Coordination Chemistry Reviews, 36 (1981) 183–265
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

ACTINIDE NITRATE COMPLEXES

UMBERTO CASELLATO and PIETRO A. VIGATO

Laboratorio di Chimica e Tecnologia del Radioelementi del C.N.R., Area della Ricerca, Corso Stati Uniti, 35100 Padova (Italy)

MAURIZIO VIDALI

Istituto di Chimica Generale ed Inorganica dell'Università, Via Loredan 4, 35100 Padova (Italy)

(Received 3 March 1980)

CONTENTS

A. INTRODUCTION

A wide range of actinide nitrate complexes has been recently characterized by X-ray or neutron diffraction techniques. Few anhydrous compounds have been prepared but hydrated nitrates are known for thorium(IV) and uranium(IV) and for protactinium, neptunium and plutonium in various valence states (Table 1). Nitrate complexes with a variety of neutral donor ligands have been prepared for all these elements.

Solid nitrates do not appear to have been characterised for the elements beyond plutonium and there are very few publications dealing with protactinium, neptunium and plutonium nitrates, the vast majority of the published information pertaining to thorium(IV) and uranium(VI) compounds. Nitrate ion is a poly-atomic ligand and can have several modes of coordination to a metal ion; it has a very short O···O distance and an obvious comparison can be made with the carbonate and acetate ions.

Several good reviews have been published on various aspects of the chemistry of actinide nitrate compounds and more generally on the coordination chemistry of the compounds containing the nitrate ion [7,15,51,89,96,117, 231—244].

The aim of the present article is to give an extensive review of the work done in the field of the preparation and physicochemical properties of solid nitrate compounds of actinides.

B. MODES OF COORDINATION OF THE NITRATE GROUP

The simple nitrate anion NO_3^- belongs to the point group D_{3h}. On coordination to a metal the symmetry of this ion is lowered and several modes of coordination have been proposed (Fig. 1).

Structural studies have identified the following types of nitrato group: unidentate, bidentate and bridging. The local symmetry of the ion is lowered to C_{2v} in both types of bidentate and bridging coordination; for unidentate bonding it may be either C_{2v} or C_S depending on the orientation of the nitrate ion to the metal (assuming always that all five atoms are coplanar). It is accordingly not possible to distinguish these modes of coordination by means of the selection rules alone. The correlation between D_{3h} and C_{2v} is given in Table 2.

The nitrate ion has four fundamental frequencies of absorption; the coordination of the ion results in the removal of the degeneracy of the E' modes, and all modes become active in both Raman and IR. In all cases the number and the activity of the fundamental modes are the same. The use of IR and Raman spectroscopy therefore offers a useful method for determining the presence of coordinated nitrate ions and a considerable amount of work has been concerned with such analyses. The following means of identifying the mode of coordination of nitrate groups have been proposed:

(a) The number of bands exhibited in the far IR region [1,2].

TABLE 1

Actinide nitrates, nitrate hydrates and nitrato complexes

Valence state	Th	Pa	U	Np	Pu
IV	$ThO(NO_3)_2$				
	$Th(NO_3)_4$				
	$Th(NO_3)_4 \cdot 2\,H_2O$			$Np(NO_3)_4 \cdot 2\,H_2O$	
	$Th(NO_3)_4 \cdot 4\,H_2O$				
	$Th(NO_3)_4 \cdot 5\,H_2O$				$Pu(NO_3)_4 \cdot 5\,H_2O$
	$M^ITh(NO_3)_5 \cdot xH_2O$ [a]				
	$M^I_2Th(NO_3)_6$ [b]		$M^I_2U(NO_3)_6$ [b]	$M^I_2Np(NO_3)_6$ [b]	$M^I_2(NO_3)_6$ [b]
	$M^{II}Th(NO_3)_6 \cdot 8\,H_2O$ [c]		$M^{II}U(NO_3)_6 \cdot 8\,H_2O$ [c]		$M^{II}Pu(NO_3)_6 \cdot 8\,H_2O$ [c]
V		$PaO(NO_3)_3 \cdot xH_2O$		$NpO(NO_3) \cdot 3\,H_2O$	
				$NpO_2(NO_3)$	
				$NpO_2(NO_3) \cdot H_2O$	
		$M^IPa(NO_3)_6$ [d]			
VI			$UO_2(NO_3)_2$		$PuO_2(NO_3)_2$
			$UO_2(NO_3)_2 \cdot H_2O$		
			$UO_2(NO_3)_2 \cdot 2\,H_2O$		$PuO_2(NO_3)_2 \cdot 2\,H_2O$
			$UO_2(NO_3)_2 \cdot 3\,H_2O$		$PuO_2(NO_3)_2 \cdot 3\,H_2O$
			$UO_2(NO_3)_2 \cdot 6\,H_2O$	$NpO_2(NO_3)_2 \cdot 6\,H_2O$	$PuO_2(NO_3)_2 \cdot 6\,H_2O$
			$M^IUO_2(NO_3)_3$ [e]	$M^INpO_2(NO_3)_3$ [e]	$M^IPuO_2(NO_3)_3$ [e]
			$M^IUO_2(NO_3)_4$ [f]		
			$M^{II}UO_2(NO_3)_4$ [g]		

[a] M^I = Na, K, NH_3Me, NH_2Me_2, NH_3Et, NH_2Et_2. [b] M^I = Variously, Rb, Cs, NH_4, NEt_4, NO and NO_2. [c] M^{II} = Variously, Mg, Zn, Co, Ni and Mn. [d] M^I = Cs, NEt_4, NMe_4. [e] M^I = Variously, K, Rb, Cs, NEt_4, NEt_2H_2, NMe_4. [f] M^I = Rb, Cs, NH_4, $NEtH_3$, PyH. [g] M^{II} = Mg and Zn.

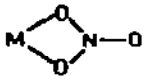
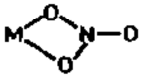
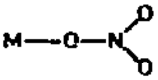
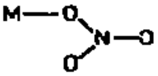
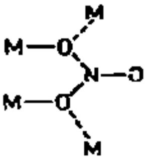
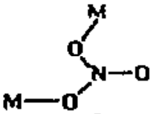
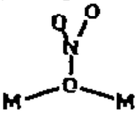
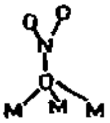
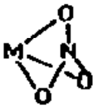
Geometry	Description	Point Group
	Symmetrically Bidentate	C_{2v}
	Unsymmetrically Bidentate	C_s
	Unidentate	C_{2v}
	Unidentate	C_s
	Bridging (syn-syn or anti-anti)	C_{2v}
	Bridging (syn-anti)	C_s
	Bridging	C_{2v}
	Bridging	C_s
	Terdentate	C_{2v}

Fig. 1. Modes of coordination of the nitrate ion.

(b) The positions of the two highest frequency N—O stretching vibrations [3,4].

(c) The depolarisation ratios of the three highest N—O stretching vibrations in the Raman spectrum [5,6].

(d) The sequence of relative intensities of the three highest frequency Raman shifts attributable to nitrate fundamentals [7].

(a) Since a bidentate nitrato group involves two metal—oxygen bonds

TABLE 2

Normal vibrations of the nitrate ion and correlation between D_{3h} and C_{2v} symmetry

Free ion (D_{3h})	ν_1 symmetric stretch A_1'(R) 1050 cm^{-1}	ν_2 out of plane bend A_2''(IR) 830 cm^{-1}	ν_3 degenerate stretch E'(IR,R) 1390 cm^{-1}		ν_4 degenerate bend E'(IR,R) 720 cm^{-1}	
Unidentate and bidentate coordination (C_{2v})	$\nu_2 A_1$(IR,R) 1050–1000 cm^{-1}	$\nu_6 B_1$(IR,R) 850–800 cm^{-1}	$\nu_1 A_1$(IR,R) 1550–1450 cm^{-1}	$\nu_4 B_2$(IR,R) 1320–1260 cm^{-1}	$\nu_3 A_1$(IR,R) 770–740 cm^{-1}	$\nu_5 B_2$(IR,R) 720–700 cm^{-1}

whereas a unidentate group involves only one, it has been suggested that bidentate nitrato groups should exhibit two metal—oxygen frequencies whereas unidentate nitrato groups should only exhibit one. According to this criterion it has been reported [2] that the far IR spectra of nitrato complexes of the type $M(NO_3)_2L_2$ (L = 2-picoline, quinoline or triphenylphosphine oxide, M = Co, Ni, Zn and Cu) show two strong bands assigned to M—O frequencies arising from metal—oxygen (nitrato) interaction. Similar frequencies have been observed for $Rb[UO_2(NO_3)_3]$ at 262 and 223 cm^{-1}, and assigned to bidentate nitrates [1]. These assignments rest largely upon three invalid assumptions [8]. First, it is assumed that one or more of the normal vibration modes of the molecules involve almost exclusively stretching of the M—O bonds; in such molecules the mechanism of the system should be carefully considered, particularly when assigning a metal—ligand vibration, for it has been shown [9,10] that even in simple systems mixing of vibrations can occur to such a degree that the assignment of metal—ligand stretching vibrations has little meaning. Secondly, even if one of the fundamental modes were shown to correspond to an M—O stretching vibration, then in a complex containing two or more coordinated nitrato groups, unless the complex were of very high symmetry, at least two M—O stretching modes would be expected, even if the groups were monodentate in their coordination. Thirdly, the unit cell composition must be considered; if the lattices contain more than one molecule per unit cell then two or more bands may be observed where only one would be predicted from consideration of an isolated molecule. These considerations show that mono and bidentate nitrato groups cannot be distinguished by the use of far IR spectroscopy. The uranyl nitrate complexes, which have bidentate nitrate groups, have up to nine IR and Raman active bands which could be assigned to U—O vibrations [11,12]. It is tempting therefore to assign bands in the region 235—190 cm^{-1} to U—O stretching modes. However, structurally related ions, as in the trinitrato complexes, do not have identical spectra or the same total number of bands or bands of corresponding activity.

(b) Normal coordinate analyses [10,13] have been carried out for symmetrically bidentate and unidentate nitrato groups in order to indicate the probable changes in frequency which would result from an increase in the polarization of the nitrate ion by the metal ion and/or an increase in the metal—oxygen covalent bonding (Fig. 2). Distinction between symmetrically bidentate and unidentate nitrato groups on the basis of this criterion requires the separation of the two highest frequency bands to be characteristic of the mode of coordination, symmetrically bidentate attachment giving rise to a greater separation than unidentate coordination [3]. In addition it has been suggested that the occurrence of two strong bands, one at a frequency greater than 1570 cm^{-1} and the other at a frequency of less than 1280 cm^{-1} might indicate the presence of bridging nitrato groups [4].

The nature of the metal cation and the other ligands coordinated to it will also influence the positions of these two bands and it is not surprising that a wide range of frequencies is observed for symmetrically bidentate, unidentate

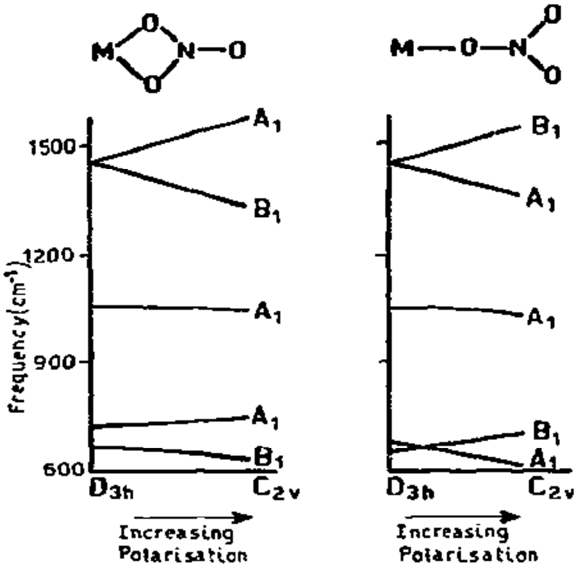


Fig. 2. Frequency shift in symmetrically bidentate and unidentate (C_{2v}) nitrato groups as the degree of polarisation increases with a fixed metal nitrate covalent interaction.

and bridging nitrato groups. Distinction between nitrato groups on the above basis must therefore be made with caution [14]. However it does appear that if the vibrational spectrum of a nitrate group coordinated to a metal atom has its highest frequency at about 1600 cm^{-1} and is separated by about 350 cm^{-1} from the next highest band, then coordination as a symmetrically bidentate or bridging ligand is likely.

(c) This criterion relies on the fact that A_1 and B_1 vibrational modes may be distinguished in the Raman spectrum since the former is Raman polarised whereas the latter is Raman depolarised. The sequence of the polarisations of the three highest frequency Raman bands expected [10,13] for symmetrically bidentate and unidentate nitrato groups are:

Unidentate C_{2v}	B_1(dp)	A_1(p)	A_1(p)
Symmetrically bidentate C_{2v}	A_1(p)	B_1(dp)	A_1(p)

It has been found that there is good agreement between the predicted and observed sequences and hence this technique would appear to offer a convenient means of distinguishing between unidentate and symmetrically bidentate nitrato groups. However it must be noted that coupling between nitrato groups may lead to complications.

Although these arguments have been developed assuming C_{2v} symmetry for unidentate nitrato groups, the conclusions for C_s are basically the same [6].

TABLE 3

Coordination bands (cm^{-1}) of the nitrate groups in uranyl(VI) nitrate complexes

Complex	Bidentate nitrate groups						
	$\nu_2 + \nu_1$	$\nu_2 + \nu_4$	Δ	$\nu_2 + \nu_3$	$\nu_2 + \nu_5$	Δ	Ref.
$UO_2(NO_3)_2 \cdot 2\ H_2O$	2580	2290	290	1767	1730	37	74
$K[UO_2(NO_3)_3]$	2545	2288	257	1767	1733	34	74
$Rb[UO_2(NO_3)_3]$	2540	2288	252	1761	1730	31	74
$Cs[UO_2(NO_3)_3]$	2540	2262	283	1756	1724	32	74
$NH_4[UO_2(NO_3)_3]$	2540	2262	283	1754	1724	30	74
$[(C_2H_5)_4N][UO_2(NO_3)_3]$	2545	2262	283	1751	1724	27	74
$UO_2(NO_3)_2(Ph_3PO)_2$	2550	2300	250	1780	1730	50	74
$UO_2(NO_3)_2(TEP)_2$	2550	2300	250	1780	1730	50	74
$UO_2(NO_3)_2(U)_2$	2540	2300	240	1788	[a]		168
$UO_2(NO_3)_2(MU)_2$	2545	2310	235	1782	1740	42	168
$UO_2(NO_3)_2(DMU)_2$	2540	2295	245	1775	[a]		168
$UO_2(NO_3)_2(PhU)_2$	2545	2280	265	1775	1750	25	169
$UO_2(NO_3)_2(DPhU)_2$	2553	2280	273	1775	1750	25	169
$UO_2(NO_3)_2(EU)_2$	2540	2305	235	1778	1743	35	169
$UO_2(NO_3)_2(DEU)_2$	2547	2290	257	1772	1746	26	169
$UO_2(NO_3)_2(PhEU)_2$	2552	2290	262	1771	1740	31	169
$UO_2(NO_3)_2(2(1\text{-}Ph)U)_2$	2565	2270	295	1780 1770	1748	32 22	169
$UO_2(NO_3)_2(Me_3NO)_2$	2530	2320	210	1790	1742	48	160
$UO_2(NO_3)_2(urea)_2$	2545	2300	245	1780	[a]		154
	Ionic nitrate groups						
	$\nu_1 + \nu_3$	$\nu_1 + \nu_4$					
$[UO_2(Me_3NO)_4](NO_3)_2$	2385 [b]	1752					160
$[UO_2(urea)_4(H_2O)](NO_3)_2$	2430 [c] 2355	[a]					154

[a] Not observed. [b] Tentative assignment. [c] Split due to hydrogen bonding.

(d) A reliable distinction between unidentate and symmetrically bidentate modes of coordination has been found in the sequence of relative intensities of the three highest Raman shifts attributable to nitrate fundamentals. The sequence for unidentate species differs from that for symmetrically bidentate species. It was found that for unidentate nitrato complexes, band 2 which is due to N—O$_{\mathrm{I}}$ + N—O$_{\mathrm{II}}$ symmetric stretching (Fig. 2), is generally fairly strong and is by no means the least intense of the three bands; in contrast, for symmetrically bidentate species band 2 due to the N—O$_{\mathrm{I}}$ antisymmetric stretching, is weak and without exception the least intense of the three bands.

It appears that the relative intensities of the three highest frequency Raman shifts, together with their depolarisation ratios, currently provides the most acceptable means of distinguishing between unidentate and symmetric-

TABLE 4

Combination bands of the nitrate groups in actinide(IV) nitrate complexes (cm^{-1})

Complex	$\nu_2 + \nu_1$	$\nu_2 + \nu_4$	Δ	$\nu_2 + \nu_3$	$\nu_2 + \nu_5$	Δ	Ref.
$Cs_2[U(NO_3)_6]$	2550	2300	250	1780	1738	42	134, 140
$U(NO_3)_4(Ph_3PO)_2$	2550	2280	270	1775	1725	50	134
$U(NO_3)_4(Ph_3AsO)_2$	2540	2290	250	1771	1722	49	134
$U(NO_3)_4(HMPA)_2$	2558	2300	258	1772	1732	40	134
$U(NO_3)_4(PTPA)_2$	2545	2290	255	1768	1729	39	134
$Th(NO_3)_4 \cdot 3\ Me_3PO$	2530	2320	210	1775	1740	35	140
$U(NO_3)_4 \cdot 3\ Me_3PO$	2520	2320	200	1775	1740	35	140
$Th(NO_3)_4 \cdot 3$ HMPA	2550	2310	235	1770	1728	42	140
$[U(NO_3)_3 \cdot 4$ HMPA$][BPh_4]$	2545	2310	235	1765	1725	40	134
$Th(NO_3)_4 \cdot 4$ HMPA	2530	2380	150	1773	1741	32	140
		2370	160		1718	55	
$Th(NO_3)_4 \cdot 5\ Me_3PO$	2395	2320	75	1770	1740	30	140
		2275	120		1715	55	
$U(NO_3)_4 \cdot 5\ Me_3PO$	2510	2400	110	1765	1745	20	140
		2280	230		1715	50	

ally bidentate coordination of the nitrate group to metals.

