11 Coordination Chemistry of the Actinides

By the end of this chapter you should be able to:

- recognize +4 and +6 as the main oxidation states for uranium and +4 as the only important oxidation state for thorium;
- appreciate that coordination numbers of >6 are the norm;
- be familiar with the main features of the chemistry of the other actinides, and appreciate the transition in chemical behaviour across the series;
- appreciate the importance of nitrate complexes;
- recognize the characteristic structures of uranyl complexes;
- suggest structures for compounds;
- explain the separation of nuclear material and the recovery of U and Pu in terms of the chemistry involved;
- appreciate the problems presented in nuclear waste disposal and understand the solutions;
- suggest safe ways to handle actinide compounds.

11.1 Introduction

Studies of the coordination chemistry of the actinides have been limited by a number of factors – the care needed in handling radioactive materials and the possibility of damage to human tissue from the radiation; toxicity (especially Pu); the very small quantities available and very short half-lives of the later actinides; radiation and heating damage to solutions; and radiation damage (defects and dislocations) to crystals.

The vast majority of the studies reported have concerned the metals thorium and uranium, particularly the latter, due to accessibility of raw materials, ease of handling, and the long lifetimes of the relatively weakly α-emitting elements Th and U. In many cases, compounds of neptunium and plutonium with similar formulae to U and Th analogues have been made and found to be isomorphous and thus presumably isostructural. This chapter will therefore commence with, and concentrate largely on, the chemistry of complexes of these elements, followed by sections on the other actinides.

11.2 General Patterns in the Coordination Chemistry of the Actinides

As noted earlier (Table 9.2), the patterns of oxidation states of the early actinides resemble those of d-block metals, with the maximum oxidation state corresponding to the number of 'outer shell' electrons. Thus the chemistry of thorium is essentially confined to the +4

state (to an even greater degree than Zr or Hf) but uranium exhibits oxidation states of $+3$, $+4$, $+5$, and $+6$, with most compounds being in either the $+4$ or $+6$ state. The reason for this is that uranium(III) compounds tend to be easy to oxidize:

$$U^{4+}(aq) + e^- \rightarrow U^{3+}(aq) \qquad E = -0.63 \, V$$
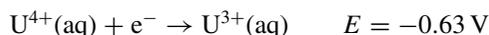
whilst under aqueous conditions the $UO_2{}^+$ ion readily disproportionates to a mixture of U^{4+} and $UO_2{}^{2+}$ [though there is a chemistry of uranium(V) in non-aqueous solvents].

As the actinide series is crossed, it becomes harder to involve the f electrons in compound formation, so that the later actinides increasingly show a chemistry in the $+3$ state, resembling the lanthanides, but with a more prominent $+2$ state.

11.3 Coordination Numbers in Actinide Complexes

As for the lanthanides, actinide complexes display high coordination numbers. A study of the aqua ions of early actinides makes an interesting comparison (Table 11.1 lists numbers of water molecules and bond lengths).

Table 11.1 Actinide aqua ions – numbers of bound water molecules and metal–water distances[a]

Ox state		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
6	$MO_2{}^{2+}$				5.0	5.0	6.0				
	$M–OH_2$ (Å)				2.40	2.42	2.40–2.45				
5	$MO_2{}^+$					5.0	4.0				
	$M–OH_2$ (Å)					2.50	2.47				
4	M^{4+}		10.0		9.0; 10.0	11.2	8 or 9				
	$M–OH_2$ (Å)		2.45		2.51; 2.42	2.40	2.39				
3	M^{3+}				9 or 10	9 or 10	10.2	10.3	10.2		8.5 ± 1.5
	$M–OH_2$ (Å)				2.61	2.52	2.51	2.48	2.45		2.4

[a] The uncertainty in the hydration number is generally in the region of 1.

The best characterized aqua ion is the hydrated uranyl ion $[UO_2(OH_2)_5]^{2+}$, which has been isolated in several salts studied by diffraction methods as well as X-ray absorption methods (EXAFS) in solution. However, similar ions are firmly believed to exist in the cases of $[MO_2(aq)]^{2+}$ (M = Np, Pu) and $[MO_2(aq)]^+$ (M = U, Np, Pu). In studying Table 11.1, two features stand out. Ions like $UO_2{}^{2+}$ are unprecedented in lanthanide chemistry, both in respect of the $+6$ oxidation state and also in the presence of strong and non-labile U=O bonds. Secondly, the coordination numbers of the hydrated $+3$ actinide ions appear to be higher than those of the Ln^{3+} ions (9 for early lanthanides, 8 for later ones), explicable on account of the slightly higher ionic radii of the actinide ions. One of the few other characterized aqua ions is the trigonal prismatic $[Pu(H_2O)_9]^{3+}$, strongly resembling the corresponding lanthanide series.

11.4 Types of Complex Formed

Table 11.2 gives some stability constants for complexes of Th^{4+} and $UO_2{}^{2+}$. Thorium forms stronger complexes with fluoride, the 'hardest' halide ion, than with chloride and bromide; this is the behaviour expected of a 'hard' Lewis acid. Thorium also forms quite

Table 11.2 Stability constants of Th^{4+} and UO_2^{2+} complexes

Stability constants for complexes of Th^{4+}					Stability constants for complexes of UO_2^{2++}		
Ligand	I (mol/dm³)	Log K_1	Log K_2	Log K_3	Log K_4	Ligand	I (mol/dm³)	Log K_1

Stability constants for complexes of Th^{4+}						Stability constants for complexes of UO_2^{2++}		
Ligand	I (mol/dm³)	Log K_1	Log K_2	Log K_3	Log K_4	Ligand	I (mol/dm³)	Log K_1
F^-	0.5	7.56	5.72	4.42		F^-	1	4.54
	1	7.46				Cl^-	1	−0.10
Cl^-	1	0.18				Br^-	1	−0.3
Br^-	1	−0.13				NO_3^-	1	−0.3
NO_3^-	1	0.67				$EDTA^{4-}$	0.1	7.4
SO_4^{2-}	2	3.3	2.42					
NCS^-	1	1.08						
$EDTA^{4-}$	0.1	25.3						
$acac^-$	0.1	8.0	7.5	6.0	5.3			

strong complexes with oxygen-donor ligands like nitrate. The hexadentate ligand $EDTA^{4-}$ forms very stable complexes, due largely to the favourable entropy change when six water molecules are replaced.

11.5 Uranium and Thorium Chemistry

11.5.1 Uranyl Complexes

The great majority of uranium(VI) compounds contain the UO_2 group and are known as uranyl compounds; exceptions are a few molecular compounds, such as the halides UOF_4, UF_6, and UCl_6, and some alkoxides such as $U(OMe)_6$. Uranyl compounds result eventually from exposure of compounds of uranium in other oxidation states to air. They characteristically have a yellow fluorescence under UV light; from the early 19th century, glass manufacturers added uranium oxide when making yellow and green glass (it is sometimes known as Vaseline glass).

Uranyl complexes can be thought of as derivatives of the UO_2^{2+} ion. There is a very wide range of them; they may be cationic, such as $[UO_2(OH_2)_5]^{2+}$ ions; neutral, e.g. $[UO_2(OPPh_3)_2Cl_2]$; or anionic, such as $[UO_2Cl_4]^{2-}$, yet all feature a *trans*-UO_2 grouping with the characteristic short U–O bonds (1.7–1.9 Å), quite comparable with those found in 'osmyl' compounds, which have the OsO_2 grouping. The presence of the uranyl group can readily be detected in the IR spectrum of a uranium compound through the presence of a strong band in the region 920–980 cm⁻¹ caused by the asymmetric O–U–O stretching vibration; a corresponding band around 860 cm⁻¹ caused by the symmetric O–U–O stretching vibration is seen in the Raman spectrum. Fine structure due to symmetric uranyl stretching vibrations can be seen on an absorption peak in the spectrum of uranyl complexes around 450 nm (Figure 12.1). There has been considerable speculation on the bonding in the uranyl ion. The essentially linear geometry of the UO_2 unit is an invariable feature of uranyl complexes; no other atoms can approach the uranium nearer than ~2.2 Å. Uranium d–p and f–p π bonding have both been invoked to explain the bonding (Figure 11.1).

An energy level diagram for the uranyl ion is shown in Figure 11.2. An electron count takes 6 electrons from uranium, four from each oxygen, deducting two for the positive charges; alternatively, if the uranyl ion is thought of as a combination of U^{6+} and two O^{2-}, taking six electrons from each oxide and none from U^{6+}, again giving 12. These completely occupy the six σ_u, σ_g, π_u, and π_g molecular orbitals ($\sigma_u^2 \sigma_g^2 \pi_u^4 \pi_g^4$). It has been suggested
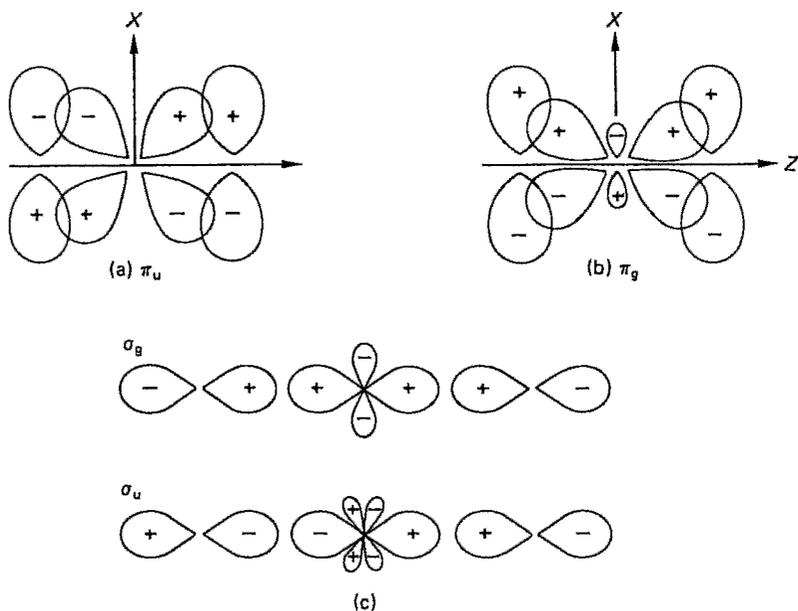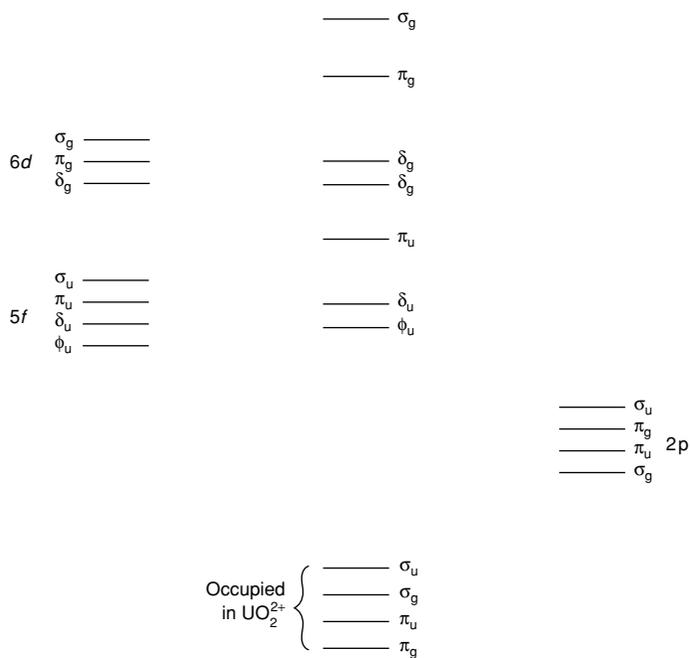
Figure 11.1
π-bonding in the uranyl, $[UO_2]^{2+}$ ion: (a) $d_{xz}-p_x$ overlap; (b) $f_{xz^2}-p_x$ overlap; (c) σ-bonding in the uranyl ion (reproduced with permission from Figure 3.24 of S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

The relative ordering of the bonding MOs is uncertain

Figure 11.2
M.O. scheme for the uranyl ion, UO_2^{2+} (reproduced with permission from Figure 3.25 of S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

that repulsion (antibonding overlap) between oxygen p orbitals and occupied uranium 6d and 5f orbitals may destabilize the bonding d molecular orbitals, causing them to be higher in energy than the π bonding orbitals, as shown. Addition of further electrons puts them in the essentially non-bonding δ_u and ϕ_u orbitals, accounting for the existence of the rather less stable MO_2^{2+} (M = Np, Pu, Am) ions.

