf are more volatile than the bromides.[48,49]

31.4.3 Element 105

Attempts at the synthesis of element 105 were first reported from Dubna in 1968 but it was a further two years before cyclotron physics, combined with a thermal-gradient variant of gas-phase chromatography, plus parent–daughter α-particle generic relations finally succeeded in convincingly establishing its formation. The main reactions studied were ^{243}Am(^{22}Ne,4n)^{261}105 and ^{243}Am(^{22}Ne,5n)^{260}105. During the later stages of this work the Berkeley group published a convincing synthesis via ^{249}Cf(^{15}N,4n)^{260}105 which was also secured, amongst much other evidence, by an α-particle generic relation with ^{256}103. The independent work from the two laboratories was essentially contemporaneous and

credit for the discovery of element 105 was shared.[5] The name now internationally accepted for element 105 is dubnium.

The pioneering gas thermochromatographic studies of I. Zvara and his group in the mid-1970s suggested that element 105 was a homologue of Nb and Ta. No further work on its chemistry was reported until 1988 when the first studies of aqueous solutions of element 105 were published.[50] Using the 35 s isotope formed by the reaction ^{249}Bk(^{18}O,5n)^{267}105, some 800 manual experiments (taking about 50 s each) were performed. It was found that, after fuming with concentrated nitric acid, atoms of element 105, dubnium, sorbed on glass surfaces just like the Group 5 elements Nb and Ta but unlike Zr and Hf in the preceding Group. Extraction studies also confirmed the affinity to Group 5, though dubnium appeared closer to Nb than to Ta, perhaps due to the influence of relativistic effects. Later work using computer-controlled procedures reduced the timescale to less than 40 s per experiment;[49] halide complexation and extraction behaviour showed element 105 to be most like Pa, a pseudo Group 5 element.

31.4.4 Element 106

Work at Berkeley-Livermore in 1974 first convincingly demonstrated the synthesis of this element via the reaction ^{249}Cf(^{18}O,4n)^{263}106. Contemporaneous work at Dubna applied their novel cold fusion method (p. 1280) to reactions such as $_{82}$Pb + $_{24}$Cr: although this methodolgy was crucial to the synthesis of all later elements (107–112) it did not at that time demonstrate the formation of element 106 with adequate conviction. Very recently, element 106 was resynthesized by a new group at Berkeley using exactly the same reaction as employed in 1974.[51] The isotope ^{263}106 decays with a half-life of 0.8 ± 0.2 s to ^{259}104 and then by a second

[47] D. C. HOFFMAN, *Proc. Robert A. Welch Foundation Conference XXXIV. Fifty Years with Transuranium Elements*, October 1990, pp. 255–76. D. C. HOFFMAN, *Chem. & Eng. News*, May 2, 24–34 (1994).

[48] B. KADKHODAYAN, A. TÜRLER, K. E. GREGORICH, M. J. NURMIA, D. M. LEE and D. C. HOFFMAN, *Nucl. Instr. and Methods in Phys. Res.* **A317**, 254–61 (1992).

[49] D. C. HOFFMAN, *Radiochim. Acta* **61**, 123–8 (1993).

[50] K. E. GREGORICH (and 11 others), *Radiochim. Acta* **43**, 223–31 (1988).

[51] K. E. GREGORICH, M. R. LANE, M. F. MOHAR, D. M. LEE, C. D. CACHER, E. R. SILWESTER and D. C. HOFFMAN, *Phys. Rev. Lett.* **72**, 1423–6 (1994).

α-particle emission to ^{255}No, both of which were positively identified. The recommended name for element 106 is seaborgium, Sg.