It has been found [74] that the separation of the $\nu_2 + \nu_5$ and $\nu_2 + \nu_3$ is greater in bidentate (about 30 cm^{-1}) than in monodentate (about 10 cm^{-1}) nitrate complexes. The frequencies observed between 2300 and 2550 cm^{-1} in the spectra of some monodentate and bidentate nitrate complexes have been assigned to $\nu_2 + \nu_1$ and $\nu_2 + \nu_4$ and the separation of these two frequencies is greater for bidentate (about 200—300 cm^{-1}) than for monodentate (about 50—200 cm^{-1}) nitrate groups. Complexes containing ionic nitrate groups show only one band in this region assignable to $\nu_1 + \nu_3$. For many actinide(IV) and (VI) complexes the separations of $\nu_2 + \nu_1$ and $\nu_2 + \nu_4$ and the separations of $\nu_2 + \nu_5$ and $\nu_2 + \nu_3$ are of the order 250 cm^{-1} and 30—50 cm^{-1}, respectively, indicating that these complexes contain bidentate nitrate groups (Tables 3 and 4). For symmetrically bidentate nitrate groups (Fig. 3) the terminal N—O distance r_3 is shorter than the N—O bonds involving the coordinated oxygen atoms r_2 and r_3, the latter being larger than those in the nitrate ion (Table 5).

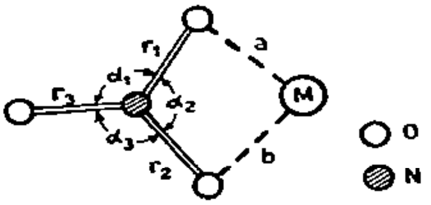


Fig. 3. The symmetrical coordination of the bidentate nitrate groups.

TABLE 5

Interatomic distances and angles [a] in actinide nitrato complexes

Compound	Bond lengths (Å) [b]					Angles (°)			Ref.
	a	*b*	r_1	r_2	r_3	1	2	3	
$Th(NO_3)_4 \cdot 5\ H_2O$									
NO_3 (1)	2.528	2.618	1.250	1.270	1.202	123.2	121.7	115.2	31
NO_3 (2)	2.554	2.573	1.264	1.275	1.206	123.0	122.5	114.5	
$MgTh(NO_3)_6 \cdot 8\ H_2O$									
NO_3 (1)	2.63	2.63	1.22	1.22	1.22	119.7	119.7	120.6	92
$(NH_4)_2Ce(NO_3)_6$									
NO_3 (1)	2.497	2.530	1.280	1.287	1.243	124.1	120.7	115.2	97
NO_3 (2)	2.510	2.488	1.272	1.289	1.235	124.5	120.9	114.6	
NO_3 (3)	2.514	2.512	1.280	1.286	1.225	115.6	120.5	113.9	
$UO_2(NO_3)_2 \cdot 2\ H_2O$									
NO_3 (Molecule I)	2.513	2.508	1.269	1.253	1.213	121.7	123.0	115.3	184
NO_3 (Molecule II)	2.491	2.477	1.275	1.262	1.190	122.1	123.5	114.4	
$UO_2(NO_3)_2 \cdot 6\ H_2O$									
NO_3 (1)	2.504	2.504	1.271	1.271	1.208	122.7	122.7	114.6	69
NO_3 (2)	2.547	2.547	1.260	1.260	1.231	122.2	122.2	115.6	
$RbUO_2(NO_3)_3$									
NO_3 (1)	2.48	2.48	1.26	1.26	1.21	121.2	121.2	117.5	107
$Rb_2UO_2(NO_3)_4$ [c]									
NO_3 (1)	2.51	2.45	1.45	1.33	1.10				112
NO_3 (2)	2.48		1.22	1.23	1.15				

[a] Apart from those in $UO_2(NO_3)_2 \cdot 2\ H_2O$ the nitrate groups designated (1) and (2) are bonded to the same metal atom. [b] The meaning of *a*, *b*, r_1, r_2, r_3, 1, 2 and 3 is shown in Fig. 3. [c] $NO_3(2)$ in $Rb_2UO_2(NO_3)_4$ is monodentate, therefore r_1 refers to the coordinate oxygen—nitrogen distance and r_2 and r_3 to the remaining distances.

C. ACTINIDE(III) NITRATES AND COMPLEXES

Solid compounds containing either covalent or ionic nitrate, or both, have been characterized for the lanthanide elements in the trivalent state. In contrast to this, no solid compounds appear to be known for the trivalent actinide elements. The absence of trivalent actinide compounds for the earlier members of the series is readily accounted for by the ease with which this valence state is oxidized for the elements up to and including plutonium [15]. However, this valence state is appreciably more stable for americium and the following elements and the present situation reflects a combination of a lack of research and the very small quantities of many of these man-made elements at present available.

D. ACTINIDE(IV) NITRATES AND COMPLEXES

(i) Nitrates

In view of the ready oxidation of protactinium(IV) it is unlikely that a tetranitrate or tetranitrate hydrates will be capable of existence. Although a di-, tri- and hexahydrate of thorium tetranitrate have been reported the existence of these phases has not been positively established.

An investigation of the thorium(IV) nitrate—nitric acid—water system has revealed that only $Th(NO_3)_4 \cdot 5\ H_2O$ and $Th(NO_3)_4 \cdot 4\ H_2O$ can be isolated as stable phases at room temperature [16]. Thorium(IV) nitrate crystallizes readily from aqueous nitric acid solution as the pentahydrate $Th(NO_3)_4 \cdot 5\ H_2O$ while the tetrahydrate crystallizes only when the nitric acid concentration is very high [16].

There have been several unsuccessful attempts to isolate uranium(IV) nitrates from aqueous solution which have all resulted in uranyl compounds [19,20]. The compound $UO(NO_3)_2$, reported to be stable to 100°C, has however been reported to precipitate during the photochemical reduction of an aqueous-ethanolic solution of uranyl nitrate [21]; more recently $UO(NO_3)_2 \cdot 4\ H_2O$ has been reported to form when uranium(IV) in 2 M nitric acid is treated with dioxan [22]. Attempts to repeat these preparations have been unsuccessful [23]. The preparation of uranium tetranitrate by reaction of uranium tetrachloride in acetone with silver nitrate in acetonitrile has been attempted [23]; the green solution, after removal of silver chloride, was evaporated under vacuum at room temperature, but as the green solid product separated in the last stages of the evaporation it oxidized spontaneously to uranium(VI). Similarly evaporation in vacuo of a solution of uranium(IV) in 2 M nitric acid yielded a green solid which oxidised spontaneously. Strong cooling of solutions of the tetranitrate in acetonitrile did not lead to separation of a solid [23]. Azeotropic distillation of uranium(IV) in dilute nitric acid with diethylether yielded a black sludge of oxide and removal of acid and water by repeatedly shaking similar solutions with ethyl acetate ultimately gave a 3% yield of a green solid of composition $UO(NO_3)_{1.03-1.54} \cdot 2.4-4.9\ H_2O$ which evolved oxides of nitrogen at 80°C and was oxidised to uranium(VI) at 100°C in air. It seems unlikely that the compound previously reported [21] to be stable at 100°C was a uranium(IV) nitrate [23].

Neptunium(IV) is fairly stable in dilute nitric acid at room temperature whereas oxidation to neptunium(V) is quite rapid in 1 M nitric acid at 90°C [24]. On vacuum evaporation of a neptunium(IV) solution in dilute nitric acid no oxidation is observed and thus the grey, moisture-sensitive dihydrate $Np(NO_3)_4 \cdot 2\ H_2O$ can be obtained on vacuum evaporation of a 0.1 M nitric acid solution of neptunium(IV) [24]. $Np(NO_3)_4 \cdot 2\ H_2O$ decomposes above 50°C at 10^{-3} mm to the dioxide, NpO_2, with no evidence for intermediate species. $Np(NO_3)_4 \cdot xN_2O_5$ ($x = 1.2$) has been prepared by reaction of neptunium(IV) tetrachloride with dinitrogen pentoxide [24]. Prolonged pumping at room temperature does not completely remove the adduct ($x \simeq 0.2$) and slight warming on a water-bath causes partial oxidation to neptunium(V). Dried neptunium(IV) hydroxide reacts with N_2O_5 to yield a similar product, confirmed by X-ray powder diffraction results, but it also undergoes partial oxidation to neptunium(V) [24]. Thermogravimetric analysis [24] of this product shows that decomposition starts at about 80°C at 10^{-3} mm. From about 190 to 210°C the decomposition curve indicates the presence of an intermediate product which appears to be $NpO_2(NO_3)_2$, although it could not be isolated pure since it is stable over such a short temperature range. The isolated sample hydrated in air and gives a weight increase corresponding to the formation of NpO_2-$(NO_3)_2 \cdot 6\ H_2O$. A short plateau occurs in the decomposition curve between about 310 and 340°C, possibly due to a higher neptunium oxide, since a small weight loss was observed above 340°C to produce NpO_2 [24].

Plutonium(IV) nitrate pentahydrate $Pu(NO_3)_4 \cdot 5\ H_2O$ forms when a nitric acid solution of plutonium(IV) is slowly evaporated at room temperature. The product crystals are green if smaller than about 1 mm; larger crystals appear to be black. They are fairly stable, both in humid and dry air [17]. A thermogravimetric study of the hydrate reveals that it begins to decompose at 40°C and to melt or deliquesce at 95 to 100°C. After rapid decomposition around 100°C a fairly unstable intermediate product forms between 150 and 220°C. Decomposition above 220°C is very rapid; at 250°C conversion to the dioxide is essentially complete although there continues to be a slight weight loss above this temperature. The ignition of the nitrate at 1250°C produces oxygen deficient plutonium dioxide [18]. $Pu(NO_3)_4 \cdot 5\ H_2O$ is readily soluble in water, the stability of the solution being dependent on the concentration of the salt. A dilute solution, initially brown, changes to green as colloidal plutonium forms. Since the colloid does not form in solutions of high nitrate ion concentration, the concentrated solutions of the salt remain brown. Solutions of the nitrate in concentrated HNO_3 are green due to plutonium nitrate complexes; acetone and diethylether solutions of the nitrate are also green.

Anhydrous nitrates are not obtained by thermal decomposition of the various hydrates although there is some evidence for the formation of nitrate-deficient lower hydrates such as $ThO_{0.15}(NO_3)_{3.7} \cdot x\ H_2O$ when $Th(NO_3)_4 \cdot 5\ H_2O$ is heated at moderate temperatures [25]. $ThO(NO_3)_2 \cdot H_2O$ is reported to form when the pentahydrate is heated at 140°C and it is suggested, on the basis of IR data, that Th—O—Th groups are present in this compound. An earlier report [26] that ionic nitrate is present in the lower hydrate produced by thermal decomposition of $Th(NO_3)_4 \cdot 4\ H_2O$ appears to be incorrect [25,27]. Anhydrous $Th(NO_3)_4$, a white, moisture-sensitive compound, is best prepared by the vacuum thermal decomposition of $Th(NO_3)_4 \cdot 2\ N_2O_5$ at ca. 150°C [28] or $Th(NO_3)_4 \cdot 2\ N_2O_4$ at 90°C [29], the former decomposes at higher temperatures (~190°C) to give the oxynitrate $ThO(NO_3)_2$.

No structural data are available for $Th(NO_3)_4$ but the crystal and molecu-

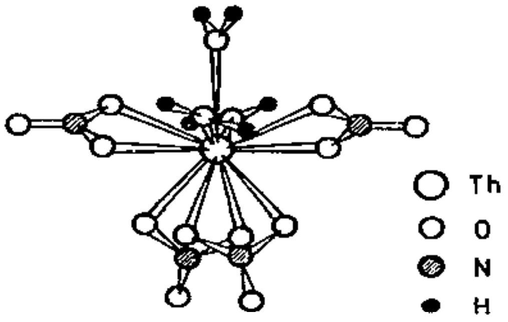


Fig. 4. The molecular structure of $Th(NO_3)_4 \cdot 5\ H_2O$.

lar structure of $Th(NO_3)_4 \cdot 5\ H_2O$ has been reported [30,31]. Determinations of the structure of $Th(NO_3)_4 \cdot 5\ H_2O$ by X-ray [30] and by neutron diffraction [31] are in excellent agreement. There are eleven oxygen atoms bound to the thorium atom, eight from four bidentate nitrate groups and three from the water molecules. The arrangement around the thorium (Fig. 4) is complex and cannot be described in terms of a coordination polyhedron, but if the nitrate groups are regarded as single units, the geometry is approximately that of a singly capped trigonal prism. The remaining two molecules of water are not bonded to the metal. The Th—O(nitrate) distances range from 2.528 to 2.618 Å and the Th—O(water) distances range from 2.438 to 2.473 Å. The hydrogen bond scheme is shown in Fig. 5. Two different types of hydrogen bonding are present: two strong water—water hydrogen bonds with bond distances of 2.70 Å (O(1)···H(1)···O(3) and O(2)···H(2)···O(3) in Fig. 5) and three weaker water—nitrate oxygen hydrogen bonds with bond distances of 2.90–2.95 Å (O(2)···H(3)···O(22), O(3)···H(4)···O(22) and O(3)···H(5)··· O(13) in Fig. 5). The water oxygen atom O(3), not bonded to the thorium atom, has an approximately tetrahedral disposition of hydrogen bonds about

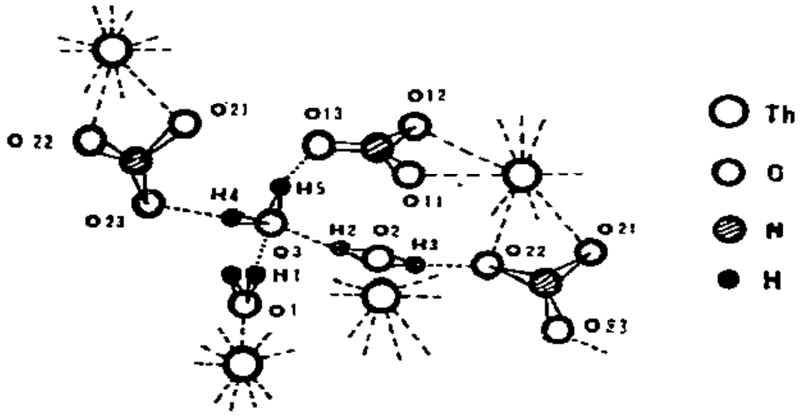


Fig. 5. The hydrogen bonding system in $Th(NO_3)_4 \cdot 5\ H_2O$.

TABLE 6

Crystallographic data for actinide nitrates and nitrato complexes

Compound	Colour	Symmetry; space group	Lattice parameters				Ref.
			a_0(Å)	b_0(Å)	c_0(Å)	β°	
$Th(NO_3)_4 \cdot 5\ H_2O$	White	O; *Fdd*2	11.191	22.889	10.579		30, 31
$Pu(NO_3)_4 \cdot 5\ H_2O$	Green	O; *Fdd*2	11.14	22.55	10.51		217
$Th_2(OH)_2(NO_3)_6 \cdot 8\ H_2O$	White	M; $P2_1/c$	6.772	11.693	13.769	102.63	41
$Th(OH)_2(NO_3)_2 \cdot xH_2O$	White	M; $C2/c$	14.25	8.95	6.11	98.0	218
$MgTh(NO_3)_6 \cdot 8\ H_2O$ [a]	White	M; $P2_1/c$	9.08	8.75	13.61	97.0	92
$(NH_4)_2Ce(NO_3)_6$ [b]		M; $P2_1/n$	13.061	6.842	8.183	91.34	97

[a] The analogous Mn, Co, Ni and Zn complexes are isostructural. [b] The analogous Th and Pu complexes are isomorphous [84].

it. The hydrogen bond scheme is in accord with the IR spectrum of $Th(NO_3)_4 \cdot 5\ H_2O$, in which a broad band at 3100 cm^{-1} corresponding to strongly hydrogen bonded water is present, with more weakly hydrogen bonded water in evidence at 3440 cm^{-1}. $Th(NO_3)_4 \cdot 5\ H_2O$ and $Pu(NO_3)_4 \cdot 5\ H_2O$ are isostructural; the crystallographic data are listed in Table 6. Infrared [23,27,32–34] and Raman [34–36] bands for $Th(NO_3)_4 \cdot 5\ H_2O$ have been assigned on the basis of the presence of bidentate covalently

TABLE 7

Infrared data (cm^{-1}) for tetravalent actinide nitrates and nitrato complexes

Compound	ν_1	ν_4	ν_2	ν_6	ν_5/ν_3	ν_{M-O}	Ref.
$Th(NO_3)_4$	1620 1560	1328 1240	1010	800	740	244	27
$Th(NO_3)_4 \cdot 5\ H_2O$	1550 1510 1420	1350 1325 1293	1040 1030	875 815 808	760 745	244 211	27
$Th(NO_3)_4 \cdot 4\ H_2O$	1550 1500	1320 1290	1040 1030	812 805	759 743	249 218	27
$Np(NO_3)_4 \cdot 2\ H_2O$	1524	1287	1034	804	765 749		24
$Cs_2Th(NO_3)_6$	1550 1527	1276	1026	805	738 702		88
$Cs_2Np(NO_3)_6$	1523	1280	1028	802	742 702		88
$MgTh(NO_3)_6 \cdot 8\ H_2O$	1520	1313 1293 1280	1037	813	750 727		34