The uranium(V) species UO_2^+ exists, but is less stable than UO_2^{2+}, possibly owing to weaker overlap; it readily decomposes by disproportionation:

$$2\ UO_2^+(aq) + 4\ H^+(aq) \rightarrow UO_2^{2+}(aq) + U^{4+}(aq) + 2\ H_2O(l)$$

In contrast to the *trans* geometry of UO_2^{2+}, isoelectronic ($6d^0\ 5f^0$) ThO_2 molecules in the gas phase or in low temperature matrices are bent ($\angle O–Th–O \sim 122°$); this is thought to be due to the thorium 5f orbitals being much higher in energy (in uranium, the 5f orbitals are well below 6d), reducing possibilities of 5f–p overlap, so that thorium resorts to using 6d orbitals in the p bonding, like transition metals, as in the case of MoO_2^{2+} ($5d^0$) and WO_2^{2+} ($6d^0$) ions which also adopt bent, *cis* geometries ($\angle O–M–O \sim 110°$).

11.5.2 Coordination Numbers and Geometries in Uranyl Complexes

An extensive range of uranyl complexes has been prepared and had their structures determined. Their structure can be summarized as a uranyl ion surrounded by a 'girdle' of 4, 5, or 6 donor atoms round its waist (a rare example of $2 + 3$ coordination is known for a complex of the uranyl ion with a calixarene ligand; another is the amide complex $[K(thf)_2]$ $[UO_2\{N(SiMe_3)_2\}_3]$). If the ligands are monodentate donors, there are usually 4 of them, unless they are small, like F or NCS, when five can be accommodated. When bidentate ligands with small steric demands like NO_3, CH_3COO, and CO_3 can be accommodated, six donor atoms can surround the uranyl group. In general if there are 4 or 5 donor atoms round the waist, they are reasonably coplanar, but puckering sometimes occurs when there are six. Table 11.3 shows examples of uranium complexes for 5-, 6-, 7-, and 8-coordination.

Table 11.3 Uranyl complexes

5-coordinate ($2 + 3$)	6-coordinate ($2 + 4$)	7-coordinate ($2 + 5$)	8-coordinate ($2 + 6$)
$[UO_2\{N(SiMe_3)_2\}_3]^-$	$Cs_2[UO_2Cl_4]$	UO_2Cl_2	UO_2F_2
	$(Me_4N)_2[UO_2Br_4]$	UO_2(superphthalocyanine)	UO_2CO_3
	$MgUO_4$	$[UO_2(NO_3)_2(Ph_3PO)]$	$[UO_2(NO_3)_2(H_2O)_2]$
	$BaUO_4$	$[UO_2(L)_5]^{2+}$	$CaUO_4$
		(L, e.g., H_2O, DMSO, urea)	$SrUO_4$
			$Rb[UO_2(NO_3)_3]$

The uranium(VI) aqua ion is now firmly established as the pentagonal bipyramidal $[UO_2(OH_2)_5]^{2+}$; it has been found in crystals of the salt $[UO_2(OH_2)_5]$ $(ClO_4)_2 \cdot 2H_2O$ (U=O 1.702 Å, U–OH_2 2.421 Å) and also found in solutions by X-ray diffraction studies. Similar $[UO_2(L)_5]^{2+}$ ions (L = urea, Me_2SO, $HCONMe_2$) also exist. Uranyl nitrate forms complexes with phosphine oxides of the type $[UO_2(NO_3)_2(R_3PO)_2]$; similar phosphate complexes $[UO_2(NO_3)_2\{(RO)_3PO\}_2]$ are important in the extraction of uranium in nuclear waste processing (Figure 11.3 and Section 11.5.5). A number of structures of these complexes are known; for example, when R=isobutyl, U=O 1.757 Å; U–O(P) 2.372 Å; U–O(N) 2.509 Å.
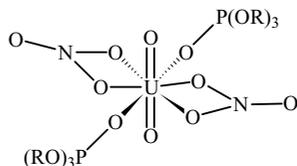
Figure 11.3
Structure of $UO_2(NO_3)_2[(RO)_3PO]_2$.

11.5.3   Some Other Complexes

Uranyl carbonate complexes have attracted considerable interest in recent years as they are intermediates in the processing of mixed oxide reactor fuels and in extraction of uranium from certain ores using carbonate leaching; more topically they can be formed when uranyl ores react with carbonate or bicarbonate ions underground, and can be present in relatively high amounts in groundwaters. The main complex formed in carbonate leaching of uranyl ores is 8 coordinate $[UO_2(CO_3)_3]^{3-}$, but around pH 6 a cyclic trimer $[(UO_2)_3(CO_3)_6]^{6-}$ has been identified.

UO_3 dissolves in acetic acid to form yellow uranyl acetate, $UO_2(CH_3COO)_2.2H_2O$. It formerly found use in analysis since, in the presence of M^{2+} (M = Mg or Zn), it precipitates sodium ions as NaM $[UO_2(CH_3COO)_3]_3.6H_2O$.
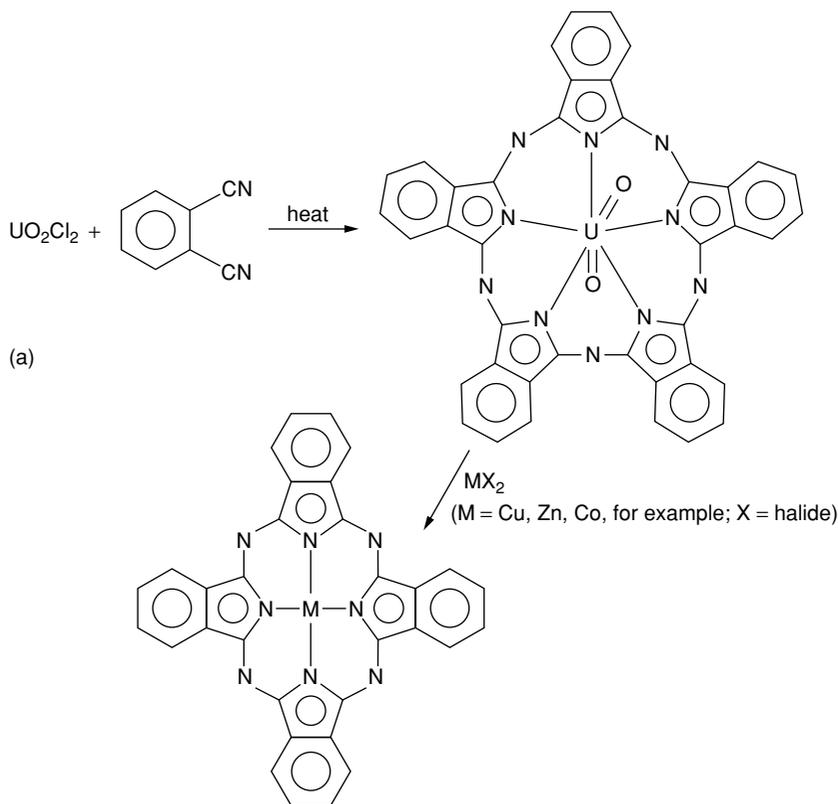

Figure 11.4
Structure and reaction of "uranyl superphthalocyanine".

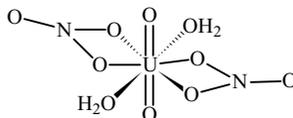**Figure 11.5**
Structure of $UO_2(NO_3)_2(H_2O)_2$.

Uranyl chloride, UO_2Cl_2, reacts on heating with *o*-phthalodinitrile to form a so-called 'superphthalocyanine' complex with $2 + 5$ coordination (Figure 11.4); other metals (lanthanides, Co, Ni, Cu) react with this, forming a conventional phthalocyanine, so that the uranyl ion has an important role in sustaining this unusual structure.

11.5.4   Uranyl Nitrate and its Complexes; their Role in Processing Nuclear Waste

Reaction of uranium oxide with nitric acid results in the formation of nitrates $UO_2(NO_3)_2.x$ H_2O ($x = 2$, 3, 6); the value of x depends upon the acid concentration. All contain $[UO_2(NO_3)_2(H_2O)_2]$ molecules; the nitrate groups are bidentate, so that uranium is 8 coordinate (Figure 11.5). Its most important property lies in its high solubility in a range of organic solvents in addition to water (Table 11.4), which is an important factor in the processing of nuclear waste.

Table 11.4   Solubility of uranyl nitrate in various solvents

Solvent	Solubility (g per g solvent)
Water	0.540
Diethyl ether	0.491
Acetone	0.617
Ethanol	0.675

By adding metal nitrates as 'salting out' agents, the solubility of uranyl nitrate in water can be decreased to favour its extraction from aqueous solution into the organic layer. Tributyl phosphate [TBP; $(C_4H_9O)_3P{=}O$] acts as a complexing agent (in the manner discussed in this chapter for a number of phosphine oxide ligands) and also as solvent, with no salting-out agent being needed. In practice, a solution of TBP in kerosene is used to give better separation, as pure TBP is too viscous and also has a rather similar density to that of water.
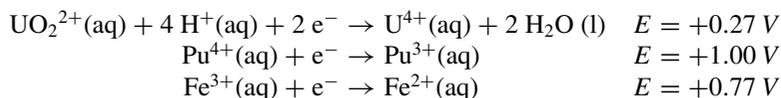
11.5.5   Nuclear Waste Processing

Nuclear fuel rods consist of uranium oxide pellets contained in zirconium alloy or steel tubes. As the fission process proceeds, uranium is used up and fission products accumulate. A lot of these fission products are good neutron absorbers and reduce the efficiency of the fission process (by absorbing neutrons before they reach uranium atoms) so that the rods are removed for reprocessing before all the ^{235}U content has undergone fission. Fission of a ^{235}U atom produces two lighter atoms of approximate relative atomic masses around 90–100 and 130–140, with the main fission products being the intensely radioactive and short lived ^{131}I ($t_{1/2} \sim 8$ d), ^{140}La, ^{141}Ce, ^{144}Pr, ^{95}Zr, ^{103}Ru, and ^{95}Nb, and longer-lived ^{137}Cs, ^{90}Sr, and ^{91}Y. These essentially useless and toxic products have to be separated from unchanged uranium and also from plutonium (the product of neutron absorption by ^{238}U), both of which can be used again as fuels.

1. The first stage of the process involves immersing the fuel rods in ponds of water for up to 3 months. This allows the majority of the short-lived and intensely radioactive fission products such as ^{131}I to decay.

2. The rods are then dissolved in rather concentrated (7M) nitric acid, producing a mixture of $UO_2(NO_3)_2$, $Pu(NO_3)_4$, and other metal nitrates.

3. The mixture is extracted with a counter-current of a solution of TBP in kerosene. Uranium and plutonium are extracted into kerosene as the complexes $[UO_2(NO_3)_2(\textbf{tbp})_2]$ and $[Pu(NO_3)_4(\textbf{tbp})_2]$, but the other nitrates, of metals such as the lanthanides and actinides beyond Pu, as well as fission products, do not form strong complexes with TBP and stay in the aqueous layer.

4. The mixture of uranium and plutonium is treated with a suitable reducing agent [iron(II) sulfamate, hydrazine, or hydroxylamine nitrate]; under these conditions, U^{VI} is not reduced and stays in the kerosene layer, but Pu^{IV} is reduced to Pu^{3+}, which is only weakly complexed by TBP and so migrates into the aqueous phase.

$$UO_2{}^{2+}(aq) + 4\,H^+(aq) + 2\,e^- \rightarrow U^{4+}(aq) + 2\,H_2O\,(l) \quad E = +0.27\,V$$
$$Pu^{4+}(aq) + e^- \rightarrow Pu^{3+}(aq) \qquad\qquad\qquad E = +1.00\,V$$
$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad\qquad\qquad E = +0.77\,V$$

The uranyl nitrate is extracted back into the aqueous phase and crystallized as the hydrate $UO_2(NO_3)_2.xH_2O$; thermal decomposition to UO_3 is followed by hydrogen reduction to re-form UO_2. The plutonium is reoxidized to Pu^{4+}, precipitated as the oxalate $Pu(C_2O_4)_2.6H_2O$, which undergoes thermal decomposition to PuO_2.

The fission products remain to be dealt with. The preferred solution at the moment is to evaporate their solution and pyrolyse the product to convert it into a mixture of oxides; on fusion with silica and borax an inert borosilicate glass is formed, which encapsulates the radioactive materials. At present the main problem seems to be choosing suitably stable geological areas where these materials will not be disturbed by earthquakes nor dissolved by underground water.

11.6 Complexes of the Actinide(IV) Nitrates and Halides

11.6.1 Thorium Nitrate Complexes

A number of thorium nitrate complexes have been synthesized and studied. Hydrated thorium nitrate, $Th(NO_3)_4.5H_2O$, contains $[Th(NO_3)_4.(H_2O)_3]$ molecules and was one of the first 11-coordinate compounds to be recognized (Figure 11.6).