Six isotopes of element 106 are now known (see Table 31.8) of which the most recent has a half-life in the range 10–30 s, encouraging the hope that some chemistry of this fugitive species might someday be revealed.[†] This heaviest isotope was synthsised by the reaction ^{248}Cm(^{22}Ne,4n)^{266}106 and the present uncertainty in the half-life is due to the very few atoms which have so far been observed. Indeed, one of the fascinating aspects of work in this area is the development of philosophical and mathematical techniques to define and deal with the statistics of a small number of random events or even of a single event.[52]

31.4.5 Elements 107, 108 and 109

These three elements were all first synthesized by the cold fusion method at GSI, Darmstadt,[5] using a very sophisticated set of techniques. For element 107 (1981) an accelerated beam of ionized ^{54}Cr atoms was made to impinge on a thin ^{209}Bi foil; the reaction recoils were separated in flight from the incoming beam and from the unwanted products of transfer reactions by a velocity filter consisting of a combination of magnetic and electric fields. This facility is known by the acronym SHIP, i.e. separated heavy-ion reaction products. The product atoms were then implanted in position-sensitive solid-state detectors which recorded α-particle decay energies or spontaneous fission events in position- and time-correlation with each other and with the time of implantation. Time-of-flight was also used to estimate the masses of these particles. Five atoms of ^{262}107 were detected and characterized in this way in the discovery experiments. Later work showed that

the half-life was 102 ± 26 ms and also established a second isotope, ^{261}107, with $t_{1/2}$ 11.8 ms having an (unsymmetrical) uncertainty at the 68% level of (+5.3, −2.8). The recommended name for element 107 is bohrium, Bh.

Element 108 was unequivocally established in 1984 using the SHIP facilities in Darmstadt to detect three atoms formed by the reaction ^{208}Pb(^{58}Fe,n)^{265}108. The half-life for α-decay was 1.8 ms with an uncertainty of (+2.2, −0.7) ms, and both the daughter and grand-daughter nuclides ^{261}106 and ^{257}104 were detected and characterized. Other isotopes of element 108 were in all probability obtained in Dubna at about the same time using reactions such as ^{209}Bi(^{55}Mn,n)^{263}108, ^{207}Pb(^{58}Fe,n)^{264}108 and ^{208}Pb(^{58}Fe,2n)^{264}108.[5] The recommended name for element 108 is hassium, Hs, after the latin name for Hesse, the region of Germany in which the GSI Laboratories are located.

Element 109 was also discovered by the Darmstadt GSI group in 1982 in an astonishingly virtuoso experiment which convincingly detected and unambiguously identified just *one atom* of ^{266}109 from the reaction ^{209}Bi(^{58}Fe,n). A further two atoms were synthesized at GSI six years later in 1988. The isotope is an α-emitter with a "half-life" of 3.4 ms (+1.6, −1.3 ms).[5] The recommended name for element 109 is meitnerium, Mt. It is salutary to contemplate the towering intellectual insights and prodigious technical achievements required to accomplish such experiments which can precisely identify a single atom amongst some 10^{18} accompanying events.

31.4.6 Elements 110, 111 and 112

These three elements were first made during a 15-month period of intense activity from late 1994 to early 1996 at GSI, Darmstadt. They therefore post-date the deliberations of the IUPAC/IUPAP international working group,[5] but the publications convincingly meet the stringent criteria for discovery elaborated by that group and have been widely accepted by the scientific community. So far, no names have been officially proposed or recommended for elements 110–112.

[†] The chemistry of 4 atoms of Sg in solution and of 3 atoms in the gas phase indicate that the element resembles its lighter homologues in Group 6, Mo and W; see M. SCHÄDEL and 17 others, *Nature* **388**, 55–7 (1997).