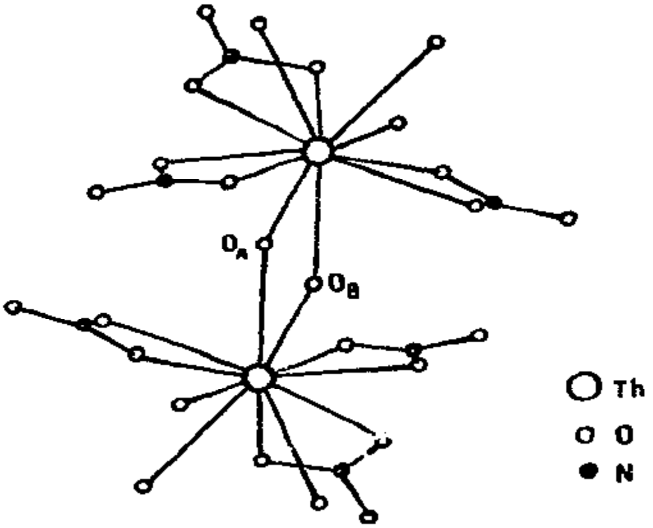


Fig. 6. The molecular structure of $Th_2(OH)_2(NO_3)_6(H_2O)_6$.

bonded nitrate groups and are consistent with the above structure. The IR frequencies together with their assignments are shown in Table 7 together with those of other actinide tetranitrate hydrates and $Th(NO_3)_4$. Although no structural information or Raman results are available to confirm the presence of bidentate nitrate groups in these other compounds it is possible that they are correct since such actinide compounds do tend to exhibit high coordination number and the presence of monodentate nitrate groups has only been demonstrated for some uranyl compounds [112,224,226]. It is interesting to note that the sequence of relative intensities of ν_1, ν_4 and ν_2 (medium, weak and strong) in the Raman spectrum [34,35] of $Th(NO_3)_4 \cdot 5\ H_2O$ indicates the presence of bidentate rather than monodentate groups. In addition the separation of ν_4 and ν_1 in the IR spectrum is of the magnitude frequently associated with bidentate nitrate groups although this criterion is admittedly less reliable than those based on either the sequence of relative intensities or the depolarisation ratios of the three highest frequency Raman shifts. Th—O stretching vibrations have been tentatively assigned at 244 cm^{-1} for $Th(NO_3)_4$, 249 and 218 cm^{-1} for $Th(NO_3)_4 \cdot 4\ H_2O$ and 244 and 211 cm^{-1} for $ThO(NO_3)_4 \cdot 5\ H_2O$. Both IR and Raman studies have demonstrated the existence in aqueous solution of the species $Th(NO_3)^{3+}$ and $Th(NO_3)_2^{2+}$ [37] for which it was not possible to demonstrate unequivocally the nature of the nitrate coordination but there was some evidence for the existence of non-equivalent groups in $Th(NO_3)_2^{2+}$. A polarised band at 230 cm^{-1} was assigned to the metal—oxygen stretching mode. Addition of hydrogen peroxide to thorium in aqueous nitric acid results in the formation of a polymeric peroxynitrate, $Th_6(OO)_{10}(NO_3)_4 \cdot 10\ H_2O$ [38]. Hydrolysis of aqueous thorium(IV) nitrate solution leads to the formation of polynuclear complexes and different suggestions have been made as to the complexes really formed [39,40], but most investigations seem to agree that the first step is the formation of a dinuclear complex. Crystals of composition $Th_2(OH)_2(NO_3)_6 \cdot 8\ H_2O$ containing discrete dinuclear complexes can be obtained from weakly hydrolyzed thorium nitrate solution [41]. The structure (Fig. 6) is built up from discrete complexes each containing two thorium atoms joined by two bridging oxygens (O_A, O_B). The Th—Th distance within a complex is 3.988 Å, whereas the shortest distance between thorium atoms belonging to different complexes is 6.77 Å. Three nitrate groups, acting as bidentate ligands, are coordinated to each thorium atom and a coordination number of eleven is achieved by coordination of three water molecules. The coordination around thorium is rather irregular; if each nitrate group is considered as a single ligand, however, the coordination polyhedron may be described as a somewhat distorted dodecahedron. The two bridging oxygens, which should be hydroxo groups, do not seem to be involved in any hydrogen bonding. There are two waters of crystallization; all the oxygen atoms of the bonded and non-bonded waters are involved in short O···O contacts (2.77—2.96 Å) indicative of hydrogen bonding. The discrete units building up the structure can thus be described by the formula $Th(OH)_2$-$(NO_3)_3(H_2O)_6 \cdot 2\ H_2O$. Each group is bound to other groups only by means of hydrogen bonds and Van der Waals contact and different groups have no oxygen atoms in common. The hydrolysis products of thorium nitrate have been studied and an X-ray investigation has been made of solutions prepared by dissolving aqueous thorium oxide in thorium nitrate solutions [41]. The variation of the scattering curves with the hydroxyl number at a total constant thorium concentration of 2 M has been measured. The coordination number found for thorium in solution is close to the values found in crystal structures. The nitrate group is coordinated to thorium as a bidentate ligand. A dominating dinuclear complex is consistent with the data for low hydroxyl numbers but for more than about 2 OH per thorium the average nuclearity is four or larger. The shortest distance between the thorium atoms in the polynuclear hydrolysis products is 3.94 Å, which is close to values found in basic thorium salts.

(ii) Nitrato complexes

Hexanitrato complexes of the type $M^I_2M^{IV}(NO_3)_6$ (M^I = univalent cation; M^{IV} = actinide element) are known for thorium(IV) [82—85,91], uranium-(IV) [23,86,89], neptunium(IV) [83,86,88] and plutonium(IV) [83,86,89,91]; there appears to have been no attempt to prepare analogous protactinium(IV) complexes. The above compounds and those of the type $M^{II}M^{IV}(NO_3)_6 \cdot 8\ H_2O$ (M^{II} = Mg, Zn, Co, Ni and Mn; M^{IV} = thorium [34,92], uranium [87] and plutonium [91]) are all conveniently obtained by mixing the appropriate tetravalent actinide and the uni- or divalent cation nitrate is nitric acid solution. $Cs_2Th(NO_3)_6$ has also been prepared by the reaction between $CsNO_3$ and $(NO_2)_2[Th(NO_3)_6]$ [29]. $Th(NO_3)_4 \cdot 2\ N_2O_5$, formulated as $(NO_2)_2$[Th-

$(NO_3)_6]$ on the basis of IR results (νNO_2^+ at 2360 cm^{-1}), is conveniently obtained by the addition of N_2O_5 to $Th(NO_3)_4 \cdot 5\ H_2O$ in anhydrous nitric acid [28]. Treatment with N_2O_4 results in the formation of $Th(NO_3)_4 \cdot 2\ N_2O_4$ (the formulation $(NO)_2[Th(NO_3)_6]$ has been inferred from the presence in the IR spectrum of a band at 2270 cm^{-1} due to the NO^+ group [29]).

Uranium(IV) hexanitrato complexes undergo oxidation when heated in air [87] decomposing at around 100°C to yield either uranyl(VI) trinitrato complexes $M^IUO_2(NO_3)_3$ ($M^I = NH_4$) or uranyl(VI) tetranitrato complexes $M_2^IUO_2(NO_3)_4$ (M^I = Rb, Cs, PyH, QuinH) and $M^{II}UO_2(NO_3)_4$ (M^{II} = Mg and Zn). The tetranitrates are unstable and decompose to the trinitrates at higher temperatures.

$[(C_2H_5)_4N]_2[M(NO_3)_6]$ (M = Th, Np, Pu) compounds have been prepared [83] by the gradual mixing of solutions of actinide(IV) nitrate and $[(C_2H_5)_4N]NO_3$ in stoicheiometric amounts.

A tetrabutylammonium salt of plutonium(IV) has been prepared in an analogous manner and was assumed from the method of preparation to be $[(C_4H_9)_4N]_2[Pu(NO_3)_6]$ [83]. Caesium and tetraethylammonium hexanitrato-uranate(IV) are precipitated when the appropriate nitrate in concentrated nitric acid saturated with sulphamic acid is added to uranium(IV) in 8 M nitric acid—sulphamic acid at 0° [23,86]. $Cs_2[U(NO_3)_6]$ can also be prepared by treating solid $Cs_2[UCl_6]$ with an acetone solution of $AgNO_3$ [23]; similar procedures have been used for the preparation of $Cs_2[Np(NO_3)_6]$ [93]. $[(C_2H_5)_4N]_2[U(NO_3)_6]$ has also been obtained [23] by adding an excess of $[(C_2H_5)_4N]NO_3$ in concentrated nitric—sulphamic acid to a solution of uranium(IV) in perchloric acid at 0° C. $[(C_2H_5)_4N]_2[U(NO_3)_6]$ is not hygroscopic and is stable at room temperature for many weeks; it decomposes at 120—125° C, oxides of nitrogen being detectable and at 150° C oxidation to uranium(VI) is rapid. The oxidised product melts at 162—164° C, releasing trapped oxides of nitrogen [23]. $Cs_2[U(NO_3)_6]$ decomposes very slowly at

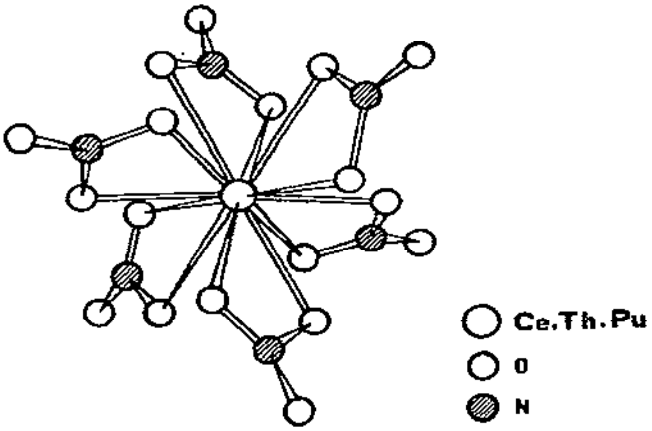


Fig. 7. The arrangement of the hexanitratocerate anion in the complex $(NH_4)_2[Ce(NO_3)_6]$.

room temperature, more rapidly when heated, oxides of nitrogen being detectable at 100--105° C; decomposition is very rapid at 155--165° C with oxidation to the hexavalent state [23].

Crystals of pale green $K_2[Pu(NO_3)_6]$ have been formed by cooling to 1°C a 12 M HNO_3 solution containing the appropriate concentrations of KNO_3 and plutonium(IV) nitrate [94,95]. The pale green $Rb_2[Pu(NO_3)_6]$ and $Cs_2[Pu(NO_3)_6]$ are formed when solutions of the respective nitrates are mixed with plutonium(IV) nitrate solutions [94,95]. $[(C_5H_5NH)]_2[Pu(NO_3)_6] \cdot 14\ H_2O$ and $[(C_9H_7NH)]_2[Pu(NO_3)_6]$ are obtained by mixing the appropriate nitrate solutions. The solubility of rubidium, caesium, pyridinium and quinolinium plutonium(IV) hexanitrates is low enough for crystallization without cooling [94--96]. The compounds $(NH_4)_2[Ce(NO_3)_6]$, $(NH_4)_2[Th(NO_3)_6]$ and $(NH_4)_2[Pu(NO_3)_6]$ have been found by X-ray analysis to be isomorphous [83] and the crystal and molecular structure of $(NH_4)_2[Ce(NO_3)_6]$ has been more recently determined [97]. The structure (Fig. 7) is composed of ammonium cations and hexanitratocerate anions. The hexanitratocerate anion results from the bidentate coordination of six nitrate groups about each ceric atom; the anion has a symmetry which closely approximates T_h with a $\bar{3}$ axis parallel to the crystallographic *b* axis. The bond distance for the nitrogen to the noncoordinating oxygen is significantly shorter than the other N—O distances in each nitrate group. The average Ce—O distance is 2.50 Å, the average N—O distance involving a coordinated oxygen is 1.28 Å and the average N—O distance involving a noncoordinated oxygen is 1.23 Å. X-ray diffraction studies of concentrated aqueous solutions of $(NH_4)_2[Ce(NO_3)_6]$ indicate a coordination number of twelve for cerium with an average Ce—O distance of 2.85 Å and an average N—O distance of 1.35 Å [98]; in the solid state the structure is held together by a three dimensional network of hydrogen bonds [97]. Although there are no X-ray structural results available for actinide(IV) hexanitrato complexes of the type $M^I_2M^{IV}(NO_3)_6$ the relative intensities

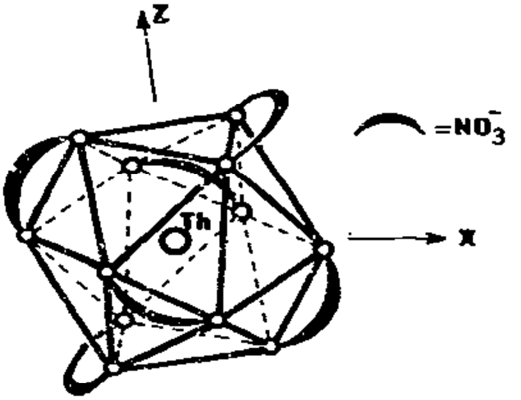


Fig. 8. The coordination around the thorium ion in the complex $[Mg(H_2O)_6][Th(NO_3)_6] \cdot 2\ H_2O$.

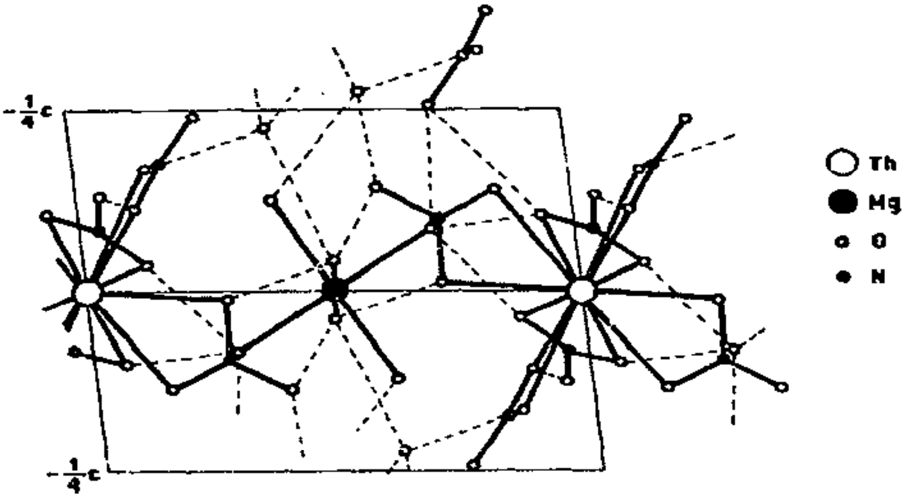


Fig. 9. The molecular structure of $[Mg(H_2O)_6][Th(NO_3)_6] \cdot 2\ H_2O$ in the (010) projection.

(m, w, s) of the three highest frequency Raman shifts recorded for certain thorium(IV) complexes (M^I = Rb and Cs) indicate [34], as one might anticipate in view of the similarity in ionic radius of cerium(IV) and thorium(IV), that bidentate nitrate groups are present. Recent IR data [88] for $Cs_2[Th(NO_3)_6]$ and $Cs_2[Np(NO_3)_6]$ are assigned on this basis in Table 7. X-ray structure analysis of magnesium thorium nitrate hydrate $MgTh(NO_3)_6 \cdot 8\ H_2O$ has been reported [92]. The compound is better formulated as $[Mg(H_2O)_6][Th(NO_3)_6] \cdot 2\ H_2O$; thus the magnesium atom is surrounded by six water molecules disposed at the corners of a nearly regular octahedron. The average $Mg—OH_2$ distance, 2.12 Å, slightly exceeds the sum of ionic radii. Each thorium atom is surrounded by twelve nitrate oxygen atoms. The lengths of the Th—O bonds are from 0.1 to 0.4 Å greater than the sum of ionic radii; the variation of thorium to oxygen distances is appreciable, ranging from 2.50 to 2.80 Å, the average distance being 2.63 Å. These oxygen atoms are at the corners of an irregular icosahedron. Two water molecules do not participate in the formation of the coordination polyhedra around the metal atoms and can be regarded as isolated waters of crystallization. The icosahedron and the octahedron do not share either edges or corners. Connection between them is effected through the weak hydrogen bonds. The other $M^{II}Th(NO_3)_6 \cdot 8\ H_2O$ complexes (M^{II} = Zn, Co, Mn, Ni) crystallize in the same space group and have similar lattice parameters, being isomorphous with $[Mg(H_2O)_6][Th(NO_3)_6]\ 2\ H_2O$ (Figs. 8 and 9). Infrared and Raman results are also now available [34] for the compounds $M^{II}Th(NO_3)_6 \cdot 8\ H_2O$ (M^{II} = Mg, Mn, Ni, and Co) the latter being consistent with the X-ray structural results.

There is evidence that solutions of the tetravalent actinides in concentrated nitric acid solution also give rise to the hexanitrato anion. Thus, the results of the extraction studies employing tri-n-octylamine in xylene are most readily interpreted on this assumption. When absorption spectra are compared, it is found that the spectra for the amine solution and for the concentrated nitric acid solution are identical with those of a solution of the hexanitrato complex and the solid. In addition, the spectrum of the metal ion in less concentrated nitric acid solution is quite different [86]. It must be remembered that in the case of uranium(IV) [99] the species present in solution will be influenced not only by nitrate ion concentration but also by other factors, such as the acidity.