Reaction of thorium nitrate with tertiary phosphine oxides in solvents like acetone or ethanol has afforded a number of complexes. In particular, when thorium nitrate reacts with Me_3PO, a wide range of complexes is obtained depending upon the stoichiometry and solvent used, compounds with formulae $Th(NO_3)_4.5Me_3PO$, $Th(NO_3)_4.4Me_3PO$, $Th(NO_3)_4.3.67Me_3PO$, $Th(NO_3)_4.3Me_3PO$, $Th(NO_3)_4.2.67Me_3PO$, and $Th(NO_3)_4.2.33Me_3PO$ having been obtained. Thorium nitrate complexes display a fascinating range of structure (Table 11.5).

11.6.2 Uranium(IV) Nitrate Complexes

Uranium(VI) nitrate complexes have been discussed in Section 11.5.4, but uranium forms complexes in the +4 state that are generally similar to those of thorium.

$$Cs_2U(NO_3)_6 + 2\,Ph_3PO \rightarrow U(NO_3)_4(OPPh_3)_2 + 2\,CsNO_3$$

Table 11.5 Thorium nitrate complexes

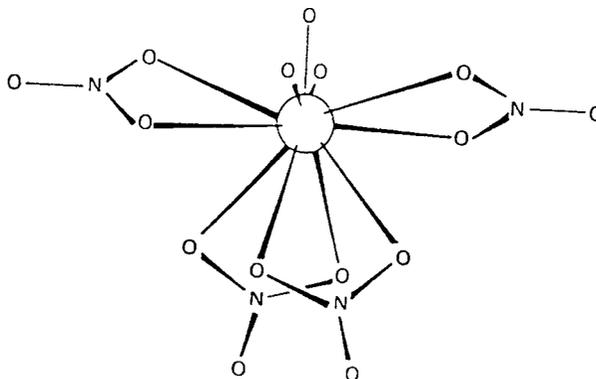| Formula	Thorium species present	Coord. No.
$MTh(NO_3)_6$ (M = Mg, Ca)	$[Th(NO_3)_6]^{2-}$	12
$Ph_4P^+ [Th(NO_3)_5(OPMe_3)_2]^-$	$[Th(NO_3)_5(OPMe_3)_2]^-$	12
$Th(NO_3)_4.5H_2O$	$[Th(NO_3)_4(H_2O)_3]$	11
$Th(NO_3)_4.2.67Me_3PO$	$\{[Th(NO_3)_3(Me_3PO)_4]^+\}_2 [Th(NO_3)_6]^{2-}$	10, 12
$Th(NO_3)_4.2Ph_3PO$	$[Th(NO_3)_4(OPPh_3)_2]$	10
$Th(NO_3)_4.5Me_3PO$	$[Th(NO_3)_2(OPMe_3)_5]^{2+}$	9

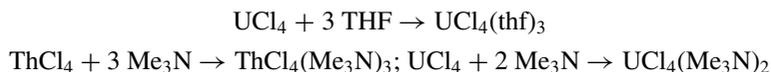
Figure 11.6
Structure of $Th(NO_3)_4(H_2O)_3$.

The reaction is carried out in a non-polar solvent like propanone; precipitated caesium nitrate is filtered off and green (the most characteristic colour of U^{IV} complexes) crystals of the nitrate complex are obtained on concentrating the solution. $U(NO_3)_4(OPPh_3)_2$ has a 10-coordinate structure (Figure 11.7) with phosphine oxide ligands *trans* to each other, and bidentate nitrates.

11.6.3 Complexes of the Actinide(IV) Halides

A large number of these have been synthesized, usually by reaction of the halides with the ligand in a non-polar solvent like MeCN or acetone, which will form a labile complex such as $[UCl_4(MeCN)_4]$ that will undergo ready substitution by a stronger donor:

$$ThCl_4 + 5 Me_2SO \rightarrow ThCl_4(Me_2SO)_5 \text{ (in MeCN)}$$
$$UCl_4 + 2 (Me_2N)_3PO \rightarrow UCl_4[(Me_2N)_3PO]_2 \text{ (in Me_2CO)}$$

Although sometimes direct reaction with a liquid ligand is possible:

$$UCl_4 + 3 THF \rightarrow UCl_4(thf)_3$$
$$ThCl_4 + 3 Me_3N \rightarrow ThCl_4(Me_3N)_3; UCl_4 + 2 Me_3N \rightarrow UCl_4(Me_3N)_2$$

Relatively few UI_4 complexes have been made. They can often be synthesized by reaction in a solvent like MeCN and, whilst relatively stable thermally, undergo ready oxidation to uranyl complexes in (moist) air. The structures of many of these compounds have been determined, such as UCl_4L_2 [L = Ph_3PO, $(Me_2N)_3PO$, Et_3AsO, $(Me_2N)_2PhPO$] and UBr_4L_2 [L = Ph_3PO, $(Me_2N)_3PO$] and $UX_4[(Me_2N)_2CO]_2$(X = Cl, Br, I). Both the 2:1 stoichiometry and *trans*-UX_4L_2 geometry are very common, but there are
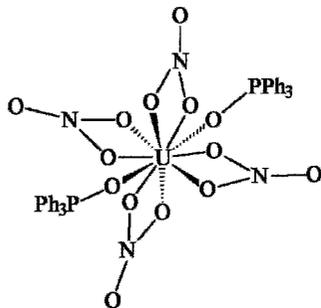
Figure 11.7
Structure of $U(NO_3)_4(Ph_3PO)_2$.

exceptions. $UCl_4(Me_2SO)_3$ is $[UCl_2(Me_2SO)_6]$ UCl_6 and $UCl_4(Me_3PO)_6$ is $[UCl(Me_3PO)_6]$ Cl_3; although no X-ray study has been carried out, $UI_4(Ph_3AsO)_2$ is almost certainly $[UI_2(Ph_3AsO)_4]$ UI_6.

Most structural reports concern uranium complexes. Many cases are known where complexes MX_4L_n (n usually 2) exist for some or all the series Th–Pu; they are generally believed to have the same structure. $UCl_4(Ph_3PO)_2$ is an exceptional compound in having a *cis* geometry, confirmed by X-ray diffraction studies on crystals obtained on recrystallization from nitromethane (Figure 11.8). The phenyl rings in neighbouring Ph_3PO molecules face each other with a ring–ring separation of $\sim$3.52 Å, an early recognized example of π–π stacking in a coordination compound. Similar compounds can be obtained for Th, Pa, Np, and Pu.

It was subsequently noted that crystals obtained immediately from the reaction mixture had an IR spectrum different to that of authentic *cis*-$UCl_4(Ph_3PO)_2$ but strongly resembling those of samples of *trans*-$UBr_4(Ph_3PO)_2$. It seems likely that a less soluble *trans*-$UCl_4(Ph_3PO)_2$ crystallizes first but on recrystallization or contact with the mother liquor it isomerizes to the thermodynamically more stable *cis*-$UCl_4(Ph_3PO)_2$.
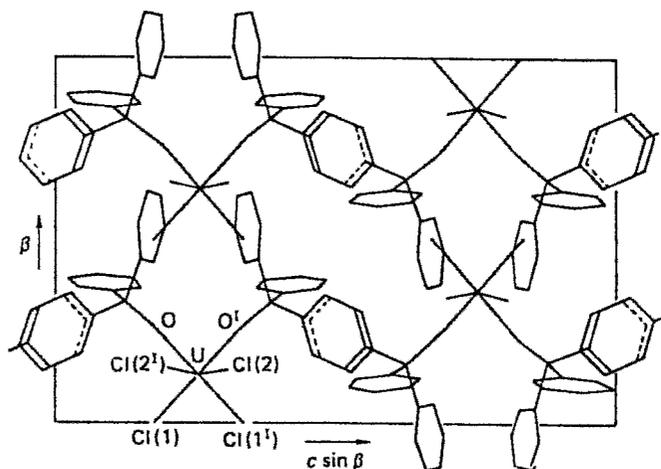

Figure 11.8
Reproduced with permission from JCS Dalton, (1975) 1875. G. Bombieri et al. Copyright (1975) RSC.

Table 11.6 Bond lengths in UX_4L_2 complexes

	$UCl_4(tmu)_2$	$UBr_4(tmu)_2$	$UI_4(tmu)_2$	$UCl_4(hmpa)_2$	$UBr_4(hmpa)_2$
Average U–O (Å)	2.209	2.197	2.185	2.23	2.18
Average U–X (Å)	2.62	2.78	3.01	2.615	2.781

*Abbreviations*: tmu = $(Me_2N)_2C=O$; hmpa = $(Me_2N)_3P=O$.

The only complete family of UX_4 complexes (X = Cl, Br, I) that has been examined crystallograpically is that with tetramethylurea, $UX_4[(Me_2N)_2CO]_2$. Table 11.6 lists structural data for these compounds and also for $UX_4[(Me_2N)_3PO]_2$(X = Cl, Br) {though the compound $UI_4[(Me_2N)_3PO]_2$ has been made, its structure is not known}. Table 11.7 shows the formulae of $ThCl_4$ and UCl_4 complexes with the same ligands. The ionic radius of U^{4+} = 1.00 Å and that of Th^{4+} = 1.05 Å (values given for eight coordination, the pattern is similar for six coordination). Since the ions are of similar size, complexes usually have similar stoichiometry (and indeed geometry). In a few cases (Me_3N, Ph_3PO, THF) the slightly greater size of thorium allows one more ligand to be attached to the metal ion.

Table 11.7 A comparison of thorium(IV) and uranium(IV) complexes isolated with the same ligand

Ligand	Thorium	Uranium
MeCN	$ThCl_4(MeCN)_4$	$UCl_4(MeCN)_4$
Ph_3PO	$ThCl_4(Ph_3PO)_3$; $ThCl_4(Ph_3PO)_2$	$UCl_4(Ph_3PO)_2$
$(Me_2N)_3PO$	$ThCl_4[(Me_2N)_3PO]_3$; $ThCl_4[(Me_2N)_3PO]_2$	$UCl_4[(Me_2N)_3PO]_2$
$(Me_2N)_2CO$	$ThCl_4[(Me_2N)_2CO]_3$	$UCl_4[(Me_2N)_2CO]_2$
Ph_2SO	$ThCl_4(Ph_2SO)_4$	$UCl_4(Ph_2SO)_4$; $UCl_4(Ph_2SO)_3$
thf	$ThCl_4(thf)_3(H_2O)$	$UCl_4(thf)_3$
Me_3N	$ThCl_4(Me_3N)_3$	$UCl_4(Me_3N)_2$
$Me_2N(CH_2)_2NMe_2$	$ThCl_4[Me_2N(CH_2)_2NMe_2]_2$	$UCl_4[Me_2N(CH_2)_2NMe_2]_2$
$Me_2P(CH_2)_2PMe_2$	$ThCl_4[Me_2P(CH_2)_2PMe_2]_2$	$UCl_4[Me_2P(CH_2)_2PMe_2]_2$

11.7 Thiocyanates

As the anhydrous actinide thiocyanates are not known {only hydrated $[M(NCS)_4(H_2O)_4]$}, thiocyanate complexes are prepared metathetically.

$$ThCl_4(Ph_3PO)_2 + 4\ KNCS + 2\ Ph_3PO \rightarrow Th(NCS)_4(Ph_3PO)_4 + 4\ KCl\ (in\ Me_2CO)$$
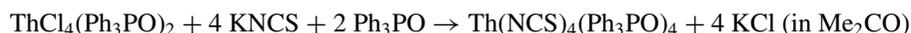
The precipitate of insoluble KCl is filtered off and the solution concentrated to obtain the actinide complex. Several structures have been reported; $Th(NCS)_4(L)_4$ [L = Ph_3PO, $(Me_2N)_3PO$]; $U(NCS)_4(L)_4$[L = Ph_3PO, $(Me_2N)_3PO$, Me_3PO] are all square antiprismatic; $Th(NCS)_4[(Me_2N)_2CO]_4$ is dodecahedral.
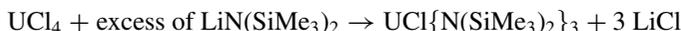
Some complexes are known where thiocyanate is the only ligand bound to uranium. The geometry of $(Et_4N)_4$ $[U(NCS)_8]$ is cubic, whilst Cs_4 $[U(NCS)_8]$ is square antiprismatic. Compared with the d-block transition metals, there is not much evidence for directional character in bonding in lanthanide and actinide compounds. Because of this, the size and geometry of the cation affects the packing arrangements in the lattice and energetically this factor must be more important than any crystal-field effects favouring a particular shape of the anion.

11.8 Amides, Alkoxides and Thiolates

Compounds $U(NR_2)_x$ and $U(OR)_x$ have been synthesized in oxidation states $+3$ to $+6$ (though the hexavalent amides are not well characterized). A limited number of thiolates $U(SR)_4$ are also known. These largely molecular species occupy a borderline between classical coordination chemistry and organometallic chemistry.