52 K.-H. SCHMIDT, C.-C. SAHM, K. PIELENZ and H.-G. CLERC, *Z. Phys. A* **316**, 19–26 (1984).

Initially, one atom of $^{269}110$ was detected on 9 November 1994 by the SHIP facilities at Darmstadt following the reaction $^{208}Pb(^{62}Ni,n)^{269}110$ and observation of the subsequent chain of four α-decays:[53,54]

$$^{269}110 \xrightarrow{393\,\mu s} {}^{265}108 \xrightarrow{583\,\mu s} {}^{261}106 \xrightarrow{72\,ms}$$
$$^{257}104 \xrightarrow{779\,ms} {}^{253}No$$

A further three atoms of $^{269}110$ were observed during the next eight days leading to an average "half-life" of $170\,\mu s$ ($+160$, $-60\,\mu s$). [Note that the decay times listed for the above single-atom observations are not identical with the best values of the statistical half-lives for the species mentioned.] Subsequent work also identified a second isotope $^{271}110$ with $t_{1/2}$ 623 μs.

Element 111 was synthesized and characterized by the same group during the period 8–17 December 1994 using the analogous cold-fusion reaction, $^{209}Bi(^{64}Ni,n)^{272}111$, followed by observation of up to five successive α-emissions which could be assigned to the chain:[54,55]

$$^{272}111 \xrightarrow{2.04\,ms} {}^{268}109 \xrightarrow{72\,ms} {}^{264}107 \xrightarrow{1.45\,s}$$
$$^{260}105 \xrightarrow{0.57\,s} {}^{256}Lr \xrightarrow{66\,s} {}^{252}Md$$

Note also the production of new isotopes of elements 107 and 109 in this chain.

Element 112 emerged close to midnight on 9 February 1996 when the team at GSI unambiguously detected one atom of the new element after two weeks of bombarding a lead target with high-energy ionized atoms of zinc $^{208}Pb(^{70}Zn,n)^{277}112$.[56] The new element emitted an α-particle after $280\,\mu s$, followed by several others which formed a coherent decay scheme down to Fm:

$$^{277}112 \xrightarrow{280\,\mu s} {}^{273}110 \xrightarrow{110\,\mu s} {}^{269}108 \xrightarrow{19.7\,s}$$
$$^{265}106 \longrightarrow {}^{263}104 \longrightarrow {}^{259}No \longrightarrow {}^{255}Fm$$

This work is particularly significant for a number of reasons. Not only does $^{277}112$ have the highest atomic number and the highest mass of any nuclide so far, but it is also expected to complete the 6d transition series of elements. Will the next elements 113, 114, etc. prove to be members of the boron and carbon groups or will relativistic effects supervene to stabilize other electronic configurations? Perhaps even more significantly, the new atomic species is approaching the "island of stability" which has been predicted on the basis of the expected nuclear closed sheels of 114 protons and 184 or 178 neutrons, and it does indeed show clear signs of this increasing stability (decreasing instability). Moreover, the decay chain generates two new isotopes of elements 110 and 108 which themselves are the heaviest (and most stable) isotopes of these elements so far. Further increases in stability might well make chemical experimentation feasible. Clearly, exciting prospects lie ahead.

At present, some 36 isotopes of the transactinide elements have been characterized and these are summarized in Table 31.8.

[53] S. HOFMANN (and 11 others), *Z. Phys. A* **350**, 277–80 (1995).

[54] M. FREEMANTLE, *Chem. & Eng. News*, 13 March, 35–40 (1995).

[55] S. HOFMANN (and 11 others), *Z. Phys. A* **350**, 281–2 (1995).

[56] S. HOFMANN (and 11 others), *Z. Phys. A* **354**, 229–30 (1996).

Table 31.8 Isotopes of the transactinide elements (1997)

Z (Discovered)	No. of isotopes	Mass range	$t_{1/2}$ range
104 (1969)	9(?10)	253–262	7 ms–65 s
105 (1970)	7	255–263	1.3 s–34 s
106 (1974)	6	259–266	3.6 ms–30 s
107 (1981)	3	261–264	12 ms–0.44 s
108 (1984)	3	264, 265, 269	80 μs–19.7 s
109 (1982)	2	266, 268	3.4 ms–70 ms
110 (1994)	3	269, 271, 273	0.1 ms–0.2 ms
111 (1994)	1	272	1.5 ms
112 (1996)	1	277	0.28 ms