The unusual complex $H_3K_3Th(NO_3)_{10} \cdot 4\ H_2O$ [34], contains both covalent and ionic nitrate groups. This observation is not surprising but, nonetheless, it would be of interest to have structural information on this complex since, like the uranyl complex $M^I_2[UO_2(NO_3)_4]$, it may contain both bidentate and monodentate nitrates.

Papers [34,82] dealing with the preparation of a series of complexes of the type $M^ITh(NO_3)_5 \cdot xH_2O$ (M^I = NH_3Me, NH_3Et and NH_2Et_2 with x = 7, 8, 5 and 11, respectively) have appeared recently but although the older literature contains reports of the existence of complexes of the type $M^I[Th_2(NO_3)_7] \cdot x\ H_2O$ these results have not been confirmed.

E. ACTINIDE(V) NITRATES AND COMPLEXES

(i) Nitrates

Fuming nitric acid solutions of protactinium(V) are reasonably stable and hydrolytic condensation of protactinium(V) is not observed after several days at room temperature. No crystallisation takes place during this time and on vacuum evaporation of the solutions obtained by dissolving protactinium halides these initially become colourless and finally deposit a white, non-crystalline compound of variable water content; the product invariably has a 3 : 1 nitrate to protactinium(V) ratio but the number of water molecules ranges from 1.5 to 4.0. Accordingly the product has been designated $PaO(NO_3)_3 \cdot xH_2O$. Attempts to obtain the anhydrous compound by prolonged pumping in vacuo at room temperature or by vacuum thermal analysis have been unsuccessful. In the latter case the hydrated compound starts to decompose at about 50°C at 10^{-3} mm with no evidence of stable phases between the hydrated oxytrinitrate and the pentoxide Pa_2O_5 [42].

Protactinium pentachloride and pentabromide react in anhydrous CH_3CN with gaseous dinitrogen tetroxide to give the white $Pa_2O(NO_3)_8 \cdot 2\ CH_3CN$ while vacuum evaporation of a dinitrogen pentoxide solution obtained on dissolution of protactinium(V) hydroxide, pentachloride, pentabromide or the chloro-complex $SO[PaCl_6]_2$ yields the white solid $HPa(NO_3)_6$, which is immediately decomposed by water and aqueous ammonia [42]. $HPa(NO_3)_6$ is insoluble in anhydrous CH_3CN and CH_2Cl_2 and does not react with Ph_3PO dissolved in these solvents. $Pa_2O(NO_3)_8 \cdot 2\ CH_3CN$ and $HPa(NO_3)_6$ are thermally unstable, starting to decompose above 50°C at 10^{-3} mm, and vacuum thermogravimetric studies have failed to characterise the anhydrous

TABLE 8

Infrared data for pentavalent oxynitrates and hexanitratoprotactinates(V)

Compound	ν_1	ν_4	ν_2	ν_6	ν_5/ν_3	$\nu_{M—O}$	Ref.
$PaO(NO_3)_3 \cdot xH_2O$	1524	1269	1021	804	746	773	42
$Pa_2O(NO_3)_8 \cdot 2\ CH_3CN$	1603	1299	1016	803	749	721	42
	1558	1256		798			
$NpO(NO_3)_3 \cdot 3\ H_2O$	1495	1292	1040	803	750	961	24
		1277	1022		739		
$NpO_2(NO_3) \cdot H_2O$	1517	1308	1044	813	752	759	24
$HPa(NO_3)_6$	1600	1299	1018	803	746		42
	1563	1267		796			
	1536						
$CsPa(NO_3)_6$	1594	1290	1015	799	751		42
	1558	1262		792	744		
	1527	1220		786			
$NEt_4Pa(NO_3)_6$	1597	1277	1023	810	750		42
	1567	1255		803	747		
	1541			799			

$Pa_2O(NO_3)_8$ or to furnish any reproducible indication of stable nitrates intermediate between the starting compounds and protactinium pentoxide [42].

Pink, deliquescent neptunium(V) oxynitrate hydrate $NpO(NO_3)_3 \cdot 3\ H_2O$ was obtained by evaporating a solution of neptunium(V) in 1 M nitric acid to dryness. Evaporation of a neutral solution of neptunium(V) in nitrate media, prepared by dissolving neptunium(V) hydroxide in the minimum volume of dilute nitric acid, yields the green deliquescent compound $NpO_2NO_3 \cdot H_2O$ [24]. An alternative formulation of $NpO(NO_3)_3 \cdot 3\ H_2O$ is $NpO_2(NO_3)_2 \cdot 0.5\ N_2O_4 \cdot 3\ H_2O$. However, the chemical behaviour of this product indicates that the neptunium(V) formulation is correct [24]. $NpO_2NO_3 \cdot H_2O$ begins to lose the water of crystallization at about 80°C at 10^{-3} mm and the anhydrous compound NpO_2NO_3, which is extremely moisture-sensitive and deliquesces in moist air, can be isolated in the temperature range 140—220°C [24]; this decomposes above 220°C at 10^{-3} mm, yielding the dioxide. Both dried neptunium(V) hydroxide and neptunium pentoxide, Np_2O_5, dissolve in N_2O_5 with partial reduction, the product isolated by vacuum evaporation containing both neptunium(IV) and neptunium(V) [24]. Structural data are not available for the actinide(V) nitrate compounds but IR results indicate the presence of covalent nitrate groups only (Table 8) [24,42].

A band at 773 cm^{-1} for $PaO(NO_3)_3 \cdot xH_2O$ and at 721 cm^{-1} for $Pa_2O(NO_3)_8$ 2 CH_3CN suggests the presence of the Pa=O—Pa group; the absence of IR vibrations associated with the Pa=O groups in $PaO(NO_3)_3 \cdot xH_2O$ is indicative of a dimeric or even polymeric structure [42].

The metal—oxygen stretching vibration in $NpO(NO_3)_3 \cdot 3\ H_2O$ is at 960 cm^{-1} while in $NpO_2NO_3 \cdot H_2O$ it occurs at a much longer wavelength, 756 cm^{-1}. The longer wavelength of the Np=O vibration in compounds containing the NpO_2^+ species has also been observed in $Cs_3NpO_2Cl_4$ [24] (800 cm^{-1}) and in concentrated neptunium(V) solutions in dilute perchloric acid (824 cm^{-1}) [24].

Although no americium(V) nitrates are known, the stability of americium(V) in aqueous solution suggests that at least the hydrate $AmO_2NO_3 \cdot xH_2O$ could be prepared [15].

(ii) Nitrato complexes

Only protactinium is known to form pentavalent nitrato complexes [42]. Products of the type $M^IPa(NO_3)_6$ (M^I = Cs, NEt_4 and NMe_4) are obtained by treatment of the appropriate hexachloroprotactinate(V) with liquid dinitrogen pentoxide at room temperature. The white hexanitrato complexes are isolated by removal of excess dinitrogen pentoxide. The complexes are immediately decomposed by water, aqueous ammonia and dilute acids but can be handled in dry air [42]. The spectra do not contain ionic nitrate vibrations (Table 8); the complexes appear to possess low symmetry. Oxides of nitrogen are evolved at approximately 90°C at 10^{-3} mmHg.

Attempts to prepare tetramethylammonium octanitratoprotactinate(V) from $(NMe_4)_3[PaCl_8]$ have been unsuccessful; the product is a mixture of $(NMe_4)[Pa(NO_3)_6]$ and NMe_4NO_3.

F. ACTINIDE(VI) NITRATES AND COMPLEXES

(i) Nitrates and nitrate hydrates

Hexavalent nitrates of the type $MO_2(NO_3)_2$ are known for both uranium and plutonium and a range of hydrated compounds is known for each of these elements (Table 1). Relatively little work has been done on the analogous neptunium(VI) system and only the hexahydrate, $NpO_2(NO_3)_2 \cdot 6\ H_2O$, is known at present but it is likely that under the correct conditions other hydrates and $NpO_2(NO_3)_2$ will exist. A variety of methods has been reported for the preparation of anhydrous uranyl nitrate [19,43,44]. Easily the most satisfactory is the thermal decomposition of the dinitrogen tetroxide adduct $UO_2(NO_3)_2 \cdot N_2O_4$ [45] which is obtained from reactions involving dinitrogen tetroxide and uranium metal, uranium oxides or uranium halides. The temperature of decomposition appears to be critical, pure uranyl(VI) nitrate being obtained at 163—165°C [43,44]. The dinitrogen pentoxide adduct, $UO_2(NO_3)_2 \cdot N_2O_5$, provides an alternative starting material; it is somewhat less stable than the dinitrogen tetroxide adduct, decomposing at 125—130°C [46]. $UO_2(NO_3)_2 \cdot N_2O_4$ has also been alternatively formulated as $(NO)[UO_2(NO_3)_3]$ [45], largely on the basis of the appearence in the IR spectrum of frequencies attributed to the NO^+ ion. Others [44] concluded that ionic species play little part in the structure of either the solid compound or in solutions. The electrical conductivity of solutions in nitromethane indicate little ionization and electrolysis in the same solvent shows that the small degree of ionization which exists, results only in cationic uranium species. Furthermore, the IR spectrum of the solid contains bands which can be attributed to molecular N_2O_4, while bands in the NO^+ region have been attributed to overtones or combinations of fundamental nitrate frequencies [44]. Anhydrous uranyl(VI) nitrate has also been reported to form as an intermediate in the thermal decomposition of the various uranyl(VI) nitrate hydrates [47—50] but this type of reaction is less important than those mentioned above on account of the possibility of hydrolysis occurring. Contamination of the product with UO_3 has, in fact, been mentioned [50].

Conditions for the preparation of uranyl(VI) hexa-, tri- and dihydrate are well established [27,51—54]. The hexahydrate is obtained by crystallization from aqueous nitric acid followed by drying over 35—40% sulphuric acid or by evaporation of ethereal extracts of uranium(VI). Crystallization from con-

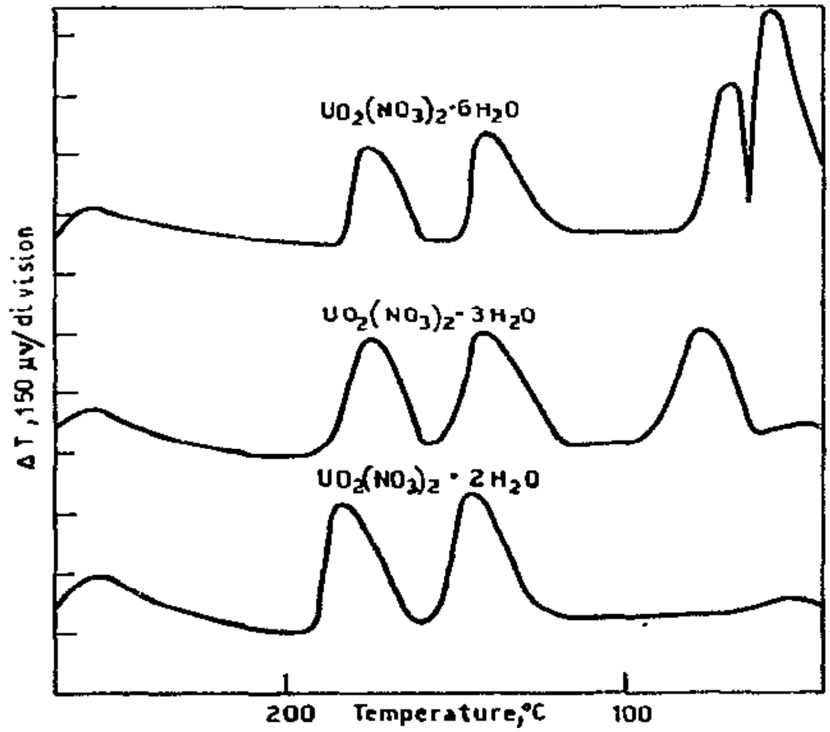


Fig. 10. DTA thermograms in dry nitrogen of $UO_2(NO_3)_2 \cdot 6H_2O$, $UO_2(NO_3)_2 \cdot 3H_2O$ and $UO_2(NO_3)_2 \cdot 2H_2O$.

centrated nitric acid or vacuum dehydration of the hexahydrate over 60—65% sulphuric acid results in the formation of $UO_2(NO_3)_2 \cdot 3\ H_2O$ whilst dehydration over 95% sulphuric acid yields the dihydrate $UO_2(NO_3)_2 \cdot 2\ H_2O$. This last compound is also formed by the thermal decomposition of $UO_2(NO_3)_2 \cdot N_2O_5 \cdot 2\ H_2O$.

Details of the dehydration and thermal decomposition of uranyl(VI) nitrate hexahydrate have been published [50,51]. Previous studies were primarily concerned with the steps of the decomposition and with the oxides produced by the decomposition rather than with the steps of dehydration. $UO_2(NO_3)_2 \cdot 6\ H_2O$ was reported [51] to melt at 65°C when heated in a stream of air and to lose four molecules of water at 110°C, another water molecule at 175°C and the last water molecule at 205°C. A more recent report gives different results [50]; the differential thermal analysis of $UO_2(NO_3)_2 \cdot 6\ H_2O$, $UO_2(NO_3)_2 \cdot 3\ H_2O$ and $UO_2(NO_3)_2 \cdot 2\ H_2O$ (Fig. 10) showed that transitions which are common to the three hydrates occur at the same temperature.

No difference is apparent between dehydrations performed in nitrogen or in air. X-ray, IR and analytical data have established that the following steps occur in the thermal dehydration of uranyl nitrate hexahydrate, trihydrate and dihydrate respectively. The dehydration is not dependent on heating rate or sample size.

Scheme 1.

$$UO_2(NO_3)_2 \cdot 6\ H_2O \rightarrow UO_2(NO_3)_2 \cdot 3\ H_2O \rightarrow UO_2(NO_3)_2 \cdot 2\ H_2O$$
$$\rightarrow UO_2(NO_3)_2 \cdot H_2O \rightarrow UO_2(NO_3)_2 \rightarrow \text{decomposition products} \qquad (A)$$

$$UO_2(NO_3)_2 \cdot 3\ H_2O \rightarrow UO_2(NO_3)_2 \cdot 2\ H_2O \rightarrow UO_2(NO_3)_2 \cdot H_2O$$
$$\rightarrow UO_2(NO_3)_2 \rightarrow \text{decomposition products} \qquad (B)$$

$$UO_2(NO_3)_2 \cdot 2\ H_2O \rightarrow UO_2(NO_3)_2 \cdot H_2O \rightarrow UO_2(NO_3)_2 \rightarrow \text{decomposition products} \qquad (C)$$

No evidence was found for the formation of $UO_2(NO_3)_2 \cdot 5\ H_2O$ and $UO_2(NO_3)_2 \cdot 4\ H_2O$. $UO_2(NO_3)_2 \cdot 6\ H_2O$ can also give, under controlled conditions, the monohydrate $UO_2(NO_3)_2 \cdot H_2O$. The results for the thermogravimetric analysis of the hexahydrate, trihydrate and dihydrate (Fig. 11) agree with those obtained by differential thermal analysis. The error in the results occurs in the transition of the monohydrate to the anhydrous material, due to the presence of a small amount of UO_3 when the last dehydration occurs [50]. The values for the 6 → 3 and 3 → 2 H_2O transitions are also close to those determined by measurements of the water vapour pressures [56]. An investigation of the self-diffusion of water in single crystals of $UO_2(NO_3)_2 \cdot 6\ H_2O$ at 35°C has shown [57] that four of the water molecules undergo exchange but the remaining two do not. This observation is compatible with the structure of the hexahydrate which is comprised of $UO_2(NO_3)_2 \cdot 2\ H_2O$ units, the remaining four molecules of water being weakly hydrogen bonded to the nitrate groups and other water molecules. The temperature dependence of the diffusive exchange can be expressed as $D = 4 \cdot 10^{-3}$ exp-

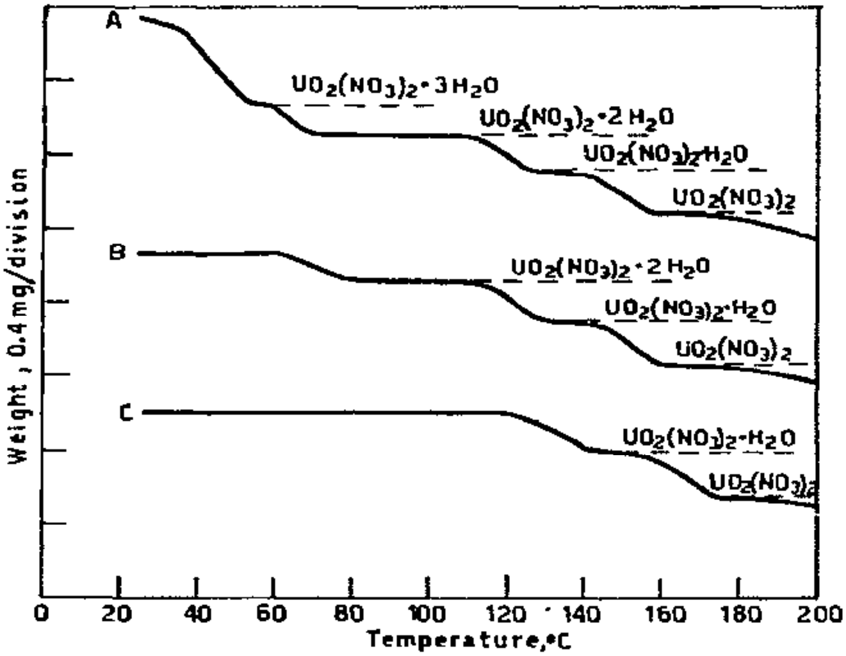


Fig. 11. Thermal analysis of $UO_2(NO_3)_2 \cdot 6\ H_2O$, $UO_2(NO_3)_2 \cdot 3\ H_2O$ and $UO_2(NO_3)_2 \cdot 2\ H_2O$.