11.8.1 Amide Chemistry

Although they have been much less studied than the range of alkoxides in the $+4$, $+5$, and $+6$ oxidation states, a number of amides of uranium(IV) have been made by 'salt-elimination' reactions in solvents such as diethyl ether or THF, examples being:

$$UCl_4 + 4\,LiNEt_2 \rightarrow U(NEt_2)_4 + 4\,LiCl$$

$$UCl_4 + 4\,LiNPh_2 \rightarrow U(NPh_2)_4 + 4\,LiCl$$

$$UCl_4 + \text{excess of } LiN(SiMe_3)_2 \rightarrow UCl\{N(SiMe_3)_2\}_3 + 3\,LiCl$$
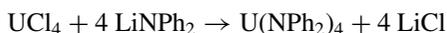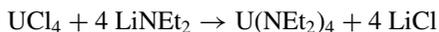
The steric demands of the ligands can be quantified in terms of the steric coordination number, CN_S [see J. Marçalo and A. Pires de Matos, *Polyhedron*, 1989, **8**, 2431; $CN_S = $ the ratio of the solid angle comprising the Van der Waals' spheres of the atoms of the ligand and that of the chloride ligand, when placed at a typical distance from the metal, values for these amide groups are: NEt_2^- 1.67; NPh_2^- 1.79; $N(SiMe_3)_2^-$ 2.17].

$U(NPh_2)_4$ is a monomer with a tetrahedral geometry, whilst in the solid state $U(NEt_2)_4$ is actually a dimer, $[U_2(NEt_2)_{10}]$, which contains five-coordinate uranium, with two bridging amides (Figure 11.9). As $N(SiMe_3)_2$ is a much bulkier ligand with larger solid cone angle, it seems likely that there is not room for a fourth amide group round uranium, hence the non-isolation of $U\{N(SiMe_3)_2\}_4$, with $MCl\{N(SiMe_3)_2\}_3$ (M = Th, U) being the most substituted species obtained; the halogen can be replaced by other groups such as methyl or tetrahydroborate. The compound $U(NMe_2)_4$ is harder to prepare. In the solid state it has a chain trimeric structure; each uranium is 6 coordinate, NMe_2 being less bulky than the other amides and has a smaller steric coordination number than even NEt_2.

So far, the amides described have all been in the $+4$ state, but one rare three coordinate U^{III} compound is $U\{N(SiMe_3)_2\}_3$(pyramidal, like the lanthanide analogues). Unusual amides
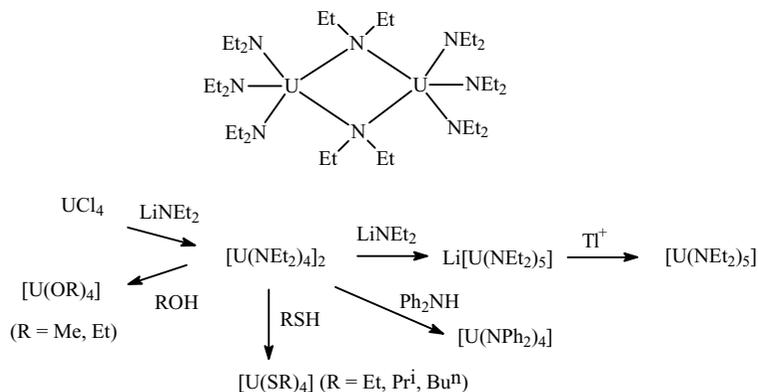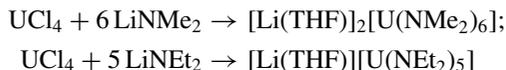

Figure 11.9
Synthesis, structure and reaction of $U(NEt_2)_4$.

have also been prepared with uranium in the +5 and +6 oxidation states. The first step in the syntheses involved preparing anionic complexes with saturated coordination spheres:

$$UCl_4 + 6\,LiNMe_2 \rightarrow [Li(THF)]_2[U(NMe_2)_6];$$
$$UCl_4 + 5\,LiNEt_2 \rightarrow [Li(THF)][U(NEt_2)_5]$$

The anions can then be oxidized to neutral molecular species using TlBPh$_4$ or, better, AgI:

$$[U(NMe_2)_6]^{2-} \rightarrow [U(NMe_2)_6]^- \rightarrow [U(NMe_2)_6];\ [U(NEt_2)_5]^- \rightarrow [U(NEt_2)_5]$$

[U(NEt$_2$)$_5$] (which can be obtained as dark red crystals) is a monomer in benzene solution whilst [U(NMe$_2$)$_6$] is only known in solution. [U(NMe$_2$)$_6$] would be expected to be octahedral and [U(NEt$_2$)$_5$] trigonal bipyramidal, but no structures are known. The most versatile of all these compounds is U(NEt$_2$)$_4$. This is a low-melting (36 °C) and thermally stable substance (but like all alkoxides and alkylamides, immediately attacked by air or water). It can be distilled at ∼40 °C at 10^{-4} mmHg pressure and on account of this volatility was investigated for some time as a possible material for isotopic separation of uranium by gaseous diffusion. U(NEt$_2$)$_4$ is a useful starting material for the synthesis of other amides, alkoxides, and thiolates (Figure 11.9)

Its utility stems from the fact that alcohols and thiols are better proton donors (more acidic) than amines, thus:

$$U(NEt_2)_4 + 4\ EtOH \rightarrow U(OEt)_4 + 4\ Et_2NH$$
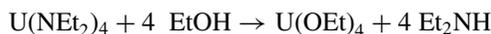
11.8.2 Alkoxides and Aryloxides

U(OR)$_n$ compounds (R = alkyl or aryl) exist in oxidation states between +3 and +6; in addition, there are some uranyl alkoxides. An unusual feature is the number of thermally stable compounds in the otherwise unstable and rare +5 state.

A few uranyl alkoxides have been made, such as golden yellow [UO$_2$(OCHPh$_2$)$_2$(thf)$_2$], but more important are the large number of octahedral U(OR)$_6$ compounds that can be made, examples being U(OMe)$_6$, U(OPr^i)$_6$, U(OBu^t)$_6$, U(OCF$_2$CF$_3$)$_6$, and U(OCH$_2$Bu^t)$_6$ (U–O 2.001–2.002 Å).

$$UF_6 + 6\ NaOMe \rightarrow U(OMe)_6 + 6\ NaF$$
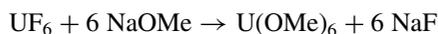
These compounds are volatile *in vacuo*, U(OCF$_2$CF$_3$)$_6$ remarkably boiling at 25 °C at 10 mmHg pressure. U(OMe)$_6$, which sublimes at 30 °C at 10^{-5} mmHg pressure, was investigated as a candidate for IR laser photochemistry leading to uranium isotopic enrichment.

Unlike the monomeric U(OR)$_6$, U(OR)$_5$ are usually associated; U(OPr^i)$_5$ is dimeric with two alkoxide bridges giving six coordination. U(OEt)$_5$ is the easiest compound to synthesize and can be converted into others by alcohol exchange (Figure 11.10).

Uranium(IV) compounds tend to be non-volatile, highly associated solids, though the aryloxide U[O(2,6-Bu$^t_2$C$_6$H$_3$)]$_4$ is made of monomeric tetrahedral molecules, doubtless owing to its very bulky ligand. A number of U^{III} aryloxide species have been synthesized, examples including U[O(2,6-Bu$^t_2$C$_6$H$_3$)]$_3$ being shown in Figure 11.11.

Since four of the same aryloxide ligands can bind to uranium in the uranium(IV) compound, a three coordinate U[O(2,6-Bu$^t_2$C$_6$H$_3$)]$_3$ is presumably coordinatively unsaturated, and so forms a uranium-ring bond; coordinative saturation can also be achieved by forming an adduct with a Lewis base.
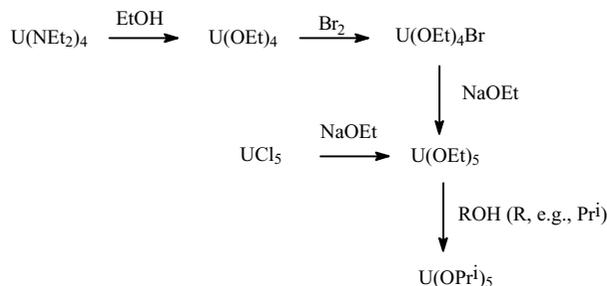
$$U(NEt_2)_4 \xrightarrow{EtOH} U(OEt)_4 \xrightarrow{Br_2} U(OEt)_4Br$$

$$\downarrow NaOEt$$

$$UCl_5 \xrightarrow{NaOEt} U(OEt)_5$$

$$\downarrow ROH\ (R,\ e.g.,\ Pr^i)$$

$$U(OPr^i)_5$$

Figure 11.10
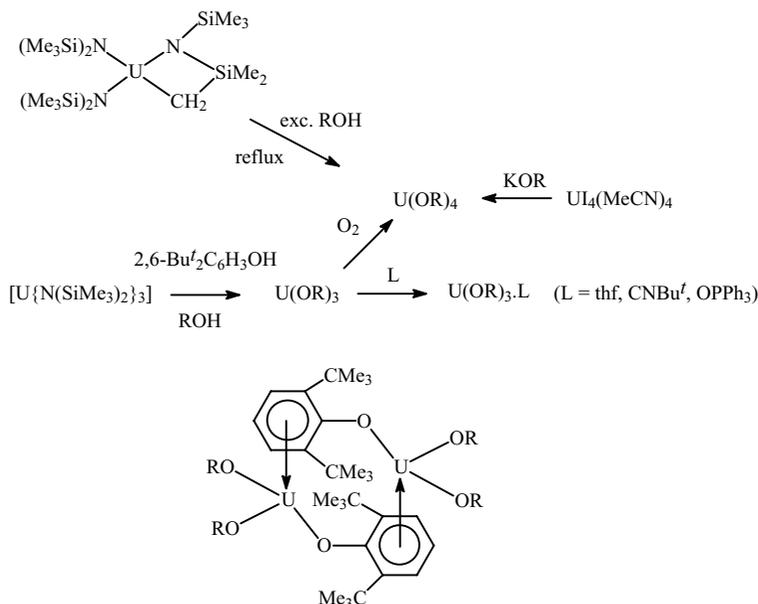Synthesis of uranium alkoxides.

Figure 11.11
Synthesis of uranium aryloxides.

11.9   Chemistry of Actinium

Little is known about the chemistry of actinium. It strongly resembles the lanthanides, especially lanthanum, with identical reduction potentials ($Ac^{3+} + 3e^- \rightarrow Ac$; $E = -2.62$ V) and similar ionic radii ($La^{3+} = 106$ pm, $Ac^{3+} = 111$ pm). Its chemistry is dominated by the (+3) oxidation state; as expected for a f^0 ion, its compounds are colourless, with no absorption in the UV–visible region between 400 and 1000 nm. ^{227}Ac is strongly radioactive ($t_{1/2} = 21.77$ y) and so are its decay products. Most of the work carried out has been on the microgram scale, examining binary compounds such as the oxides and halides, and little is known about its complexes. Actinium metal itself is a silvery solid, obtained by reduction of the oxide, fluoride, or chloride with Group I metals; it is oxidized rapidly in moist air. Like lanthanum, it forms an insoluble fluoride (coprecipitating quantitatively with lanthanum on the tracer scale) and oxalate $Ac_2(C_2O_4)_3.10H_2O$.

Since the chemistry of actinium is confined to the Ac^{3+} ion, it can readily be separated from thorium (and the lanthanides, for that matter) by processes like solvent extraction with thenoyltrifluoroacetone (TTFA) and by cation-exchange chromatography. The latter is an excellent means of purification, as the Ac^{3+} ion is much more strongly bound by the resin than its decay products.

11.10   Chemistry of Protactinium

Although its chemistry is not greatly studied at present, quite a lot of protactinium chemistry has been reported. The main isotope is the alpha-emitter ^{231}Pa, which has a long half-life ($t_{1/2} = 3.28 \times 10^4$ y) so few problems arise, once appropriate precautions are taken with the α-emission, the only other point of note being the ready hydrolysis of Pa^V in solution. Protactinium metal itself, formed by reduction (Ba) of PaF_4, or thermal decomposition of PaI_5 on a tungsten filament, is a high-melting (1565 °C), dense (15.37 g cm^{-3}), ductile silvery solid, which readily reacts on heating with many non-metals.
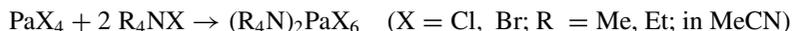
The aqueous chemistry is dominated by the readily hydrolysed Pa^{5+} ion, which in the absence of complexing ligands (e.g., fluoride) tends to precipitate as hydrated $Pa_2O_5.nH_2O$. A PaO_2^+ ion would be isoelectronic with the uranyl ion, UO_2^{2+}, but there is no evidence for it. However, solutions of Pa^V in fuming HNO_3 yield crystals of $PaO(NO_3)_3.x\ H_2O$ (x =1–4), which may have Pa=O bonds; the sulfate $PaO(HSO_4)_3$ also exists. Reduction of Pa^V with zinc or Cr^{2+} gives Pa^{4+}(aq), only stable in strongly acidic solution, as, at higher pH, ions like $Pa(OH)_2^{2+}$, PaO^{2+}, and $Pa(OH)_3^+$ are believed to exist.

Many of the complexes of Pa that have been studied are halide complexes, falling into two types; anionic species with all-halide coordination, and neutral Lewis base adducts, usually of the chloride $PaCl_4$.

Historically, the fluoride complexes are most important. Aristid Von Grosse (1934) used K_2PaF_7 in his determination of the atomic mass of Pa in 1931. Colourless crystals of this and other complexes $MPaF_6$, M_2PaF_7, and M_3PaF_8 (M = K, Rb, Cs) can be obtained by changing the stoichiometry, e.g.:

$$2\ KF + PaF_5 \rightarrow K_2PaF_7 \quad \text{(in 17M HF, precipitate with propanone)}$$

This complex has tricapped trigonal prismatic nine coordination of Pa, whilst $MPaF_6$ has dodecahedral 8 coordination and Na_3PaF_8 the very rare cubic 8 coordination. Other halide complexes can be made by appropriate methods:

$$PaX_4 + 2\ R_4NX \rightarrow (R_4N)_2PaX_6 \quad \text{(X = Cl, Br; R = Me, Et; in MeCN)}$$
$$PaCl_4 + 2\ CsCl \rightarrow Cs_2PaCl_6 \quad \text{(in } SOCl_2/ICl)$$
$$PaI_4 + 2\ MePh_3AsI \rightarrow (MePh_3As)_2PaI_6 \quad \text{(in MeCN)}$$

Six-coordinate $[PaX_6]^{2-}$ ions have been confirmed by X-ray diffraction for $(Me_4N)_2PaX_6$ (X = Cl, Br) and Cs_2PaCl_6.

Many adducts of the tetrahalides of ligands like phosphine oxides have been synthesized by direct interaction of the tetrahalides with the ligands in solution in solvents like acetonitrile or propanone. These have similar stoichiometries and structures to analogous complexes of Th, U, Np, and Pu, examples being *trans*-$PaX_4[(Me_2N)_3PO]_2$ (X = Cl, Br); *cis*-$PaCl_4(Ph_3PO)_2$; $PaCl_4(MeCN)_4$; $PaCl_4(Me_2SO)_5$ {possibly $[PaCl_3(Me_2SO)_5]^+\ Cl^-$}

and $PaCl_4(Me_2SO)_3$ {possibly $[PaCl_2(Me_2SO)_6]^{2+}$ $[PaCl_6]^{2-}$}. In addition, a few adducts of the pentahalides, $PaX_5(Ph_3PO)_n (n = 1,2)$ exist.
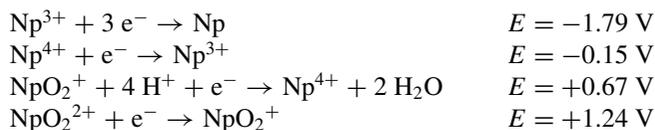
In addition to these, a number of other complexes have been isolated, such as the β-diketonates $[Pa(PhCOCHCOPh)_4]$ and antiprismatic $[Pa(MeCOCHCOMe)_4]$, which, like the TTFA complex $[Pa(C_4H_3SCOCHCOCF_3)_4]$, are soluble in solvents like benzene, and suitable for purification by solvent extraction. Pa forms a volatile borohydride $[Pa(BH_4)_4]$. These compounds are typical of those formed by other early actinides, such as Th and U.

11.11   Chemistry of Neptunium

The metal itself is a dense (19.5 g cm^{-3}) silvery solid, which readily undergoes oxidation in air. Chemical study uses one isotope, the long-lived ^{237}Np ($t_{1/2} = 2.14 \times 10^6$ y). The chemistry of neptunium shows interesting points of comparison between U and Pu, which flank it (and like them it shows a wide range of oxidation states). Thus, whilst the (+6) oxidation state is found in the $[NpO_2]^{2+}$ ion as well as in the halide NpF_6 (note that there is no $NpCl_6$, unlike U), the (+6) state is less stable than in the case of uranium, though it is more stable than Pu^{VI}. However, the (+5) state is more stable for neptunium than for uranium, with the $[NpO_2]^+$ ion showing no signs of disproportionation, though easily undergoing reduction by Fe^{2+} to Np^{4+}.

Np^{4+} is in many ways the most important oxidation state. It is formed by reduction of the higher oxidation states, and by aerial oxidation of Np^{3+}. Strong oxidizing agents like Ce^{4+} oxidize it back to $[NpO_2]^{2+}$, whilst electrolytic reduction of Np^{4+} affords Np^{3+}, which is stable in the absence of air (unlike U).

As neptunium has one more outer-shell electron than uranium, it has the possibility of a (+7) oxidation state, a possibility realized in alkaline solution, when ozone will oxidize Np^{VI} to Np^{VII}, an oxidation also achieved by XeO_3 or IO_4^- at higher temperatures. The potential for this is estimated as -1.24V (1M alkali). The relevant standard potentials for neptunium (1M acid) are:

$$Np^{3+} + 3\,e^- \rightarrow Np \qquad\qquad\qquad E = -1.79\ V$$
$$Np^{4+} + e^- \rightarrow Np^{3+} \qquad\qquad\qquad E = -0.15\ V$$
$$NpO_2^+ + 4\,H^+ + e^- \rightarrow Np^{4+} + 2\,H_2O \qquad E = +0.67\ V$$
$$NpO_2^{2+} + e^- \rightarrow NpO_2^+ \qquad\qquad\qquad E = +1.24\ V$$

11.11.1   Complexes of Neptunium

A significant amount of structural information has been gathered on neptunium complexes. For the main, they resemble corresponding U and Pu complexes. However, an EXAFS study of alkaline solutions of Np^{VII} found evidence for a *trans* dioxo ion of the type $[NpO_2(OH)_4(OH_2)]^{1-}$.

In the VI state, the 8 coordinate $Na[NpO_2(OAc)_3]$, $[NpO_2(NO_3)_2(H_2O)_2].4H_2O$, $K_4[NpO_2(CO_3)_3]$, and $Na_4[NpO_2(O_2)_3].9H_2O$ [where $(O_2)_3$ indicates three peroxide dianion ligands] are isostructural with the U, Pu, and Am analogues. They demonstrate a contraction of $\sim$0.01 Å in the M=O distance per unit increase in atomic number. Eight coordination is also found in $[NpO_2(NO_3)_2(bipy)]$. The aqua ion appears to be seven

coordinate $[NpO_2(H_2O)_5]^{2+}$. Like the uranyl ion, the neptunyl ion complexes with expanded porphyrins like hexaphyrin, amethyrin, pentaphyrin, and alaskaphyrin.

In the Np^V state, structural comparison of $Ba[Np^VO_2(OAc)_3]$ with $Na[Np^{VI}O_2(OAc)_3]$ indicates a lengthening of 0.14 Å in the neptunium–oxygen bond length on going from Np^{VI} to Np^V, consistent with an electron added to an antibonding orbital. As with the V state, the aqua ion is believed to be seven coordinate $[NpO_2(H_2O)_5]^+$; in the related $[NpO_2(urea)_5](NO_3)$ the neptunium atom has a typical pentagonal-bipyramidal environment with five oxygen atoms in the equatorial plane. A similar geometry is found in the acetamide complex of neptunium V nitrate, $[(NpO_2)(NO_3)(CH_3CONH_2)_2]$, where the pentagonal bipyramidal coordination of Np is completed (in the solid state) using oxygens of neighbouring NpO_2 groups; similarly in $NpO_2ClO_4.4H_2O$, the neptunyl(V) ion has four waters and a distant neptunyl oxygen occupying the equatorial positions. Eight and six coordination are, respectively, found in the crown ether complex, $[NpO_2(18\text{-crown-}6)]ClO_4$, and in $[NpO_2(OPPh_3)_4]ClO_4$. Carbonate complexes have been investigated as they could represent a means of leaching transactinides from underground deposits. EXAFS studies of Np^V carbonate complexes indicate the existence of $[NpO_2(H_2O)_3(CO_3)]^-$, $[NpO_2(H_2O)_2(CO_3)_2]^{3-}$ and $[NpO_2(CO_3)_3]^{5-}$; similar Np^{VI} species like $[NpO_2(CO_3)_3]^{4-}$ are indicated.

Among neptunium(VI) complexes, $[Np(S_2CNEt_2)_4]$ and $[Np(acac)_4]$ have dodecahedral and antiprismatic coordination of neptunium. A reminder of the small differences in energy between different geometries is that $[Me_4N]_4[Np(NCS)_8]$ has tetragonal antiprismatic coordination, whilst $[Et_4N]_4[Np(NCS)_8]$ has cubic coordination of Np. Neptunium(IV) is also eight coordinate in $[Np(urea)_8]SiW_{12}O_{40}\cdot2Urea\cdot H_2O$.

As with Th, Pa, U, and Pu, a variety of neutral complexes are formed between the tetrahalides (and nitrate) and ligands like phosphine oxides, such as *trans*-$[NpX_4\{(Me_2N)_3PO\}_2]$ (X = Cl, Br); *cis*-$[NpCl_4(Ph_3PO)_2]$; $NpCl_4(Me_2SO)_3$ (possibly $[NpCl_2(Me_2SO)_6]^{2+}$ $[NpCl_6]^{2-}$); $[Np(NCS)_4(R_3PO)_2]$ (R = Ph, Me, Me_2N), and $[Np(NO_3)_4(Me_2SO)_3]$.

Only a few complexes of Np^{III} have been characterized, notably the dithiocarbamate Et_4N $[Np(S_2CNEt_2)_4]$, which has distorted dodecahedral coordination like the Pu and lanthanide analogues. $[NpI_3(thf)_4]$ and the silylamide $[Np\{N(SiMe_3)_2\}_3]$ are analogous to those of U and the lanthanides, the former potentially being a useful starting material. The amide reacts with a bulky phenol:

$$[Np\{N(SiMe_3)_2\}_3] + 3\ ArOH \rightarrow [Np(OAr)_3] + 3\ HN(SiMe_3)_2$$
$$(Ar = 2,6\text{-}Bu_2^tC_6H_3)$$
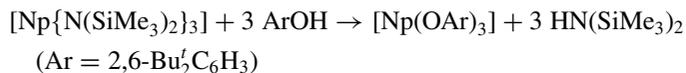
11.12 Chemistry of Plutonium

Plutonium presents particular problems in its study. One reason is that, since ^{239}Pu is a strong α-emitter ($t_{1/2} = 24,100$ years) and also tends to accumulate in bone and liver, it is a severe radiological poison and must be handled with extreme care. A further problem is that the accidental formation of a critical mass must be avoided.

11.12.1 Aqueous Chemistry
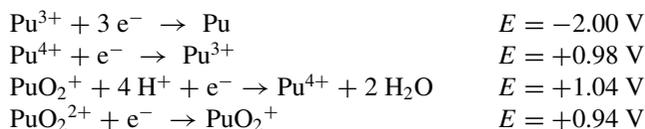
Because of the complicated redox chemistry, not all the oxidation states +3 to +7 are observed under all pH conditions. Blue Pu^{3+}(aq) resembles the corresponding Ln^{3+} ions whilst the brown Pu^{4+} ion requires strongly acidic conditions (6M) to prevent oligomerization

and disproportionation. The purple-pink PuO_2^+ ion readily disproportionates, whilst the orange-yellow PuO_2^{2+} ion resembles the uranyl ion, but is less stable, tending to be reduced, not least by its own α-decay. Blue Pu^{VII}, possibly PuO_5^{3-}(aq) or some oxo/hydroxy species like $[PuO_2(OH)_4(OH_2)]^{3-}$, exists only at very high pH; it is formed by ozonolysis of Pu^{VI}, and some Pu^{VIII} may be generated.