($-7600/RT$) for the approximate temperature range 227 to 300 K. Although four water molecules undergo exchange at temperatures below −20°C only three are lost at such temperatures when single crystals are maintained in vacuo [58]. At higher temperatures further water is lost but at a somewhat slower rate than the first three molecules. The activation energy for the isothermal dehydration (−60°C to −30°C) $UO_2(NO_3)_2 \cdot 6\ H_2O \rightarrow UO_2(NO_3)_2 \cdot 3\ H_2O$ is 40 ± 4 kJ(mole $H_2O)^{-1}$. It appears [58] that the reactant-product interface is not the seat of the reaction and the model envisaged for the mechanism requires the hexahydrate lattice to be able to accomodate a large density of highly mobile H_2O vacancies, the high self-diffusion coefficient for water also being important. The slow step is the desorption of water from the surface of the crystals. At higher temperatures, 313 to 343 K, under controlled pressures of water vapour, the kinetics of dehydration are limited by a three dimensional contracting volume process, the energy of activation being appreciably higher than that recorded for vacuum dehydration [59]. With crushed crystals the rate of dehydration is controlled by diffusion of water vapour through the powder bed, even for very shallow bed depths. During these latter studies an interesting observation was made concerning the rate of dehydration of single crystals. Thus, this increases with temperature up to the melting point of the hexahydrate (333 K) at which temperature

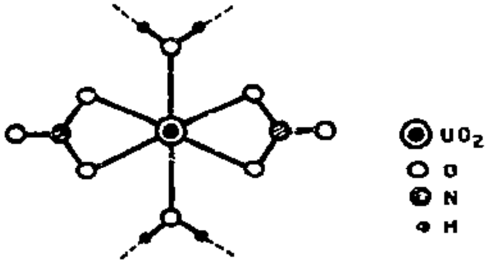


Fig. 12. The configuration about the uranium atom for $UO_2(NO_3)_2(H_2O)_2 \cdot 4\ H_2O$.

the dehydration ceases. This phenomenon is not observed for powder samples and it is suggested that a cementing process occurs at the melt—dehydration product interface which seals the core of the crystal from continued water loss. No value for the heat of formation of $NpO_2(NO_3)_2 \cdot 6\ H_2O$ is available but the free energy and heat of solution in water were recently determined [60] to be −2.94 kcal mol^{-1} and 5.06 kcal mol^{-1}, respectively, the estimated entropy for this compound being 123.4 e.u. On the basis of IR data [61] a structure of the type $[UO_2(H_2O)_6](NO_3)_2$ was suggested and such a model was also proposed from an X-ray diffraction study [62]. Other IR studies [27,44,54,64—67] have indicated covalent bonding of the nitrate groups; this structure $[UO_2(NO_3)_2(H_2O)_2]\ 4\ H_2O$ has also been proposed as a result of a two-dimensional X-ray study [63]. Both X-ray [68] and neutron diffraction [69] investigations have subsequently confirmed such interpretations. The configuration about the uranium atom is shown in Fig. 12. The linear uranyl group is equatorially surrounded by an irregular hexagon of six oxygen atoms, two from two equivalent water molecules and four from two bidentate nitrate groups. The uranium atom, the nitrate groups and the water oxygen atoms are approximately coplanar. The uranyl distances are not quite

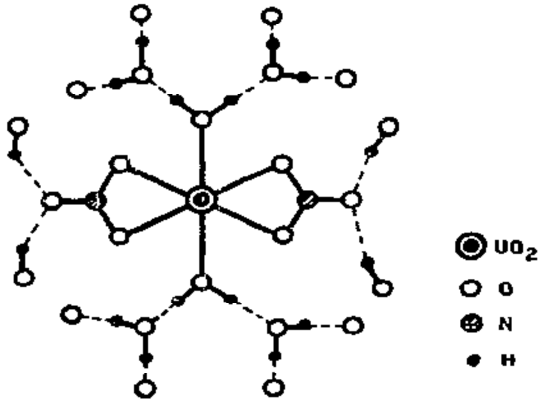


Fig. 13. The hydrogen bonding system for $[UO_2(NO_3)_2(H_2O)_2] \cdot 4\ H_2O$.

equivalent (1.770 ± 0.007 Å and 1.749 ± 0.007 Å) and in addition the two bidentate nitrate groups are also non-equivalent, although each itself is symmetrically bonded to the uranium atom. In the nitrate groups the N—O bonds involving coordinated oxygens are 0.03—0.05 Å longer than the N—O bonds involving the non-coordinated oxygen atoms; also the O—N—O angles differ significantly from 120°. All hydrogens are involved in hydrogen bonding and these may be divided into O(water)···O(water) hydrogen bonds of length 2.68—2.75 Å and weaker O(water)···O(nitrate) hydrogen bonds of lengths 2.93 and 2.99 Å (Fig. 13). The water molecules associate into sheets perpendicular to the *a* axis.

Early IR studies [61] of $UO_2(NO_3)_2 \cdot 3\ H_2O$ were interpreted by assuming that in this compound the nitrate groups and water molecules were coordinated to uranium; one nitrate group was regarded as bidentate and the other as monodentate; the two variants of the structure of $UO_2(NO_3)_2 \cdot 3\ H_2O$ proposed are shown in Fig. 14. Another IR investigation [64] indicated the non-equivalence of the water molecules. The X-ray structure determination [70] agrees with this conclusion. The linear uranyl ion is surrounded equatorially by two bidentate NO_3^- groups and two water molecules. The third water molecule lies considerably further away from the sphere of the uranyl ion and is attached to the oxygen of the nitrate group by a hydrogen bond. The structure is shown in Fig. 15.

An early X-ray diffraction study of the dihydrate $UO_2(NO_3)_2(H_2O)_2$ gave [71] U—O bond lengths which were not in agreement with those found in other compounds. Thus the U—O (uranyl) bond distance was found to be 1.9(1) Å and the U—O (equatorial) distances 2.0 and 2.1 Å, while for $[UO_2(NO_3)_2(H_2O)_2]\ 4\ H_2O$ the same distances are 1.77, 1.75 and 2.50, 2.55 and 2.40 Å. Since the two compounds exhibit sixfold oxygen coordination about

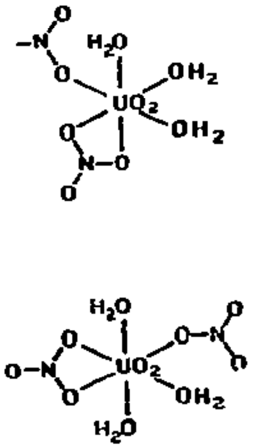


Fig. 14. The two variants proposed, on the basis of earlier IR studies, for $UO_2(NO_3)_2 \cdot 3\ H_2O$.

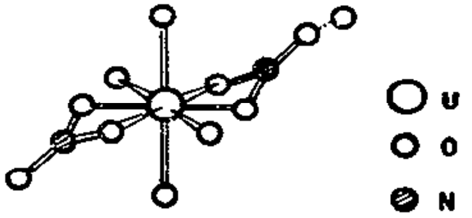


Fig. 15. The molecular structure of $UO_2(NO_3)_2 \cdot 3\ H_2O$.

the linear uranyl ion, the chemically similar bonds should be about equal in length.

More recently the crystal structure of this compound has been determined accurately by neutron diffraction [72]. The coordination around the uranium atom is shown in Fig. 16. The linear uranyl group is perpendicular to the nearly planar hexagon composed of four oxygen atoms from the two equivalent bidentate nitrate groups and two oxygen atoms from the equivalent water molecules. Such a coordination had been previously proposed from IR studies [73] and is identical to the basic coordination found in $[UO_2(NO_3)_2(H_2O)_2]\ 4\ H_2O$. The IR investigation [73] also indicated that no evidence existed for loosely bound water molecules outside the first coordination sphere and that the nitrate groups were bidentate since their symmetry was C_{2v}. There are two pairs of non-equivalent molecules (I and II) in each unit cell. The uranium—oxygen bond lengths for the uranyl groups in molecules I and II are 1.754 and 1.763 Å, respectively, and those of the symmetrically bonded nitrate groups are 2.513 and 2.508 (I) and 2.491 and 2.477 Å (II). It is seen from the N—O bond distances (Table 5) that the terminal N—O distance (r_3) is shorter than those involving the coordinated oxygen atoms (r_1 and r_2) as indeed is the case for other actinide compounds for which values

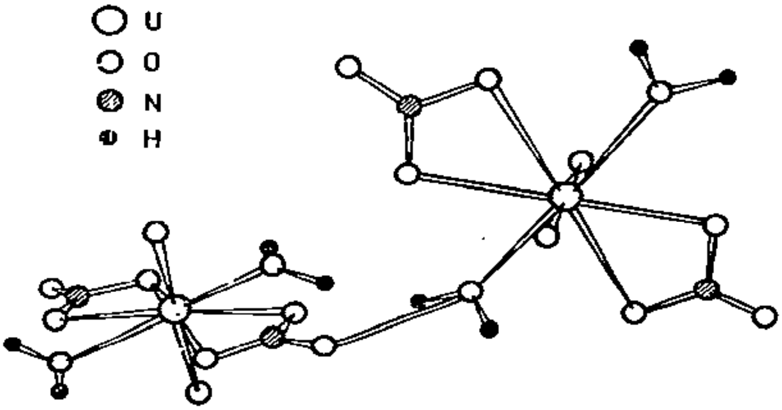


Fig. 16. The molecular structure of $UO_2(NO_3)_2(H_2O)_2$.

TABLE 9

Crystallographic data for actinide nitrate hydrates and oxynitrato complexes

Compound	Symmetry; space group	Lattice parameters				Ref.
		a(A)	b(A)	c(A)	β°	
$UO_2(NO_3)_2 \cdot 6\ H_2O$	O; $Cmc2_1$	13.197	8.035	11.467		69
$UO_2(NO_3)_2 \cdot 3\ H_2O$ [a]	T; $P1$	5.73	6.99	7.21	119.5	70
$UO_2(NO_3)_2 \cdot 2\ H_2O$	M; $P2_1/c$	14.124	8.432	7.028	108.0	72
$NpO_2(NO_3)_2 \cdot 6\ H_2O$	O; $Cmc2_1$	13.25	8.00	11.40		24
$RbUO_2(NO_3)_3$	H; $R\bar{3}c$	9.36		18.88		107
$CsUO_2(NO_3)_3$	H; $R\bar{3}c$	9.64		19.51		108
$(NH_4)_2UO_2(NO_3)_4$	M; $P2_1/c$	6.39	7.74	12.87	107.89	112
$Rb_2UO_2(NO_3)_4$	M; $P2_1/c$	6.42	7.82	12.79	108.67	112
$Cs_2UO_2(NO_3)_4$	M; $P2_1/c$	6.74	7.99	13.29	110	112

[a] $\alpha = 115°$, $\gamma = 82°$.

are also shown in Table 5. Water molecules associated with molecule 1 are not involved in hydrogen bonding (U—O 2.457 Å) whereas those in molecule II (U—O = 2.446 Å) link the basic structural units by two distinct types of hydrogen bonding which, respectively, involve the non-coordinated oxygen of a nitrate (molecule II) and a uranyl oxygen (molecule I). It is interesting to note that the nitrogen—oxygen bond distance for the oxygen involved in the hydrogen bonding (r_3, molecule II, Table 5) is shorter than the corresponding distance in molecule I. It is not certain whether this is due to a hydrogen bonding effect but, since it occurs in compounds not containing hydrogen bonding, it is unlikely. Unit cell dimensions for $UO_2(NO_3)_2(H_2O)_2$ and $UO_2(NO_3) \cdot$ 6 H_2O are listed in Table 9 together with those of $NpO_2(NO_3)_2 \cdot 6\ H_2O$ which is isostructural with the uranyl analogue. Infrared data for the uranyl(VI) nitrate hydrate and $NpO_2(NO_3)_2 \cdot 6\ H_2O$ have been interpreted on the basis of coordinated bidentate nitrate groups in accordance with X-ray results [24,69]. The distance between the antisymmetric and the symmetric stretching of the nitrate group is related to the tendency of the metal to share electrons with the nitrate ion in the solvent used [80]. An approximate value of 100 cm^{-1} has been set [81] as the boundary between spectra due to covalently bonded and electrostatically bonded nitrates. Using this criterion lithium nitrate in acetone solution with $\Delta\nu = 80\ cm^{-1}$ is on the electrostatic side while UO_2-$(NO_3)_2 \cdot 6\ H_2O$ ($\Delta\nu = 249\ cm^{-1}$) shows a very high degree of covalency. The $\Delta\nu$ value found in tributylphosphate (242 cm^{-1}) [81] and in tri-n-octylphosphine oxide solution in CCl_4 (227 cm^{-1}) [82] are very close indicating that the same structure is maintained in all these media [78].

An interpretation of the nitrogen 14 NMR and PMR results of $UO_2(NO_3)_2 \cdot$ 6 H_2O [79], is in accord with the neutron diffraction results.

The IR spectrum of anhydrous uranyl nitrate is somewhat unusual [27,44,54,64—66,74] and it will obviously be of value to have X-ray or neutron diffraction results for this compound. Since there are no other coordinating groups, a planar arrangement of six oxygen atoms around the uranium atom can only be achieved if some nitrate groups use all three oxygen atoms in coordination, as occurs, for example, for solid copper(II) nitrate [76]. The spectrum gives an indication of the presence of both local D_{3h} and C_{2v} symmetry nitrate groups; strongly coordinated bidentate nitrate is indicated by absorptions at 1625 and 1641 cm^{-1}, and the absence of nitrate ions by the failure to observe the out-of-plane bending frequency in the 830 cm^{-1} region. It is possible that the D_{3h} nitrates are coordinated through all three oxygens [77].

Neptunium(VI) nitrate hydrate can be isolated by vacuum concentration of a 1 M HNO_3 aqueous solution as $NpO_2(NO_3)_2 \cdot 1{-}2\ H_2O$, which is transformed into the hexahydrate $NpO_2(NO_3)_2 \cdot 6\ H_2O$ on exposure to moist air [24]. Concentration of a solution of $NpO_3 \cdot H_2O$ in N_2O_5 results in the formation of $NpO_2(NO_3)_2 \cdot N_2O_5 \cdot H_2O$; since the IR spectrum of this compound shows the typical absorption band of the nitronium ion, it should be formulated as $NO_2[NpO_2(NO_3)_3] \cdot H_2O$ [24]. Although it has not been isolated, $NpO_2(NO_3)_2$ appears to be formed at 190°C during the vacuum thermal decomposition of $Np(NO_3)_4 \cdot xN_2O_5$ [24].

Pink to brown plutonyl(VI) nitrate hexahydrate, $PuO_2(NO_3)_2 \cdot 6\ H_2O$, has been obtained by evaporation of a HNO_3 solution containing plutonium(VI) over P_2O_5 at room temperature [55]. The pink crystals turn brown or dark red when allowed to stand in air. When $PuO_2(NO_3)_2 \cdot 6\ H_2O$ is heated at 130°C, water of crystallization is gradually evolved with the successive formation of the tetra-, tri- and dihydrate. Anhydrous $PuO_2(NO_3)_2$ can be obtained by heating the hexahydrate at 150°C for 76 h. The last two molecules of water are much more difficult to remove than the first four, which indicates that they are bound in the inner coordination sphere of the molecule. When $PuO_2(NO_3)_2$ or its hydrates are stored in air for about four months, complete reduction to plutonium(IV) occurs; further reduction to plutonium(III) takes place after storage for an additional 18 months. Such changes in oxidation states have not been observed on storage over P_2O_5 [96].

(ii) Nitrato complexes

Solid uranyl(VI) complexes of the type $M^I[UO_2(NO_3)_3]$ (M^I = for example, K, NH_4, Rb, Cs, NEt_4, NH_2Et_2, NMe_4 [12, 61, 75, 86, 100—102]) and $M^I_2[UO_2(NO_3)_4]$ (M^I = for example, NH_4, $NEtH_3$, Rb and Cs) are obtained [100—105] by reaction in either aqueous nitric acid or N_2O_4. Analogous neptunyl(VI) [86,102,106] and plutonyl [86,102] trinitrato complexes are known although they have not been so extensively studied, but tetranitrato complexes appear not to have been characterized. Uranyl(VI) tetranitrato complexes of the type $M^I_2[UO_2(NO_3)_4]$ (M^I = Rb, Cs, PyH and QuinH) and $M^I[UO_2(NO_3)_4]$ (M^{II} = Mg and Zn) are also formed during the thermal decomposition of hexanitratouranates(IV) [87].