11.12.2   The Stability of the Oxidation States of Plutonium

In comparison with uranium, the $(+3)$ state has become much more stable (Table 9.5), witness the standard reduction potential of $+0.98$ V for $Pu^{4+} + e \rightarrow Pu^{3+}$, the comparative value for uranium being -0.63V. This means that quite strong oxidizing agents such as manganate(VII) are needed to effect this oxidation in the case of plutonium.
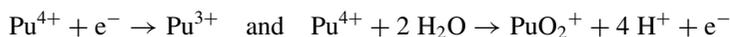
The relevant standard potentials for plutonium are:

$$
\begin{array}{ll}
Pu^{3+} + 3\,e^- \;\rightarrow\; Pu & E = -2.00\ V \\
Pu^{4+} + e^- \;\rightarrow\; Pu^{3+} & E = +0.98\ V \\
PuO_2^+ + 4\,H^+ + e^- \rightarrow Pu^{4+} + 2\,H_2O & E = +1.04\ V \\
PuO_2^{2+} + e^- \;\rightarrow\; PuO_2^+ & E = +0.94\ V
\end{array}
$$

The Pu^{III}–Pu^{IV} and the Pu^{V}–Pu^{VI} couples are both reversible, but not the Pu^{IV}–Pu^{V}, as the latter involves the making and breaking of Pu=O bonds and significant changes in geometry (cf. uranium). Reactions involving the making and breaking of Pu=O bonds are also kinetically slow, so that it is possible for ions in all four oxidation states between $(+3)$ and $(+6)$ to coexist in aqueous solution under certain conditions. The even spacing of the potentials linking the four oxidation states means that disproportionation and reproportionation reactions are feasible. For example, a possible route for disproportion of Pu^{4+} in aqueous solution can be written:

$$2\,Pu^{4+} + 2\,H_2O \rightarrow Pu^{3+} + PuO_2^+ + 4\,H^+$$

This is composed of two redox processes:

$$Pu^{4+} + e^- \rightarrow Pu^{3+} \quad \text{and} \quad Pu^{4+} + 2\,H_2O \rightarrow PuO_2^+ + 4\,H^+ + e^-$$
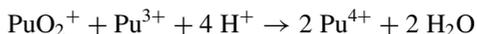
Because the potentials are of roughly equal magnitude (and of opposite sign in this case), the free energy change is small (<20 kJmol^{-1}). The following process:

$$2\,PuO_2^+ + 4\,H^+ \rightarrow PuO_2^{2+} + Pu^{4+} + 2\,H_2O$$

is also favoured; overall, the two can be combined as:

$$3\,Pu^{4+} + 2\,H_2O \rightarrow 2\,Pu^{3+} + PuO_2^{2+} + 4\,H^+.$$

Another feasible reproportionation reaction is of course:

$$PuO_2^+ + Pu^{3+} + 4\,H^+ \rightarrow 2\,Pu^{4+} + 2\,H_2O$$

A further problem is that compounds in the $+5$ and $+6$ oxidation states tend to be reduced (autoradiolysis), as ^{239}Pu is a strong α-emitter (1 mg ^{239}Pu emits over a million α-particles a second) decomposing water molecules into •H, •OH and •O radicals which, in turn, participate in redox reactions. In acidic solution, decomposition of the solvent to H_2O_2 and the acid can occur. In nitric acid, for example, both HNO_2 and nitrogen oxides are formed, so that, starting with plutonium(VI), ions in the lower oxidation states are generated
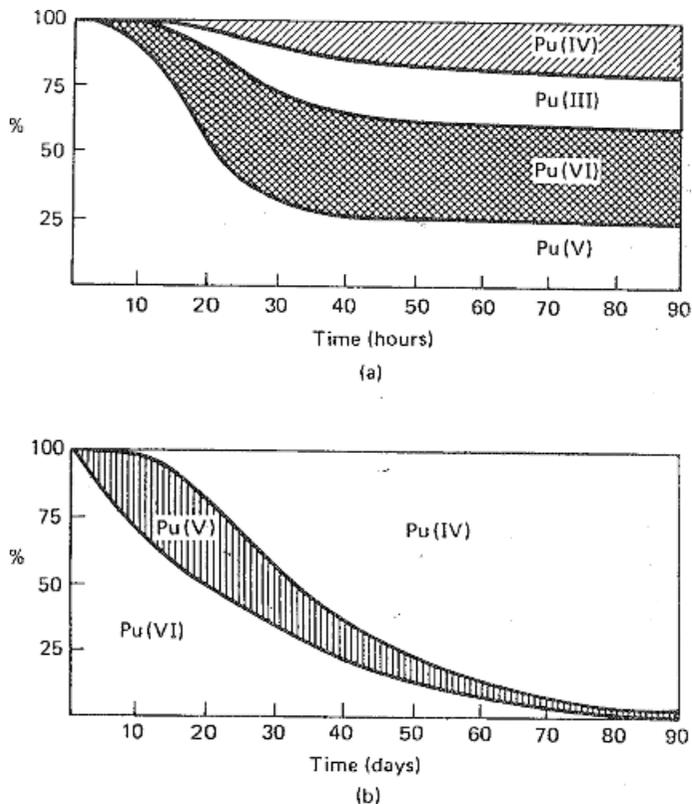
Figure 11.12
(a) Disproportionation of Pu^V in 0.1M HNO$_3$ + 0.2 M NaNO$_3$. (b) Self-reduction of Pu^{VI} due to its own α-emission, in 5M NaNO$_3$ (after P.I. Artiukhin, V.I. Medicedovskii, and A.D. Gel'man, *Radiokhimiya*, 1959, **1** 131; *Zh. Neorg. Khim.*, 1959, **4**, 1324) (permission applied for reproduction).

by both the reduction and disproportionation/reproportionation reactions described above. Figure 11.12 shows the effects of these processes. In Figure 11.12(a), the disproportionation of Pu^V into all the (+3) to (+6) states can be seen, whilst in Figure 11.12(b), over a longer time scale, the self-reduction of Pu^{VI} to Pu^{IV} is observed.

In perchloric acid, the (+4) state is less abundant, and the (+3) state more abundant, a reflection of the higher oxidizing power of nitric acid.

11.12.3 Coordination Chemistry of Plutonium

In its coordination chemistry, plutonium(VI) resembles uranium, where corresponding complexes exist. Thus crystallization of solutions of Pu^{VI} in concentrated nitric acid affords red-brown to purple crystals of the hexahydrate PuO$_2$(NO$_3$)$_2$.6H$_2$O, which is isostructural with the U analogue, and contains 8-coordinate [PuO$_2$(NO$_3$)$_2$(H$_2$O)$_2$] molecules. An X-ray absorption spectroscopy study of tributyl phosphate complexes of [AnO$_2$(NO$_3$)$_2$] (An = U, Np, Pu) in solution, probably present as [AnO$_2$(NO$_3$)$_2$(tbp)$_2$], has indicated major changes in the actinide's coordination sphere on reduction to the An^{IV} state, but no significant changes across the series UO$_2{}^{2+}$, NpO$_2{}^{2+}$, PuO$_2{}^{2+}$. An actinide contraction of

about 0.02 Å between successive actinides was detected (M $=$ O changes overall from 1.79 to 1.75 Å on passing from U to Pu).

Adding acetate ions to a Pu^{VI} solution, in the presence of the appropriate Group I metal (M), results in precipitation of M $[PuO_2(OAc)_3]$, also 8 coordinate, with bidentate acetates, isostructural with the U, Np, and Am analogues. Other examples of polyhedra resembling the corresponding uranyl complexes are to be found in the $[PuO_2Cl_4]^{2-}$ (*trans*-octahedral) and $[PuO_2F_5]^{3-}$ (pentagonal bipyramidal) ions. Plutonium(VI) carbonate complexes are important in the preparation of ceramic materials. The PuO_2^{2+} ion is precipitated from aqueous solution by carbonate ion, but this is soluble in excess of carbonate.
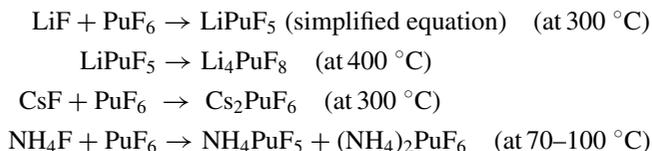
$$PuO_2^{2+}(aq) \rightarrow PuO_2CO_3(s) \rightarrow [PuO_2(CO_3)_2]^{2-}(aq) \quad \text{and} \quad [PuO_2(CO_3)_3]^{4-}(aq)$$

In the latter ion, Pu has $(2+6)$ coordination {X-ray diffraction of $[C(NH_2)_4]$ $[PuO_2(CO_3)_3]$}. The ammonium salt undergoes two-stage thermal decomposition, via (the isolable) PuO_2CO_3:

$$(NH_4)_4 [PuO_2(CO_3)_3] \rightarrow PuO_2CO_3 + 4 NH_3 + 2 H_2O + 2 CO_2 \text{ (at 110–150 °C)}$$
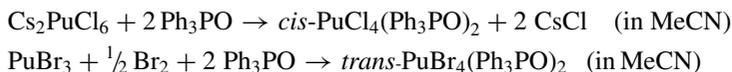$$PuO_2CO_3 \rightarrow PuO_2 + \tfrac{1}{2} O_2 + CO_2 \text{ (at 250–300 °C)}$$
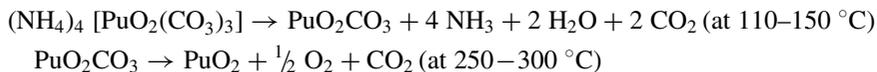
Few Pu(+5) compounds have been characterized in the solid state.

In the (+4) oxidation state, plutonium forms many halide complexes, both anionic and neutral, contrasting with the absence of $PuCl_4$ and $PuBr_4$ (though no iodides are known). $Pu^{4+}(aq)$ reacts with conc. HX forming $[PaX_6]^{2-}$ ions (X $=$ Cl, Br) isolable as salts such as $(Et_4N)_2PuBr_6$ and Cs_2PuCl_6, both probably containing octahedrally coordinated Pu, and useful as starting materials for making Pu^{IV} halide complexes. Various fluoride complexes can be made, often relying on the instability of PuF_6:
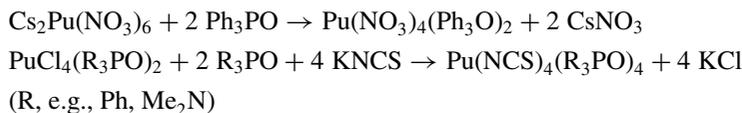
$$LiF + PuF_6 \rightarrow LiPuF_5 \text{ (simplified equation)} \quad \text{(at 300 °C)}$$
$$LiPuF_5 \rightarrow Li_4PuF_8 \quad \text{(at 400 °C)}$$
$$CsF + PuF_6 \rightarrow Cs_2PuF_6 \quad \text{(at 300 °C)}$$
$$NH_4F + PuF_6 \rightarrow NH_4PuF_5 + (NH_4)_2PuF_6 \quad \text{(at 70–100 °C)}$$

High coordination numbers are usual in fluoride complexes; $(NH_4)_4PuF_8$ has nine-coordinate Pu.

Neutral halide complexes are usually got starting from $[PuX_6]^{2-}$ salts (X $=$ Cl, Br), though bromides can also be made by bromine oxidation of Pu^{III} species.

$$Cs_2PuCl_6 + 2 Ph_3PO \rightarrow cis\text{-}PuCl_4(Ph_3PO)_2 + 2 CsCl \quad \text{(in MeCN)}$$
$$PuBr_3 + \tfrac{1}{2} Br_2 + 2 Ph_3PO \rightarrow trans\text{-}PuBr_4(Ph_3PO)_2 \quad \text{(in MeCN)}$$

A wide range of these complexes, also involving nitrate and thiocyanate ligands, has been made:

$$Cs_2Pu(NO_3)_6 + 2 Ph_3PO \rightarrow Pu(NO_3)_4(Ph_3O)_2 + 2 CsNO_3$$
$$PuCl_4(R_3PO)_2 + 2 R_3PO + 4 KNCS \rightarrow Pu(NCS)_4(R_3PO)_4 + 4 KCl$$
$$(R, e.g., Ph, Me_2N)$$

Others include *trans*-$PuX_4[(Me_2N)_3PO]_2$ (X $=$ Cl, Br); $PuCl_4(Ph_2SO)_n(n = 3, 4)$; $PuCl_4(Me_2SO)_n$ ($n = 3, 7$); $PuCl_4(Me_3PO)_6$ {probably $[PuCl(Me_3PO)_6]^{3+}$ $(Cl^-)_3$}. Structurally, they resemble the corresponding complexes of Th, Pa, U, and Np. The tridentate

ligand 2,6-[Ph$_2$P(O)CH$_2$)]$_2$C$_5$H$_3$NO combines two phosphine oxide and one N-oxide functional groups; it forms a 2:1 Pu^{IV} complex which has the same structure, [PuL$_2$(NO$_3$)$_2$](NO$_3$)$_2$, in both the solid state and solution. The 2:1 complex of the bidentate ligand 2-[Ph$_2$P(O)CH$_2$]C$_5$H$_4$NO with plutonium nitrate also has an ionic structure [PuL$_2$(NO$_3$)$_3$]$_2$[Pu(NO$_3$)$_6$]. As is the case with uranium, nitrate complexes are important in the separation chemistry of plutonium. Solutions of Pu^{4+}(aq) in conc. HNO$_3$ deposit dark green crystals of Pu(NO$_3$)$_4$.5H$_2$O, which contain 11-coordinate [Pu(NO$_3$)$_4$(H$_2$O)$_3$] molecules (as is the case with Th). [Pu(NO$_3$)$_6$]$^{2-}$ ions can be fished out of very concentrated (10–14M) nitric acid solutions as salts R$_2$Pu(NO$_3$)$_6$(R = Cs, Et$_4$N). [Pu(NO$_3$)$_6$]$^{2-}$ is strongly adsorbed by anion-exchange resins, and this is made use of in the purification of Pu commercially.

Plutonium carbonate complexes are important as they contribute to an understanding of what happens to plutonium in the environment, Pu(+4) being the most stable oxidation state under normal conditions. [Pu(CO$_3$)$_5$]$^{6-}$ has been identified by EXAFS as the Pu^{IV} species in solution at high carbonate concentration; the structure of crystalline [Na$_6$Pu(CO$_3$)$_5$]$_2$.Na$_2$CO$_3$.33H$_2$O has also been determined; it features 10-coordinate plutonium. The sulfate complex K$_4$Pu(SO$_4$)$_4$.2H$_2$O contains dimeric [(SO$_4$)$_3$Pu(μ-SO$_4$)$_2$Pu(SO$_4$)$_3$]$^{8-}$ anions with nine-coordinate Pu.

In many aspects of its coordination chemistry, Pu^{IV} compounds resemble their uranium analogues; thus it forms eight-coordinate complexes with diketonate ligands, like [Pu(acac)$_4$], and similar complexes with 8-hydroxyquinolinate and tropolonate. There is a limited alkoxide chemistry, [Pu(OBu^t)$_4$] being volatile at 112 °C (0.05 mmHg pressure) and very likely being a monomer. The borohydride [Pu(BH$_4$)$_4$] is a blue-black volatile liquid (mp 15 °C) and has a 12 coordinate molecular structure, with tridentate borohydride ligands, like the neptunium analogue, but unlike 14 coordinate [U(BH$_4$)$_4$].

Little coordination chemistry is as yet known in the (+3) state, but these compounds are interesting. Reaction of Pu with iodine in THF affords off-white [PuI$_3$(thf)$_4$], a useful starting material; [PuI$_3$(dmso)$_4$] and [PuI$_3$(py)$_4$] have also been reported. The σ-alkyl [Pu{CH(SiMe$_3$)$_2$}$_3$] and the silylamide [Pu{N(SiMe$_3$)$_2$}$_3$] are analogous to those of U and the lanthanides, the latter potentially being a useful starting material (though neither has been completely characterized). The amide reacts with a bulky phenol forming the aryloxide [Pu(OAr)$_3$] (Ar = 2,6-Bu$_2^t$C$_6$H$_3$), which is probably three coordinate. Plutonium forms insoluble oxalates Pu$_2$(C$_2$O$_4$)$_3$.x H$_2$O (x = 10, 11) similar to those of the lanthanides.

Reaction of plutonium metal with triflic acid affords blue Pu(CF$_3$SO$_3$)$_3$.9H$_2$O, isostructural with the lanthanide triflates and which contains tricapped trigonal prismatic [Pu(H$_2$O)$_9$]$^{3+}$ ions; similarly, Pu reacts with AgPF$_6$ (or TlPF$_6$) in MeCN suspension, dissolving to form [Pu(MeCN)$_9$] (PF$_6$)$_3$, in which the coordination polyhedron is rather more distorted.

11.12.4 Plutonium in the Environment

Actinides are potentially present in the environment from a number of sources, not just the 'natural' thorium and uranium. Nuclear power plants and uses in nuclear weapons are obvious areas for concern, raised in recent times by possibilities that terrorist groups could gain control of such weapons, possibly 'dirty' bombs. Plutonium is an obvious source of concern. Any plutonium in the environment is believed to be largely present as rather insoluble Pu^{IV} species. Pu^{IV} ions are hydrolysed easily, unless in very acidic solution, forming light green colloidal species, which age with time, their solubility decreasing. The possibility of colloid-facilitated transport of plutonium occurring was raised by the observation of

migration of plutonium in ground water by rather more than a mile from the location of underground weapons testing in Nevada, USA, over a period greater than 20 years. It is therefore necessary to consider the interaction of plutonium, not just with inorganic ions like carbonate (see Section 11.12.3), phosphate, silicate and sulfate, but with natural organic substances like humic acid.

Disposal of nuclear waste materials – especially the high-level waste from the cores of reactors and nuclear weapons – so that they do not escape into the environment is a pressing problem. Currently the preferred solution in the USA and most of Europe is immobilization in a suitable geological repository. The waste materials are evaporated if necessary, then heated with silica and borax to form a borosilicate glass, encased in an inert (e.g., lead) material, then buried in a stable zone, such as rock salt or clay. The conditions surrounding such sites are important. Yucca Mountain, Nevada, is the leading candidate among possible American sites. Solubility studies have shown that Np is more than 1000 times more soluble in the Yucca Mountain waters than is Pu, because under the ambient conditions Pu tends to adopt the (+4) state, associated with insolubility, whilst Np adopts the (+5) state, where compounds are much more soluble. However, at the WIPP site in New Mexico, which is built on a deep salt formation, the very salty brines favour formation of soluble Pu(+6) complexes such as $[PuO_2Cl_4]^{2-}$, which will present much more of a problem unless reducing conditions can be generated.

As a potential environmental hazard, plutonium is particularly toxic because of the remarkable similarity of Pu^{IV} and Fe^{III} – which means that Pu can be taken up in the biological iron transport and storage system of mammals. This similarity is being used in a biomimetic approach to Pu-specific ligands for both *in-vivo* actinide decorporation and nuclear waste remediation agents. It has also been suggested that plutonium could be solubilized by microbial siderophores. These are ligands used by bacteria to bind Fe^{3+} (an ion which, like Pu^{4+}, is essentially 'insoluble' at near-neutral pH) and carry it into cells. In fact, such siderophores bind plutonium strongly (log $\beta = 30.8$ for the desferrioxamine B complex), only taking it up as Pu^{IV} with plutonium in other oxidation states being oxidized or reduced appropriately. They do not solubilize plutonium rapidly, however; they are, in fact, less effective in solubilizing plutonium than are simple complexing agents like EDTA and citrate, leading to the suggestion that the siderophores passivate the surface of the plutonium hydroxide. (The overall formation constant for [Pu-EDTA] in acidic solution is log $\beta = 26.44$; the strength of the complexation means that the possibility of EDTA, widely used in former nuclear weapons programmes, solubilizing and transporting plutonium is a present concern).

Unlike the exclusively 6-coordinate iron(III) siderophore complexes, higher coordination numbers are possible with plutonium; the complex of Pu^{IV} with desferrioxamine E (DFE; a hexadentate iron-binding siderophore ligand) has shown it to contain 9-coordinate $[Pu(dfe)(H_2O)_3]^+$ ions with a tricapped trigonal prismatic geometry (Figure 11.13).

The microbe *Mycena flavescens* has been found to take up Pu (but not U) in the form of a siderophore complex though at a much slower rate than it takes up iron; the Fe and Pu complexes inhibit each other, indicating competition for the same binding site on the microbe. It has similarly been found that pyoverdin, the main siderophore in iron-gathering capacity produced by *Pseudomonas aeruginosa*, will also transport plutonium across cell membranes. It has been suggested that using phytosiderophores such as desferrioxamine and mugineic acids could solubilize actinides and promote their uptake by plants and consequent removal from the soil.
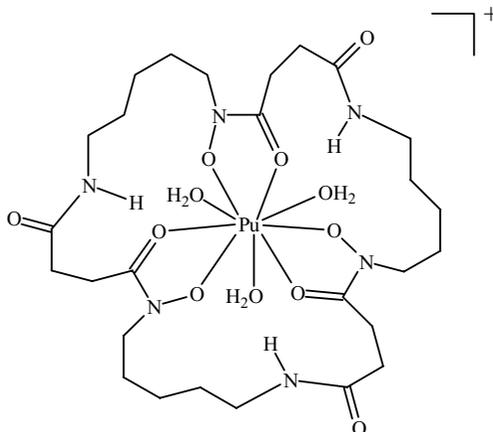
Figure 11.13
Structure of a Pu^{iv} complex of a siderophore.

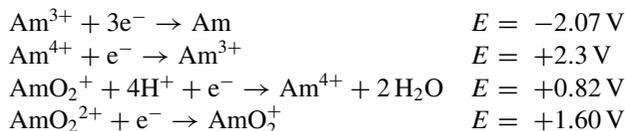## 11.13   Chemistry of Americium and Subsequent Actinides

Two isotopes, ^{241}Am ($t_{1/2} = 433$ y), a decay product of ^{241}Pu, and ^{243}Am ($t_{1/2} = 7380$ y), have half-lives suitable for their use in chemical reactions. The metal itself is a silvery, ductile and malleable solid, which is obtained by metallothermic (Ba, Li) reduction of the trifluoride; alternatively by heating the dioxide with lanthanum and using the difference in boiling point between La (bp 3457 °C) and americium (2607 °C) to displace the equilibrium to the right as americium distils.

$$3\,AmO_2 + 4\,La \rightleftharpoons 2\,La_2O_3 + 3\,Am$$
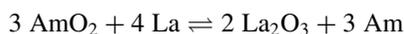
Americium undergoes slow oxidation in air and dissolves in dil. HCl, as expected from its favourable potential [E(Am/Am^{3+}) = −2.07 V].

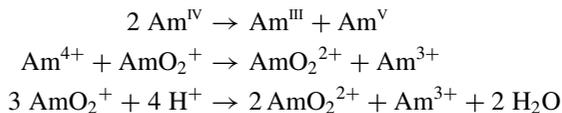### 11.13.1   Potentials

The relevant standard potentials for americium (1M acid) are:

$$
\begin{array}{lll}
Am^{3+} + 3e^- \rightarrow Am & E = & -2.07\,V \\
Am^{4+} + e^- \rightarrow Am^{3+} & E = & +2.3\,V \\
AmO_2^+ + 4H^+ + e^- \rightarrow Am^{4+} + 2\,H_2O & E = & +0.82\,V \\
AmO_2^{2+} + e^- \rightarrow AmO_2^+ & E = & +1.60\,V
\end{array}
$$

The tendency for the (+3) state to become more stable in the sequence U < Np < Pu continues with americium (and dihalides, AmX$_2$, make their appearance for the first time). The pink Am^{3+} ion is thus the most important species in aqueous solution, Am^{IV} being unstable in the absence of complexing agents. Hypochlorite oxidizes Am^{3+} in alkaline solution to what may be Am(OH)$_4$, soluble in NH$_4$F solution, very likely as the fluoride complex [AmF$_8$]$^{4-}$. The (+5) state is accessible, again through oxidation in alkaline solution (e.g., with O$_3$ or peroxydisulfate, S$_2$O$_8^{2-}$), as the AmO$_2^+$ ion, though this tends to disproportionate to Am^{III} and Am^V; the (+6) state, in the form of the AmO$_2^{2+}$ ion, is obtained by oxidation (Ag^{2+} or S$_2$O$_8^{2-}$) of lower oxidation states in acid solution.

The tendency noted for plutonium for disproportionation occurs here, as both Am^{IV} and Am^{V} tend to disproportionate in solution:

$$2\,Am^{IV} \rightarrow Am^{III} + Am^{V}$$
$$Am^{4+} + AmO_2^+ \rightarrow AmO_2^{2+} + Am^{3+}$$
$$3\,AmO_2^+ + 4\,H^+ \rightarrow 2\,AmO_2^{2+} + Am^{3+} + 2\,H_2O$$

There is also again the tendency to autoradiolysis, the reduction of high oxidation states through the effects of the α-radiation emitted.

Relatively few complexes of americium have been characterized; those that have tend to resemble the corresponding compounds of the three previous metals. Many are halide complexes, such as $(NH_4)_4\,[AmF_8]$, which resembles the U analogue, $Cs_2NaAmCl_6$, and $(Ph_3PH)_3AmX_6$ (X = Cl, Br).