X-ray and neutron diffraction studies have demonstrated the presence of

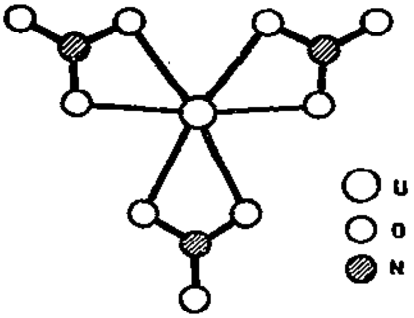


Fig. 17. Configuration of the nitrate groups about the uranium atom in the anion $[UO_2(NO_3)_3]^-$.

bidentate nitrate groups in $Rb[UO_2(NO_3)_3]$ [107] and $Cs[UO_2(NO_3)_3]$ [108, 109]. The configuration of oxygen atoms about the uranium atom in $Rb[UO_2(NO_3)_3]$ is shown in Fig. 17. The uranyl ion is symmetrical and linear (U—O = 1.79 Å). A hexagon of six oxygen atoms from three bidentate nitrate groups surrounds the O—U—O group equatorially. The hexagon is slightly puckered as the oxygen atoms are alternately 0.09 Å above and below the plane. The three nitrate groups are symmetrically distributed around the uranium atom, the U—O(nitrate) distance being 2.48 Å in $Rb[UO_2(NO_3)_3]$ [107] and 2.50 Å in the isostructural caesium salt [108]. The configuration around the uranium atom is thus an irregular hexagonal bipyramid, each nitrate group acting as a bidentate chelate forming a four membered ring system. The rubidium atom has twelve oxygen atoms as its near neighbours. Infrared data are consistent with the presence of only covalent nitrate groups in the trinitrato complexes [12,61,74,110]. It was reported that $[UO_2(NO_3)_4]^{2-}$ ions do not exist in appreciable concentrations in non-aqueous media [100] and earlier IR studies [104] are stated to indicate the presence of ionic nitrate in the solids. On the basis of other spectral studies [102] discrete $[UO_2(NO_3)_4]^{2-}$ ions were reported to exist in nitromethane solution in the presence of high concentrations of NEt_4NO_3 and some recent polarized IR studies [111] are interpreted on the basis of the presence of this ion with both mono- and bidentate nitrate groups in certain solid complexes. These deductions have been recently confirmed by single crystal X-ray investigations [112]. The crystals of the isomorphous uranyl(VI) tetranitrates $M_2[UO_2(NO_3)_4]$ (M = NH_4, Rb and Cs) [112] consist of cations M^+ and the complex anion $[UO_2(NO_3)_4]^{2-}$. The structure of the uranyl tetranitrate anion is shown in Fig. 18. The centrosymmetric complex anion consists of a linear uranyl group and four nitrate groups, two of which are bonded to the uranium atom through two oxygen atoms and two others which are linked through one oxygen atom; this represents the only reasonable arrangement of four nitrate groups linked to a uranyl group. The unsymmetrical U—O bonds to the chelate nitrate are attributed to an interac-

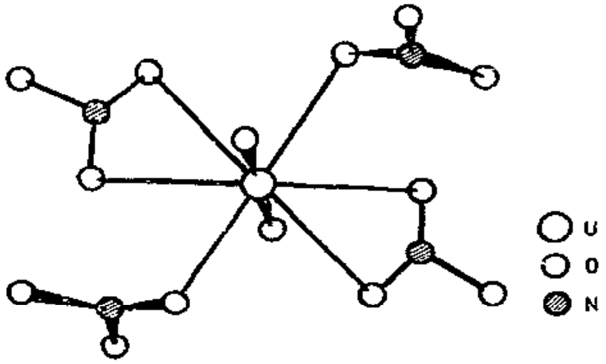


Fig. 18. The molecular structure of the uranyl(VI) tetranitrate anion $[UO_2(NO_3)_4]^{2-}$.

tion between the NH_4^+ cation and the oxygen atom involved in the longer bond.

The IR and Raman spectra of ammonium, potassium, rubidium and caesium uranyl trinitrate $NH_4[UO_2(NO_3)_3]$, $K[UO_2(NO_3)_3]$, $Rb[UO_2(NO_3)_3]$ and Cs-

TABLE 10

Fundamental nitrate and actinyl frequencies (cm^{-1}) for actinide(VI) oxynitrates

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_1O—M—O	ν_3O—M—O	Ref.
$UO_2(NO_3)_2 \cdot 6\ H_2O$	1530 1480 1452	1050 1038	748	1337 1303		806	871	959	11, 53, 74
$NpO_2(NO_3)_2 \cdot 6\ H_2O$	1520 1489	1045 1031	746	1308 1282	741	799		952	24, 74
$UO_2(NO_3)_2 \cdot 3\ H_2O$	1535 1501	1041 1028	743	1303 1277		800		952	53
$UO_2(NO_3)_2 \cdot 2\ H_2O$	1536 1505	1023	751	1263	708	801		949	53
$UO_2(NO_3)_2 \cdot H_2O$	1618 1540	1028 1008	755	1270 1240	698	802 787		960 945	219
$KUO_2(NO_3)_3$	1530	1025	741	1272	715	805	871, 878	950, 960	74
$RbUO_2(NO_3)_3$	1535	1021	738	1272	710	806	890	956	74
$CsUO_2(NO_3)_3$	1518 1545	1021	740	1270	712	808	895	956	74
$NH_4UO_2(NO_3)_3$	1525	1020	735, 739	1265	711	804	895	952	74
$(C_2H_5)_4NUO_2(NO_3)_3$	1540	1018	747	1257	723	800	895	936	74

$[UO_2(NO_3)_3]$ have been reported [11,74] and normal coordinate analyses have been made as a six body problem $[UO_2(X_3)]^-$ ($X = NO_3^-$) neglecting the outer cations [113,114]. The fundamental vibrational modes of the nitrate group in the complexes have been determined from the assumption of the C_{2v} point group, for which the nitrate group has the six IR and Raman active fundamental vibrations (Table 10). In the Raman spectra the $B_1(\nu_4)$ and the $B_2(\nu_6)$ bands are absent for all the complexes and even the $B_2(\nu_5)$ band for $Rb[UO_2(NO_3)_3]$; it has been suggested that these bands are not observed clearly [114] because their Raman intensities, i.e. the changes in polarizabilities of the complexes, may be very small. The non-degenerate asymmetric stretching frequency ν_3 of the O—U—O group is IR- allowed and occurs in the region of 950 cm^{-1}; this vibration is Raman-forbidden whereas the degenerate ν_1O—U—O symmetric stretching frequency is IR forbidden. Moreover, the latter has been reported as a weak absorption in the region 870—880 cm^{-1} in the IR. Thus $K[UO_2(NO_3)_3]$ displays a weak doublet at 871 and 878 cm^{-1} in the IR which corresponds to a strong Raman band at 870 cm^{-1}; the others have only one weak shoulder on the low-frequency edge of ν_3. From a consideration of the fact that this band occurs only in the crystal, it seems most reasonable to conclude that its appearence results from the crystal field effect which causes the symmetry lowering of the whole ion. It has been deduced on the basis of IR and Raman results [111,115] that two different orientations of $[UO_2(NO_3)_3]^-$ ions are present in the unit cell of $K[UO_2(NO_3)_3]$. Thus ν_3 for the O—U—O group is split into three bands at 930 cm^{-1}, 952 cm^{-1} and 966 cm^{-1} for this compound whereas it occurs as a single band at ca. 970 cm^{-1} for the ammonium, rubidium and caesium analogues. It has also been reported [11] that ν_3 is split into a doublet for $K[UO_2(NO_3)_3]$ in the solid IR spectrum. It was suggested [11] that as ν_3 is non-degenerate, Fermi resonance could account for these observations. Conductance measurements in nitromethane (102 Ω^{-1} cm^2) show that this complex does not dissociate in this solvent and the IR spectrum of the solution has only one ν_3 band which suggests that the double absorptions observed are due to unit cell coupling [11] rather than to Fermi resonance. The values of ν_3 are shown in Table 10 together with the positions recorded for the Raman active mode ν_1; bond lengths within the linear uranyl(VI) group, calculated on the basis of these values, are in the range 1.72 to 1.73 Å compared with 1.78 Å obtained for $Rb[UO_2(NO_3)_3]$ by neutron diffraction studies [107]. In connection with the latter compound it is interesting to note that there is some evidence, based on NMR studies [79] and also on X-ray data [116] (cell dimensions and space group only) that a second crystal modification exists. It would be interesting to have confirmation of these observations.

Values for the symmetric stretching frequencies ν_1 O—U—O of the uranyl ions in uranyl nitrate di- and hexahydrate have recently been published [74] together with similar values for a range of other uranyl nitrate complexes and the corresponding values for the asymmetric stretching frequencies ν_3O—U—O. Earlier studies [27,44,54,64—66,74] have assigned bands in the range 249—260 cm^{-1} to the U—O (nitrate) vibration and have assigned the

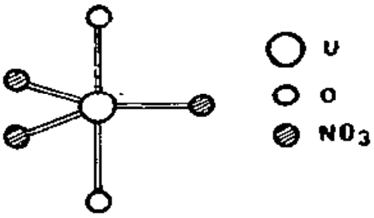


Fig. 19. The schematic D_{3h} representation of $[UO_2(NO_3)_3]^-$.

bending mode of the O—U—O (ν_2) to bands observed below 152 cm^{-1}. This last assignment of the ν_2O—U—O mode in the IR spectrum of the uranyl nitrate hydrate have been shown [12,75] to be in error by recent comparison of the spectra of a wide range of uranyl(VI) nitrato-, halogeno-, perchlorato- and carbonato-complexes from which it appears that the bending mode occurs in the range 248 to 260 cm^{-1}, being observed for $UO_2(NO_3)_2 \cdot 6\ H_2O$ at 248 cm^{-1} [12]. More recent work has indicated that the uranyl nitrate species present in acetone solution contain bidentate nitrate groups [78].

It was suggested that bands in the region 235—190 cm^{-1} could be attributed to U—O(NO_3) stretching modes; however such assignments must be considered tentative at present. In the region below 200 cm^{-1}, three bands have been observed at near 150, 120 and 90 cm^{-1} for each of the *trinitrato* complexes. The 150 cm^{-1} band is somewhat arbitrarily assigned to the equatorial X—U—X bending vibration and the band at 120 cm^{-1} to the X—U—O bending vibration assuming that the $[UO_2(NO_3)_3]^-$ complex possesses a D_{3h} symmetry of the type illustrated in Fig. 19. The weak band at near 90 cm^{-1} may be assigned to the lattice vibration resulting from the interaction between the $[UO_2X_3]^-$, and M^+ (NH_4, K, Rb, Cs) [113,114].

Spectral results and the absorption and fluorescence spectra of uranyl(VI) nitrato complexes have been reviewed in the past [117]. More recent publications contain spectral data for uranium, neptunium and plutonium complexes in non-aqueous media such as nitromethane or dinitrogen tetroxide [83,86,100]; solid state spectral data for a variety of uranyl(VI) trinitrato and tetranitrato complexes [118,120] have also been reported. The PMR spectrum of NpO_2^{2+} doped $Rb[UO_2(NO_3)_3]$ and the optical absorption spectrum of NpO_2^{2+} doped $Cs[UO_2(NO_3)_3]$ have been reported [119,121]. The latter results lead to the assignment of four pure electronic excitations within the $5f^1$ configuration (6458, 9420, 17841 and 20815 cm^{-1}) and the assignment of five electronic levels (13914, 16071, 16093, 17968 and 21021 cm^{-1}) to excitations of a bonding electron in the 5*f* shell.

G. ACTINIDE(IV) NITRATE COMPLEXES WITH LIGANDS CONTAINING NITROGEN DONORS

Reaction of thorium(IV) nitrate hydrate with 1,10-phenanthroline (phen) in ethylacetate yields the complex $Th(NO_3)_4 \cdot 2$ phen while in nitric acid the hexanitratothorate(IV) complex $(Hphen)_2[Th(NO_3)_6]$ has been obtained [227]. The ring vibrations of the 1,10-phenanthroline in the 1600—1400 cm^{-1} region shift to higher frequency on complexing with thorium(IV) and on protonation [227]. The ligand 2-(2′-pyridyl)benzimidazole (PBH) is structurally similar to 2,2′-bipyridyl and 1,10-phenanthroline in containing the grouping —N=C—C=N. It reacts with thorium(IV) nitrate in ethanolic solution to give the white complex $Th(NO_3)_4(PBH)_2$, which is stable at room temperature for several weeks [211]. The IR spectra show the ligand is coordinated in a bidentate manner through the unsaturated nitrogen atom and the nitrogen atom of the pyridine ring; no absorption band near 1380 cm^{-1} is present while the bands at 1505, 1295, 1030, 820, 749 and 725 cm^{-1} correspond to the presence of bidentate nitrate groups. Thus the coordination number of thorium seems to be twelve. In solution considerable dissociation occurs. The thermogravimetric studies of the free ligand show it is stable up to 120°C and then loses weight very rapidly, volatilizing completely at 240°C. In the thorium complex loss of the ligand occurs at about 350°C; the final product is ThO_2.

There appears to have been no further work done recently on nitrogen donor complexes with actinide tetranitrates.

H. ACTINIDE (VI) NITRATE COMPLEXES WITH LIGANDS CONTAINING NITROGEN DONORS

It has been shown [74,212—214] that the composition of uranyl(VI) complexes with neutral bidentate ligands (NN) is $UO_2(NO_3)_2(NN)$ while the composition of the complexes with neutral monodentate ligands (N) is $UO_2(NO_3)_2(N)_2$; the complexes previously reported as $UO_2(NO_3)_2(NN)_2$ appear to be incorrectly formulated [74]. The various complexes have generally been prepared by mixing uranyl nitrate hexahydrate and the appropriate neutral ligand in a suitable organic solvent. The IR spectra for all the nitrato complexes show the presence of bidentate nitrate groups; thus the coordination number of uranium is eight. It has also been reported [216] that there is a linear relationship between the ν_3 asymmetric and the ν_1 symmetric O—U—O stretching frequencies in a range of uranyl complexes, several of which contain nitrogen donor ligands. A similar relationship is also reported for ν_3 and the magnetic susceptibility of the uranyl ion in the various complexes. However the linear relationships illustrated [216] leave much to be desired; it must be realised that the identification of ν_1O—U—O symmetric stretching frequency as a weak band around 800—870 cm^{-1} in the IR spectra of complexes containing both nitrate and organic ligands can only be considered tenuous. $UO_2(NO_3)_2(H_2O)(py)$ is prepared by addition of dry pyridine to an n-pentanol solution of $UO_2(NO_3)_2 \cdot 6\ H_2O$ and by washing the precipitate with $CHCl_3$ or ether [214]. The α-picoline and α-benzylpyridine uranyl complexes $UO_2(NO_3)_2(H_2O)(\alpha\text{-pic})$ and $UO_2(NO_3)_2(H_2O)(\alpha\text{-benzylpy})$ have been prepared similarly [214]. $UO_2(NO_3)_2(py)_2$ was prepared by dissolving UO_2-

TABLE 11

Infrared spectra of uranyl(VI) nitrate complexes with neutral ligands containing nitrogen donor atoms

Compound [a]	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_3O—U—O	Ref.
$UO_2(NO_3)_2(H_2O)(py)$	1540	1025	741	1270	720	807	928	74
$UO_2(NO_3)_2(H_2O)$(α-pic)	1530			1276			924	214
$UO_2(NO_3)_2(H_2O)$·(α-benzylpy)	1530			1275			921	214
$UO_2(NO_3)_2(py)_2$	1500	1028	741	1285	725	812	930	74
$UO_2(NO_3)_2$(bipy)	1539			1278			940	214
$UO_2(NO_3)_2$(phen)	1530 1515	1030		1285		805	940	74

[a] py = pyridine, α-pic = α-picoline, α-benzylpy = α-benzylpyridine, bipy = bipyridyl, phen = 1,10-phenanthroline.

$(NO_3)_2(py)(H_2O)$ in pyridine and precipitating by cooling after the addition of ether [219,228]. If a saturated solution of 1,10-phenanthroline hydrate in ethanol is added to a solution of $UO_2(NO_3)_2 \cdot 6\ H_2O$ a yellow solid of UO_2-$(NO_3)_2$(phen) is produced [74]. A previous paper [229] stated the product contains a 2 : 1 mole ratio of 1,10-phenanthroline to uranium but reported no analytical data. The nitrate groups are bidentate (Table 11) and the ν_3O—U—O increases when the unidentate pyridine and its derivatives are replaced by bidentate bipyridyl and phenanthroline. Thermogravimetric data on UO_2-$(NO_3)_2(H_2O)(py)$ show that at 125°C the water molecule is lost, at 195°C the pyridine molecule is lost and that at about 550°C the decomposition is complete, giving rise to U_3O_8. For $UO_2(NO_3)_2$(dipy) the bipyridyl molecule is

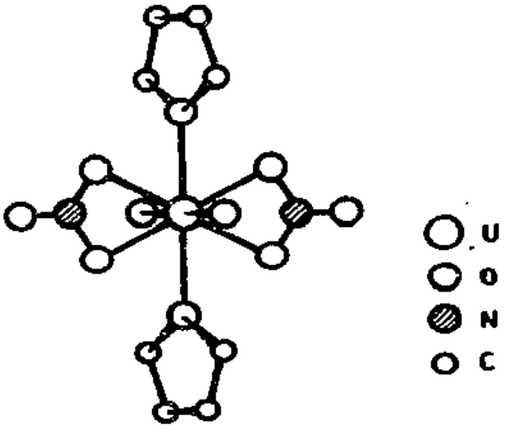


Fig. 20. The molecular structure of $UO_2(NO_3)_2(THF)_2$.

lost at 310°C and further decomposition to U_3O_8 takes place at about 500°C. For $UO_2(NO_3)_2(PBH)$ (PBH=2-(2′-pyridyl)benzimidazole), loss of the organic ligand takes place at about 400°C [211].

I. ACTINIDE(VI) NITRATE COMPLEXES WITH ETHERS

The etherate $UO_2(NO_3)_2(Et_2O)_2$ has been prepared by dissolving anhydrous uranyl(VI) nitrate in ethyl ether at reduced temperature (−40 to −20°C) [215]. The bidentate nature of the nitrate ion in this complex is confirmed by the six IR active vibrations at 1530, 1510 cm^{-1} (ν_1), 1250, 1270 cm^{-1} (ν_4), 1025 cm^{-1} (ν_2), 808 cm^{-1} (ν_6), 750 cm^{-1} (ν_3) and 735 cm^{-1} (ν_5). ν_3O—U—O lies at 935 cm^{-1} and ν_1O—U—O at 863 cm^{-1}, but bands at 1124 cm^{-1} (ν_{asym} COC) and at 1077 cm^{-1} (ν_{sym} COC) characteristic of the liquid ether are absent [215]. The solubilities of the ternary systems uranyl nitrate—isopropyl ether—water and uranyl nitrate—n-propyl ether—water have been measured [223]. The following solid phases have been isolated: $UO_2(NO_3)_2 \cdot 3\ H_2O \cdot 3\ Pr^i_2O$, $UO_2(NO_3)_2 \cdot 2\ H_2O \cdot 4\ Pr^i_2O$, $UO_2(NO_3)_2 \cdot 2\ Pr^i_2O$ in the system with isopropyl ether, and $UO_2(NO_3)_2 \cdot 6\ H_2O$, $UO_2(NO_3)_2 \cdot 3\ H_2O \cdot Pr^n_2O$, $UO_2(NO_3)_2 \cdot 2\ H_2O \cdot 2\ Pr^n_2O$, $UO_2(NO_3)_2 \cdot 2\ Pr^n_2O$ in the system with n-propyl ether. The solubility of uranyl(VI) nitrate in isopropyl ether on the whole is much lower than in ethers with a normal carbon chain [223].