The AmO_2^+ and AmO_2^{2+} ions form well-defined complexes; thus in HCl solution, where it likely forms $[AmO_2Cl_4]^{3-}$ and $[AmO_2Cl_4]^{2-}$, the symmetric Am=O stretching vibrations can be detected at 730 (AmO_2^+) and 796 cm^{-1} (AmO_2^+), respectively. $Na[AmO_2(OAc)_3]$ has eight coordination with bidentate acetates, just like the U–Pu analogues, the same coordination number also being found in AmO_2F_2, $M\,[AmO_2F_2]$ (M = Rb, K), and $M\,[AmO_2CO_3]$ (M = Rb, K, Cs). Six coordination occurs in $Cs_2[AmO_2Cl_4]$ and in $NH_4[AmO_2PO_4]$.

A significant chemistry occurs in the (+3) state, similar to that of Ln^{3+} ions, with studies often made in the context of separating Am from lanthanide fission products. Amide ligands like N, N, N', N'-tetraethylmalonamide (TEMA) have been investigated as possible extractants. Solution studies are assisted by some of the newer spectroscopic techniques; thus EXAFS (Extended X-ray Absorption Fine Structure) studies on solutions of $[Am(TEMA)_2(NO_3)_3]$ indicate a similar geometry to $[Nd(TEMA)_2(NO_3)_3]$. Carboxylate-derived calix[4]arenes show high selectivity for Am^{3+}, whilst complexation of Am^{3+} by crown ethers and diazacrown ethers has also been studied. The resemblance extends to complexes isolated. The sulfate $Am_2(SO_4)_3.8H_2O$ is isomorphous with the 8-coordinate lanthanide analogies (Pr–Sm) and insoluble oxalates $Am_2(C_2O_4)_3.x\,H_2O$ (x = 7, 11) have been characterized. The resemblance extends to diketonate complexes such as $[\{Am(Me_3CCOCHCOCMe_3)_3\}_2]$, a dimer with seven-coordinate Am, like the Pr analogue. The adduct $[Am(CF_3CCOCHCOCCF_3)_3\{(BuO)_3PO\}_2]$ is volatile at 175 °C and potentially could be used in separations. In the iodate complex $K_3Am_3(IO_3)_{12}\cdot HIO_3$, the $[AmO_8]$ polyhedra are made of eight $[IO_3]$ oxygen atoms in a distorted bicapped trigonal prismatic array. There is additionally one very long Am–O contact to complete a distorted tricapped trigonal prismatic Am coordination sphere.
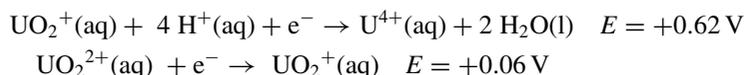
11.14 Chemistry of the Later Actinides

The succeeding actinides (Cm, Bk, Cf, Es, Fm, Md, No, Lr) mark the point where the list of isolated compounds tends to involve binary compounds (oxides, halides and halide complexes, chalcogenides, and pnictides) rather than complexes. Those studies of complexes that have been made are usually carried out in solution and, from Fm, onwards, have been tracer studies.
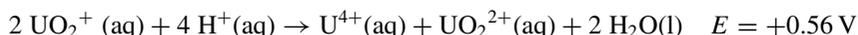
Fermium coprecipitates with lanthanide fluorides and hydroxides, showing it to form lanthanide-like Fm^{3+} ions. These elute from cation-exchange resins slightly before Es^{3+}, whilst its chloride and thiocyanate complexes are eluted from anionic exchange resins just

after Es^{3+}. This shows that Fm^{3+} forms slightly stronger complexes than does Es^{3+}, as expected purely on electrostatic considerations for a slightly smaller ion. In the case of nobelium, slightly different results have been obtained. Nobelium ions coprecipitate with BaF_2, rather than with LaF_3, suggesting that they are present as No^{2+} ions, but, after adding Ce^{4+} oxidant to the initial solution, nobelium precipitated with LaF_3, indicating that the cerium had oxidized the nobelium to No^{3+} ions. Complexing studies using Cl^- ions also indicated alkaline-earth-like behaviour.

Question 11.1 Use the reduction potentials to show why the $UO_2^+(aq)$ tends to disproportionate.

$$UO_2^+(aq) + 4\ H^+(aq) + e^- \rightarrow U^{4+}(aq) + 2\ H_2O(l) \quad E = +0.62\ V$$
$$UO_2^{2+}(aq) + e^- \rightarrow UO_2^+(aq) \quad E = +0.06\ V$$

Answer 11.1 Combining the potentials shows that for

$$2\ UO_2^+(aq) + 4\ H^+(aq) \rightarrow U^{4+}(aq) + UO_2^{2+}(aq) + 2\ H_2O(l) \quad E = +0.56\ V$$

Since E is positive, the reaction is energetically feasible; although this only predicts that the UO_2^+ (aq) ion is *thermodynamically unstable* with respect to disproportionation and says nothing about *kinetic stability*, the fact is that the uranium(V) aqua ion is very short-lived.

Question 11.2 Write the expression for K_1 and K_2 for complex formation between Th^{4+} and F^- ions.
Answer 11.2

$$K_1 = [ThF^{3+}(aq)]/[Th^{4+}(aq)][F^-(aq)];\ K_2 = [ThF_2^{2+}(aq)]/[ThF^{3+}(aq)][F^-(aq)]$$

Question 11.3 The highest occupied orbitals in the uranyl ion have the electronic arrangement $\sigma_u^2\ \sigma_g^2\ \pi_u^4\ \pi_g^4$. By referring to Figure 11.2, suggest the electronic arrangements similarly of UO_2^+ and PuO_2^{2+}.
Answer 11.3 UO_2^+ is $\sigma_u^2\ \sigma_g^2\ \pi_u^4\ \pi_g^4\ (\delta_u,\ \phi_u)^1$ and PuO_2^{2+} is $\sigma_u^2\ \sigma_g^2\ \pi_u^4\ \pi_g^4$ $(\delta_u,\ \phi_u)^2$ (The relative positions of δ_u and ϕ_u are uncertain).

Question 11.4 Suggest reasons why actinides from Cm onwards do not appear to form similar ions like CmO_2^{2+}.
Answer 11.4 Heavier actinides such as Cm do not display high oxidation states as the f orbitals appear to be more contracted and their electrons are not available for bonding, (and could be required for π bonding, for example). A further factor is that the additional electrons would need to be placed in antibonding orbitals such as σ_u^* and π_u^*, which would destabilize such an ion.

Question 11.5 Suggest coordination numbers for each of the following complexes. (a) $[UO_2F_5]^{3-}$; (b) $[UO_2Br_4]^{2-}$; (c) $[UO_2(NO_3)_3]^-$; (d) $[UO_2(NCS)_5]^{3-}$; (e) $[UO_2(CH_3COO)_3]^-$; (f) $[UO_2(NO_3)_2(H_2O)_2]$; (g) $[UO_2(NO_3)_2(Ph_3PO)_2]$; (h) $[UO_2(CH_3COO)_2(Ph_3PO)]$.
**Answer 11.5** (a) 7; (b) 6; (c) 8 (nitrate is bidentate) (d) 7; (e) 8 (acetate is bidentate) (f) 8; (g) 8; (h) 7.

Question 11.6 Explain why you can get $2 + 6$ coordination in $[UO_2(OH_2)_2(O_2NO)_2]$, $[UO_2(O_2NO)_3]^-$, etc. rather than the $2 + 5$ coordination in the uranyl aqua ion.
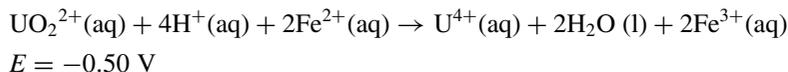
Answer 11.6 Although bidentate in most complexes, nitrate groups take up little space (they are said to have a small 'bite angle').

Question 11.7 Read section 11.5.5 and explain why Pu^{4+} can be reduced by Fe^{2+}, but UO_2^{2+} can't be so reduced.

Answer 11.7 $Fe^{3+}(aq)$ has a more negative reduction potential than $Pu^{4+}(aq)$, making Fe^{2+} a better reducing agent, one that will reduce $Pu^4(aq)$. Thus for:

$$Pu^{4+}(aq) + Fe^{2+}(aq) \rightarrow Pu^{3+}(aq) + Fe^{3+}(aq) \qquad E = +0.23\,V$$
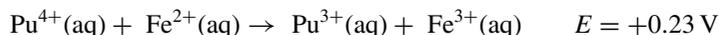
and the process is energetically feasible. However, for:

$$UO_2^{2+}(aq) + 4H^+(aq) + 2Fe^{2+}(aq) \rightarrow U^{4+}(aq) + 2H_2O\,(l) + 2Fe^{3+}(aq)$$
$$E = -0.50\,V$$

and the reduction is not energetically feasible under these conditions.

Question 11.8 The infrared spectrum of $Th(NO_3)_4.4\,Me_3PO$ displays bands due to bidentate nitrate and ionic nitrate groups. Suggest a possible structure affording a reasonable coordination number.

Answer 11.8 Phosphine oxide ligands and bidentate nitrate groups take up different amounts of space round thorium. Assuming that all the phosphine oxide groups are bound to thorium, reference to Table 11.5 suggests that a coordination number of 10 is likely; four Me_3PO groups bound would leave room for three bidentate nitrates. The suggested structure is $[Th(NO_3)_3(Me_3PO)_4]^+NO_3^-$.

Question 11.9 (Refer to section 11.6.2 in connection with this) Hexamethylphosphoramide (HMPA), $OP(NMe_2)_3$, is a good σ-donor, behaving like a typical monodentate phosphine oxide ligand such as Ph_3PO. A number of complexes of HMPA with uranium(IV) nitrate have been prepared. Green crystals of $U(NO_3)_4(hmpa)_2$ are made thus:

$$Cs_2(NO_3)_6 + 2\,HMPA\,(acetone) \rightarrow 2\,CsNO_3 + U(NO_3)_4(hmpa)_2$$
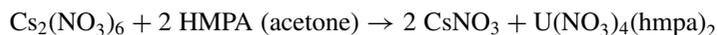
The IR spectrum of this compound shows only one type of nitrate group; all are coordinated.

Question A How are the nitrates likely to be bound in $U(NO_3)_4(hmpa)_2$? Suggest a coordination number and coordination geometry for uranium.

Answer A By analogy with $U(NO_3)_4(OPPh_3)_2$, a 10-coordinate compound with a *trans* geometry and bidentate nitrates is probable (*this is known to be the case*).

Using excess of HMPA, a green compound $U(NO_3)_4(hmpa)_4$ is obtained. Its IR spectrum shows two different modes of nitrate coordination, and no ionic nitrate.

Question B Suggest a credible structure for the compound $U(NO_3)_4(hmpa)_4$, indicating the coordination number of uranium.

Answer B Various structures are possible. It is unlikely that all nitrates are bidentate, as this product would be 12 coordinate. If one nitrate is monodentate, the compound would be 11 coordinate $U(O_2NO)_3(ONO_2)(hmpa)_4$.

If $U(NO_3)_4(hmpa)_4$ is dissolved in non-polar solvents such as CH_3CN, a non-conducting solution is obtained, but with a simpler IR spectrum possibly indicating just one type of nitrate coordination.

Question C Suggest a structure for the compound present in solution.
Answer C One alternative is an 11-coordinate complex $U(NO_3)_4(hmpa)_3$ formed by dissociation of one hmpa ligand.

When $U(NO_3)_4(hmpa)_4$ is treated with $NaBPh_4$, a crystalline solid is obtained which has the analysis $U(NO_3)_3(hmpa)_4BPh_4$. This is a 1:1 electrolyte in solution. Its IR spectrum shows only one type of nitrate group, and no ionic nitrate.
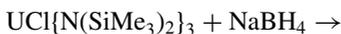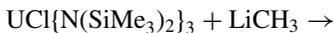
Question D Suggest a credible structure for this compound, indicating the coordination number of uranium.
Answer D Assuming all nitrates are bidentate and that the BPh_4^- group remains ionic, a structure $[U(NO_3)_3(hmpa)_4]^+(BPh_4)^-$ would contain 10-coordinate uranium.

Question 11.10 Comment on the patterns in bond length in Table 11.6.
Answer 11.10 The U–X distances increase with increasing radius of halogen, as expected. There appears to be a slight decrease in U–O distance as the σ-donor power of the halogen decreases, possibly because this means that the ligands are competing for metal orbitals.

Question 11.11 Complete these equations:

$$UCl\{N(SiMe_3)_2\}_3 + LiCH_3 \rightarrow$$
$$UCl\{N(SiMe_3)_2\}_3 + NaBH_4 \rightarrow$$

Answer 11.11

$$UCl\{N(SiMe_3)_2\}_3 + LiCH_3 \rightarrow U(CH_3)\{N(SiMe_3)_2\}_3 + LiCl$$
$$UCl\{N(SiMe_3)_2\}_3 + NaBH_4 \rightarrow U(BH_4)\{N(SiMe_3)_2\}_3 + NaCl.$$