The preparation of the tetrahydrofuran complex $UO_2(NO_3)_2(THF)_2$ has been recently reported and its crystal structure determined [123]; a 1 : 1 compound had been previously reported [123]. $UO_2(NO_3)_2(THF)_2$ is obtained by dissolving $UO_2(NO_3)_2 \cdot 6\ H_2O$ in tetrahydrofuran at room temperature and allowing the resulting solution to stand for two days. Due to the high ether vapour pressure, the crystals had to be mounted in a glovebag with an atmosphere saturated with tetrahydrofuran. The crystals are monoclinic, space group $P2_1/a$ and $Z = 2$ with $a = 9.412$, $b = 12.649$ and $c = 7.237$ Å; $\beta = 117.1°$. The molecular structure is shown in Fig. 20. It consists of a uranium atom on a centre of symmetry coordinated to eight oxygen atoms. The two uranyl oxygen atoms are perpendicular to the plane of the remaining oxygen atoms and with them form a hexagonal bipyramid about the uranium atom. The tetrahydrofuran molecule in this structure appears disordered as it does in most crystallographic determinations [124—127] presumably as a result of pseudorotation [128]; therefore interatomic distances in this ligand do not represent the true values for a single conformation.

J. ACTINIDE(IV) NITRATE COMPLEXES WITH CROWN ETHERS

The synthesis and some spectroscopic studies of the thorium(IV) nitrate complexes with the ligand 18-crown-6 have been reported [190].

$Th(18\text{-crown-}6)(NO_3)_4 \cdot H_2O$ and $Th(18\text{-crown-}6)(NO_3)_4 \cdot THF \cdot 3\ H_2O$ have been obtained by mixing in solution $Th(NO_3)_4 \cdot 6\ H_2O$ and 18-crown-6.

The first complex was obtained from methanol and the second from tetrahydrofuran.

It has been suggested from the IR data that the distortion of the nitrate groups from the D_{3h} symmetry is quite strong and a description of the local symmetry of the nitrate groups as C_{2v} appears to be more appropriate.

K. ACTINIDE(VI) NITRATE COMPLEXES WITH CROWN ETHERS

The chelating ability of the crown ether with respect to uranyl(VI) nitrate salt has been studied [190—198]. The complex UO_2(18-crown-6)$(NO_3)_2 \cdot 4\ H_2O$ has been obtained by mixing at 0°C the 18-crown-6 ligand and $UO_2(NO_3)_2 \cdot 6\ H_2O$ in absolute ethanol. On the basis of spectroscopic data it has been suggested that the uranyl(VI) ion is located at the centre of the cyclic ligand, the two nitrate ions being ionic [190]. The same complex of the uranyl(VI) nitrate with two water molecules instead of four has been obtained from $UO_2(NO_3)_2 \cdot 6\ H_2O$ and 18-crown-6 in tetrahydrofuran [190,191]. Again it was reported from IR and Raman spectra, that ionic NO_3^- was present [190,191].

UO_2(18-crown-6)$(NO_3)_2 \cdot 5\ H_2O$ has been prepared by the same procedure and the existence of an additional hydrate, possibly the hexahydrate, has been confirmed but not well characterized [191]. Alternative syntheses and the molecular structures of UO_2(18-crown-6)$(NO_3)_2 \cdot 4\ H_2O$ [192] and UO_2(18-crown-6)$(NO_3)_2 \cdot 2\ H_2O$ [193,194] have recently been reported. UO_2-(18-crown-6)$(NO_3)_2 \cdot 4\ H_2O$ has been prepared by dissolving $UO_2(NO_3)_2 \cdot 6\ H_2O$ and the cyclic ligand in warm acetonitrile and allowing the resulting solution to stand overnight at —10°C [192]. The crystals are triclinic, space group $P\bar{1}$ with $a = 7.526$, $b = 11.27$ and $c = 7.802$ Å, $\alpha = 97.51$, $\beta = 95.22$ and $\gamma = 105.95°$, $Z = 1$. The uranyl group (Fig. 21) is not located within the crown ether group. The structure consists of neutral $UO_2(NO_3)_2(H_2O)_2$ molecules and 18-crown-6 molecules connected into infinite chains via hydrogen bonding through intermediary water molecules. Thus the crown ether is not bound directly to the uranyl group as previously suggested [195]. The linear uranyl(VI) group occupies a crystallographic inversion centre and exhibits characteristic coordination, forming an angle of 86.6° with the least-squares equatorial plane containing the six donor atoms. The six equatorial ligand

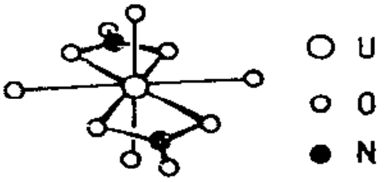


Fig. 21. View of the $UO_2(NO_3)_2(H_2O)_2$ unit in the complex UO_2(18-crown-6)$(NO_3)_2 \cdot 2\ H_2O$.

atoms, which are coplanar and alternate above and below the UO_6 least-square plane are provided by two water molecules (U—O = 2.434 Å) and by two symmetrically bidentate nitrate groups (U—O = 2.482 and 2.486 Å). In $UO_2(NO_3)_2(H_2O)_2$ · 18-crown-6 the uranyl oxygen is not involved in bonding to any atom other than uranium and the U—O distance is 1.693 Å. The coordinated water molecule is connected by a moderately strong hydrogen bond to a lattice water molecule. The ether molecule itself has a customary crown conformation with normal internal distances and angles [199—201]. The ring is slightly puckered, the six oxygen atoms being alternately 0.23 Å above and below the six-atom least-square plane. As reported above this complex was isolated from acetonitrile, whereas the previous synthesis used ethanol [195]; nevertheless, the X-ray powder patterns, IR mull spectra and decomposition temperatures are indistinguishable for products from the two preparations. The IR bands generally correspond, with small shift, to a superposition of the spectra of $UO_2(NO_3)_2 \cdot 6\ H_2O$ and 18-crown-6. The observed minor shifts in the crown ether bands have been attributed to slight conformational changes including those due to the hydrogen bonding with the oxygen of a lattice water molecule [195,201—203].

The compound UO_2(18-crown-6)$(NO_3)_2 \cdot 2\ H_2O$ crystallizes in the triclinic system with a = 9.073, b = 9.144 and c = 8.323 Å, α = 64.53, β = 104.23 and γ = 110.72°, space group $P\bar{1}$ and Z = 1 [193,194]. Again the structure consists of $UO_2(NO_3)_2(H_2O)_2$ units packed with crown molecules in 1 : 1 ratio, but with hydrogen bonds between coordinated water molecules and the etheric oxygens. The cyclic ether molecules assume two statistically non-equivalent sites in the crystal (occupancy factor 0.7 and 0.3 respectively) related to each other by a 180° rotation about O(7)···O(7'), (Figs. 22 and 23). The whole hexaether molecule is devoid of a strong conformational stress. Nevertheless the conformation adopted is different from the one observed

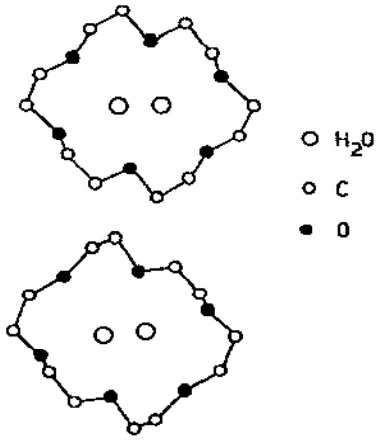


Fig. 22. Molecular models of the 18-crown-6 molecule in the two observed orientations for the complex UO_2(18-crown-6)$(NO_3)_2 \cdot 4\ H_2O$.

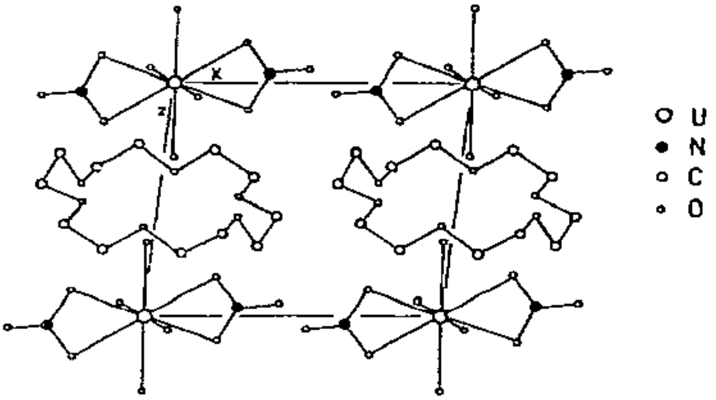


Fig. 23. The molecular structure of $UO_2(18\text{-crown-}6)(NO_3)_2 \cdot 4\ H_2O$.

for the isolated molecule [204] and from the one observed in the hydrated form, $UO_2(NO_3)_2(H_2O)_2 \cdot 2\ H_2O \cdot$ 18-crown-6 [192]. The uncomplexed crown molecule adopts in the crystal a centrosymmetric conformation with an internal cavity of a non-circular shape: oxygen to centre distances are 2.13, 2.64, and 3.57 Å. In $UO_2(NO_3)_2(H_2O)_2 \cdot$ 18-crown-6 the weak crown—water interaction suffices to induce a more circular shape and in the hydrated form $UO_2(NO_3)_2(H_2O)_2 \cdot 2\ H_2O \cdot$ 18-crown-6 the additional lattice water molecules cause an even more symmetric conformation very close to the one observed in alkali thiocyanate crown ether complexes [205—207].

It was also concluded from NMR results that the 18-crown-6 also forms complexes of 1 : 1 stoicheiometry in solution, the cation being inside the macrocyclic cavity [195,208]; further studies led to the conclusion that there is no direct bonding between the uranyl cation and the ligand [198,209].

The complexes $UO_2(\text{dicyclohexyl-18-crown-6})(NO_3)_2 \cdot 2\ H_2O$ have also been prepared [191]. These complexes are soluble in polar solvents such as acetone and alcohols and are insoluble in non-polar solvents such as benzene and cyclohexane. The preparation of the uranyl (VI) nitrate-15-crown-5 complex has also been reported but no physicochemical data other than melting point are available [191].

The synthesis and the characterization of the uranyl(VI) nitrate complexes with the cyclic polyethers dibenzo-18-crown-6 (L_A) and benzo-15-crown-5 (L_B) have been reported [209]. The yellow complexes have the compositions $UO_2(L_A)(NO_3)_2 \cdot 2\ H_2O$ and $UO_2(L_B)(NO_3)_2 \cdot 5\ H_2O$ and are soluble in acetonitrile and light alcohols. The visible spectra show the vibronic structure of the bands in the 350—500 nm range to be essentially determined by the trianionic O—U—O entity. The spectra are basically similar to those of the corresponding uranyl(VI) nitrate salt in the same solvent; some peaks appear to be slightly shifted. No ligand—uranium charge-transfer band is observed. Infrared data indicate that both the nitrate groups remain coordinated to the uranyl ion. The conductivity values are about 25 ohm^{-1} cm^2 M^{-1} in acetonitrile solution; these indicate the non electrolytic behaviour of the complexes, confirming the coordination of both the nitrate groups.

The thermogravimetric and differential thermal analysis curves for $UO_2(L_A)(NO_3)_2 \cdot 2\ H_2O$ and $UO_2(L_B)(NO_3)_2 \cdot 5\ H_2O$ show mass-loss in the temperature range 90—140°C corresponding to the loss of all the water molecules; the dehydration of both complexes begins endothermically, but two exothermic processes immediately follow before the first is completed; rearrangements probably occur in these two complexes with the contribution of the nitrate groups. After the dehydration process, both complexes are more or less stable in a temperature range 30—50°C, after which an exothermic decomposition begins; this behaviour suggests the possibility of a ligand decomposition process with the contribution of the nitrate groups during the thermal dissociation [209].

The crystal and molecular structure of uranyl(VI) nitrate dihydrate-1,4,7,10-tetraoxacyclododecane has been reported [197]; the complex is of the form 1 : 1. The crystals are monoclinic, space group $P2_1/c$ with $a = 9.048$, $b = 14.366$ and $c = 6.720$ Å, $\beta = 99.38°$ and $Z = 2$. It is reported that the molecule has a crystallographic centre of symmetry which is occupied by the uranium atom. The proposed structure is shown in Fig. 24. The uranyl ion is said to be surrounded equatorially by a near planar hexagon comprised of four oxygen atoms from the ether ring and two water oxygen atoms; intermolecular binding would be the result of the hydrogen bonds between nitrate oxygen atoms and the water molecule. It seems unlikely that the structure is correct.

L. ACTINIDE(IV) AND ACTINIDE(VI) NITRATE COMPLEXES WITH CRYPTATES

1 : 1 thorium(IV) nitrate and uranyl(VI) nitrate hexaoxadiamine macrobicyclic complexes have been prepared by direct combination of 4,7,13,16,21,

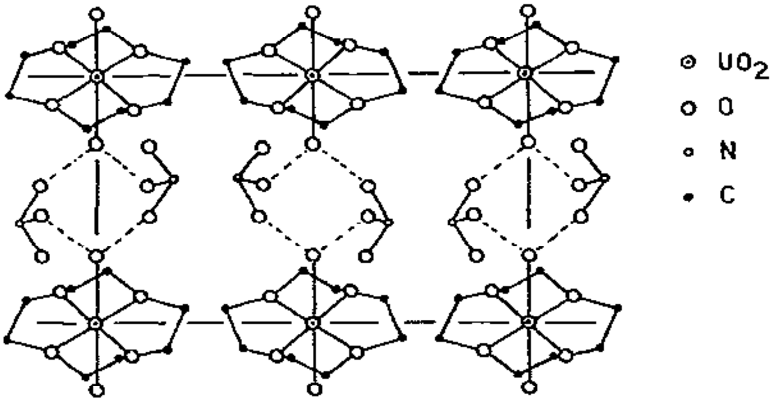


Fig. 24. The proposed structure of the complex uranyl(VI) nitrate dihydrate 1,4,7,10-tetraoxacyclododecane.

24-hexaoxa-1,1-diazabicyclo-(8,8,8)-hexacosane (crypt) with the hydrated metal nitrate [208]. The thorium(IV) complex Th(crypt)$(NO_3)_4 \cdot 4\ H_2O$ is white, whilst the uranyl(VI) complex UO_2(crypt)$(NO_3)_2 \cdot 4\ H_2O$ is golden coloured. On the basis of IR and ^1H NMR data coordination was supposed to occur in solution and in the solid state. A potentiometric study of the interaction between uranyl(VI) and the ligand in aqueous solution has shown [210] that the UO_2^{2+} group is not complexed by these diazapolyoxamacrocycles. These results are confirmed by the fact that the electronic spectra of solutions with and without ligand are identical. It is not impossible that complexation of actinide ions could occur. However, more physicochemical data are necessary to resolve the problem.

M. ACTINIDE(IV) NITRATE COMPLEXES WITH UREA

Displacement of nitrate by urea is observed in the series of complexes formed by thorium(IV) tetranitrate; thus thorium complexes of the general type $Th(NO_3)_4 \cdot x$ urea $\cdot\ yH_2O$ which precipitate from aqueous ethanol ($x = 6$ and 4 with $y = 2$ and 4, respectively) or are obtained by grinding together $Th(NO_3)_4 \cdot 5\ H_2O$ and the appropriate quantity of ligand ($x = 10, 7, 6$ and 2 with $y = 0.1, 2.5$ and 2 respectively) contain both ionic and covalent nitrate groups whereas $Th(NO_3)_4 \cdot 2$ urea $\cdot\ 6\ H_2O$ and $Th(NO_3)_4 \cdot 11$ urea $\cdot\ 2.5\ H_2O$ contain only covalent and ionic groups, respectively [180]. The increase in urea: thorium ratio is accompanied by the gradual displacement of nitrato groups from the coordination sphere by urea. The IR spectra of $Th(NO_3)_4 \cdot$ 2 urea $\cdot\ H_2O$ and $Th(NO_3)_4 \cdot 2$ urea $\cdot\ 6\ H_2O$ do not show absorption in the range 1370—1390 cm^{-1}, but an intense band at 1300 cm^{-1}, due to a covalently bound nitrato group; the IR spectrum of $Th(NO_3)_4 \cdot 4$ urea $\cdot\ 4\ H_2O$ shows the presence of both coordinate and ionic nitrate groups. In the compound $Th(NO_3)_4 \cdot 10$ urea the inner coordination sphere of thorium probably contains one bidentate nitrato group while the compound $Th(NO_3)_4 \cdot 11$ urea $\cdot$ 2.5 H_2O apparently does not contain coordinated nitrato groups or free urea molecules. For the complexes $MgTh(NO_3)_6 \cdot 6$ urea $\cdot\ 4\ H_2O$ and $NiTh(NO_3)_6 \cdot$ 5 urea $\cdot\ 3H_2O$, in addition to the absorption bands of urea coordinated through the oxygen atom, there are bands due to the coordinated nitrato groups and the nitrate anions. It was proposed also that especially in the complexes with a low urea : thorium ratio, thorium may achieve a high coordination number as a result of the coordination of water molecules, but no further evidence besides the IR data have been published [180].

N. ACTINIDE(VI) NITRATE COMPLEXES WITH UREA

Solid state interaction between urea and uranyl nitrate hexahydrate or uranyl nitrate diurea, results in the formation of a series of complexes with metal to urea ratios 1 : 2, 1 : 3 and 1 : 5 [181]. The physicochemical data suggest the complex "$UO_2(NO_3)_2$(urea)$_4$" is a mixture of [$UO_2(NO_3)$(urea)$_3$]NO_3 and [UO_2(urea)$_5$]$(NO_3)_2$. Two modifications of UO_2(urea)$_2(NO_3)_2$ have been prepared [181]. The α-form, the more stable of the two modifications, is converted to the β-form at temperatures above 145°C. The latter is stable in vacuo for one month whereas exposure to the atmosphere for a week affects a transition to the α-form. The α modification has been also obtained from $UO_2(NO_3)_2 \cdot 6\ H_2O$ and urea in alcoholic solution by slow evaporation overnight in the dark; if rapid crystallization is induced by continuous stirring, the β-form is obtained [181]. The coordination of the uranyl(VI) ion in $[UO_2(H_2O)(\text{urea})_4](NO_3)_2$ has been a matter of some disagreement. On the basis of IR results, it was postulated [182] that the complex should be formulated as $[UO_2(H_2O)(\text{urea})_4(NO_3)]NO_3$ with the uranyl ion surrounded by six oxygen atoms, four from urea ligands, one from a water ligand and one from a monodentate nitrato group. A polymeric structure with sixfold coordination about the uranyl ion, consisting of four oxygen atoms from urea ligands, one oxygen atom from a water ligand and a uranyl oxygen from a neighbouring complex was also postulated [183]. A neutron diffraction study [184] shows that the complex is correctly formulated as $[UO_2(H_2O)(\text{urea})_4](NO_3)_2$. The compound is monoclinic with space group $P2_1/c$ and $Z = 4$ with $a = 9.99$, $b = 14.99$ and $c = 13.18$ Å, $\beta = 100.08°$. Preliminary X-ray data have been used to locate the approximate positions of the uranium and non-hydrogen atoms of the urea and water ligands, utilizing the heavy atom method. The uranyl(VI) ion is almost linear with a O—U—O angle of 177.7°, with the oxygens occupying the apical positions of the pentagonal bipyramid polygon of the heptacoordinated uranium atom (Fig. 25). Five oxygen atoms, four from urea molecules and one from a water molecule, lie in the equatorial plane forming a slightly irregular pentagon. The oxygens in the pentagon are slightly puckered. Both nitrate ions are bound to the water oxygen by hydrogen bonds. In such a situation the deviation of the ion from D_{3h} symmetry would not be as large as that which occurs in bidentate nitrato groups [185]. The results of the diffraction experiment support this view. The average N—O bond length was found to be 1.22 Å and none of the O—N—O angles differed significantly from 120°. The atoms of each nitrate ion are coplanar.

In a recent study [154] only two complexes, $UO_2(NO_3)_2(\text{urea})_2$ and $[UO_2$-

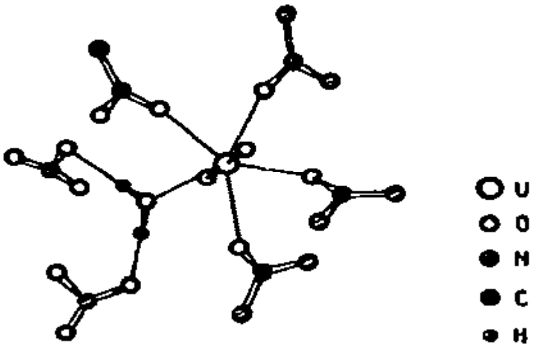


Fig. 25. The molecular structure of $\{UO_2(H_2O)[CO(NH_2)_2]_4\}(NO_3)_2$.

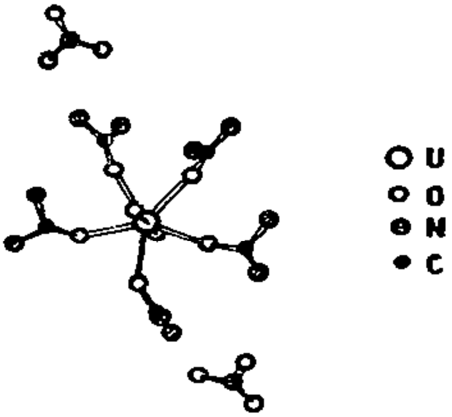


Fig. 26. The molecular structure of $\{UO_2[CO(NH_2)_2]_5\}(NO_3)_2$.

$(H_2O)(urea)](NO_3)_2$ were obtained. In the IR spectra of the complex $[UO_2(H_2O)(urea)_4](NO_3)_2$ (Table 17) the separation $(\nu_4 - \nu_1)$ is 80 cm^{-1} whilst the corresponding Δ in $UO_2(NO_3)_2(urea)_2$ which contains bidentate nitrate groups is 240 cm^{-1}. The interaction of the nitrate ions with the water molecule of $[UO_2(H_2O)(urea)_4](NO_3)_2$ via hydrogen bonds should explain a symmetry lower than D_{3h}. The ionic nitrates in $[UO_2(H_2O)(urea)](NO_3)_2$ cannot be replaced by the tetraphenylborate or perchlorate anion, the reactions leading to decomposition [154].

Spectral results suggest [186—188] that the complex $[UO_2(urea)_5](NO_3)_2$ contains only ionic nitrate groups; no splitting is observed in the ν_3 of the ionic nitrate groups, due to distortion of this group in the crystal lattice. The crystal structure of $[UO_2(urea)_5](NO_3)_2$ confirms the presence of the ionic nitrates [230]. The crystals are monoclinic, space group $P2_1/n$ and $Z = 4$ with cell parameters $a = 15.944$, $b = 8.952$ and $c = 15.394$ Å, $\beta = 106.3°$. The molecular structure (Fig. 26) consists of a uranium atom at the centre of a pentagonal bipyramid with two uranyl oxygens at the apices and five urea oxygen atoms on the equator. The complex is thus monomeric and not a polymer as suggested earlier [181]. The average U—O(urea) distance is 2.38 Å. Hydrogen bonding in the structure is mostly rather weak.

Only one nitrate ion in $UO_2(H_2O)(urea)_4(NO_3)_2$ is replaced with sodium halide in aqueous solution; the iodide nitrate and the bromide nitrate form mixed complexes with the composition $[UO_2(H_2O)(urea)_4]X(NO_3)$ where X = I or Br [186]. With chloride nitrate the two compounds $[UO_2(H_2O)(urea)_4]Cl(NO_3)$ and $[UO_2(H_2O)(urea)_4]Cl_{0.5}(NO_3)_{1.5}$ [186] have been prepared. In alcoholic solution $[UO_2(H_2O)(urea)_4](NO_3)_2$ reacts with I^- to form $[UO_2(H_2O)(urea)_4](I)_2$ and $[UO_2(H_2O)(urea)_4]I_n(NO_3)_{2-n}$ ($n = 1.4$—2). In both alcoholic and aqueous solution $[UO_2(urea)_5](NO_3)_2$ gives with I^- $[UO_2(urea)_5](I)_2$ and also non-stoicheiometric iodide nitrate complexes of composition $[UO_2(urea)_5]I_n(NO_3)_{2-n}$ (n = 1.43—1.27). The compound $[UO_2(urea)_5]Cl(NO_3)$ has also been isolated [186]. The IR and luminescence spectra of $[UO_2(H_2O)(urea)_4]X_n(NO_3)_{2-n}$ ($X = I^-$, n = 1.1, 1.7; $X = Br^-$, n = 1; $X = Cl^-$, n = 0.5) and $[UO_2(urea)_5]X(NO_3)$ ($X = I^-$ or Cl^-) show that urea is always present in the inner sphere and the nitrate ions in the outer sphere [188]. Uranyl(VI) nitrate complexes with the substituted ureas N,N,N′,N′-tetramethylurea (dmu), the cyclic propylene urea 2(1 H)-tetrahydropyrimidinone (pu) and the cyclic ethylene urea 2-imidazolidinone (eu) have been prepared by mixing uranyl(VI) nitrate hexahydrate and the appropriate ligand in hot ethanol; the complexes are of the type $UO_2(NO_3)_2(L)_2$ [189]. IR spectra have demonstrated that in all cases the ureas are monodentate via the oxygen atom and that only bands attributable to the C_{2v} symmetry of the nitrate groups are present [189]. The appearence of two groups of combination bands at 2560 and 2300 cm^{-1} and at 1780 and 1730 cm^{-1}, assigned respectively to the $\nu_2 + \nu_1$, $\nu_2 + \nu_4$, $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$ modes, undoubtedly indicate bidentate nitrate groups. The complexes behave in nitromethane—ethanol (9 : 1) solution as non-electrolytes.

O. ACTINIDE(VI) NITRATE COMPLEXES WITH CARBAMATES

Monomeric complexes of formula $UO_2(NO_3)_2L_2$ (L = N-substituted ethylcarbamates) have been synthesized by dissolving uranyl(VI) nitrate hexahydrate in the corresponding substituted ethylcarbamate followed by sublimation of excess ligand under vacuum [166,167] or by extraction of the complex with diethyl ether and precipitation with n-hexane [168].

A series of uranyl(VI) nitrate complexes with substituted ethylcarbamates has been prepared more recently by dissolving uranyl(VI) nitrate hexahydrate and the ligand in a 1 : 2 molar ratio in diethyl ether. The yellow oils initially formed crystallise in about half an hour [169]. The crystal and molecular

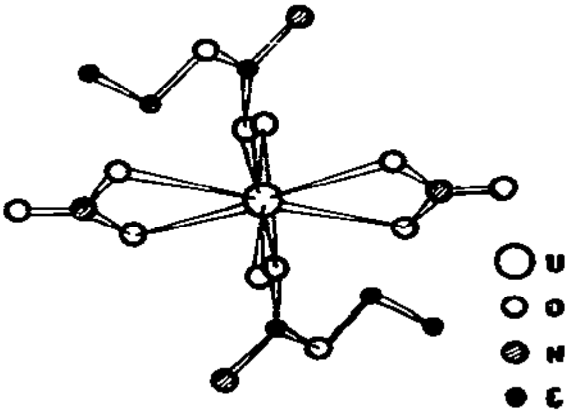


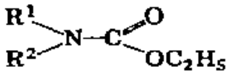
Fig. 27. A view of the complex $UO_2(NO_3)_2(EU)_2$.

structure has been determined for bis-(ethylcarbamate)-dinitrato dioxouranium(VI), $UO_2(NO_3)_2(EU)_2$ [167]; the crystals are monoclinic, space group $P2_1/a$ with $a = 12.176$, $b = 8.364$ and $c = 7.847$ Å, $\beta = 90.42°$ and $Z = 2$. A view of the molecule $UO_2(NO_3)_2(EU)_2$ is shown in Fig. 27. Eight coordination of the uranium atom is realised by an irregular hexagon of six oxygen atoms bonded in the equatorial plane which is normal to the linear uranyl(VI) group (U=O, 1.73 Å). The two nitrate groups, crystallographically equivalent, are bidentate and lie approximately in the base plane, together with the two oxygen atoms from the equivalent ethylcarbamate groups so that the symmetry of the immediate coordination of the uranium atom is D_{2h}. The six oxygen atoms are coplanar. The D_{3h} symmetry of the free nitrate group is lowered to C_{2v} in the complex because of asymmetry introduced by coordination; the nitrate group is perfectly planar and is tilted 4.5° with respect to the equatorial plane. The ethylcarbamate ligand is coordinated to the uranium atom through the amidic oxygen atom. The U—O(carbamate) distance of 2.40 Å is very simi-

TABLE 12

Infrared spectra of uranyl(VI) nitrate complexes with carbamates (cm^{-1}) [a]

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	νC—O	ν_3O—U—O	Ref.
$UO_2(NO_3)_2(U)_2$	1525	1028	740	1290 1270		800			167
$UO_2(NO_3)_2(MU)_2$	1500	1040 1020	742	1280	715	802	1640	940	168
$UO_2(NO_3)_2(DMU)_2$	1530	1010 1030	745	1270	715	805	1635	940	168
$UO_2(NO_3)_2(EU)_2$	1500	1027	741	1275		805	1633	935 930	169
$UO_2(NO_3)_2(DEU)_2$	1520 1500	1028	744	1298 1275	720	809	1620	945 938	169
$UO_2(NO_3)_2(PhU)_2$	1514	1018		1275	720	800	1662	940	169
$UO_2(NO_3)_2(DPhU)_2$	1528	1028	743	1280		803	1630	945 938	169
$UO_2(NO_3)_2(PhEU)_2$	1528	1025 1016	741	1268	719	802	1610	932	169
$UO_2(NO_3)_2(1\text{-}PhU)_2$	1540	1020 1006	742	1280		800	1621	930	169

[a] Abbreviations used for the carbamates  $R^1R^2N{-}C(=O)OC_2H_5$ are: $R^1 = R^2 = H$ (U); $R^1 = H$, $R^2 = Me$ (MU); $R^1 = R^2 = Me$ (DMU); $R^1 = H$, $R^2 = C_2H_5$ (EU); $R^1 = R^2 = C_2H_5$ (DEU); $R^1 = H$, $R^2 = C_6H_5$ (PhU); $R^1 = R^2 = C_6H_5$ (DPhU); $R^1 = C_6H_5$, $R^2 = C_2H_5$ (PhEU); $R^1 = H$, $R^2 = C_6H_5(CH_3)CH$ (1-PhU).

lar to that found for U—O(water) in $[UO_2(NO_3)_2(H_2O)_2] \cdot 4\ H_2O$ (2.39 Å) [69].

A similar structure can be suggested for the other N-substituted ethylcarbamate uranyl(VI) nitrate complexes. The IR spectra of all these complexes exhibit bands characteristic of bidentate nitrate groups (Table 12). The value of the antisymmetric stretching frequency ν_3O—U—O, in the range 930—940 cm^{-1}, suggests that N-substituted ethylcarbamates are weaker donors than trimethylamine-, triphenylphosphine- or triphenylarsine-oxide [160,170,171] and have a donor ability comparable to that of urea [74,154,167]. Coordination of carbamates to the uranium atom through the carbonyl oxygen is confirmed by the lowering of the νC=O stretching frequency relative to that of the free ligands.

In the case of the monosubstituted carbamates (methyl methane and ethyl methane) hindered rotation leads to the possibility of *cis—trans* isomerism and the presence of the ligand coordinated in both its isomeric forms has been suggested for the complexes $UO_2(NO_3)_2(BU)_2$ and $UO_2(NO_3)_2(MU)_2$ [168,169]. The signals in the ^{1}H NMR spectra of the free ligands due to the O—CH_2—CH_3 protons are near 1 ppm (CH_3) and 4 ppm(CH_2); on complexation the CH_2 resonance shifts downfield, whereas the CH_3 resonance remains practically unchanged. The ^{1}H NMR spectrum of dimethyl methane in $CDCl_3$ at 27°C shows one signal for the N—CH_3 protons suggesting free rotation about the C—N bond [172—174]. Its spectrum in benzene is similar, except that all the resonances are shifted upfield. The complex $UO_2(NO_3)_2(DMU)_2$ shows in $CDCl_3$ two 1 : 1 signals for the N—CH_3 protons, shifted downfield with respect to the single free ligand signal. The coordination of the carbonyl group to the central metal leads to hindered rotation about the N—C bond. In benzene the separation is larger than in $CDCl_3$ and all the resonances are shifted upfield. Both these effects can be attributed to interactions with the solvent. The N—CH_3 signals tend to get closer on increasing the temperature, but are far from coalescence at 70°C, indicating in the adduct a free energy of activation for the hindered internal rotation substantially higher than that in the free ligand [168]. The same behaviour has been found for $UO_2(NO_3)_2(DEU)_2$ [169]. Neither complex dissociates in benzene.

P. ACTINIDE(IV) NITRATE COMPLEXES WITH AMIDES

Thorium(IV) tetrachloride forms a complex with N,N-dimethylacetamide (DMA) of composition $ThCl_4 \cdot 4$ DMA from which the corresponding nitrate $Th(NO_3)_4 \cdot 2.5$ DMA has been prepared [175]; this complex melts with decomposition at 126—128°C. A hydrated complex of composition $Th(NO_3)_4 \cdot 3$ DMA $\cdot\ 3\ H_2O$ has been reported to be formed from hydrated thorium(IV) tetranitrate by treatment with an excess of dimethylacetamide [176]. The nitrate groups are covalently bonded and a shift towards lower frequency of the C=O stretching of the monodentate ligand has been observed ($\Delta\nu_{C=O} \sim 44$—37 cm^{-1}) [175] (Tables 13 and 14).

TABLE 13

Infrared spectra of the actinide(IV) nitrate complexes with amides (cm^{-1}) [a]

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	νC—O	Ref.
$Th(NO_3)_4 \cdot 2.5$ DMA	1500	1027	744 739	1306 1286	702	809	1610	175
$U(NO_3)_4 \cdot 2.5$ DMA	1517	1020	743 739	1277	702	807	1610	23
$Np(NO_3)_4 \cdot 2.5$ DMA	1515	1033 1025	751 744	1278 1253		807		24
$Th(NO_3)_4 \cdot 3$ EA [b]	1510	1030	741	1300	720	810	1615	179
$U(NO_3)_4 \cdot 2.5$ EA	1560	1030	741	1275	715	809	1600	179
$Pu(NO_3)_4 \cdot 2$ EA	1530	1015	740	1275		800	1610	179
$Th(NO_3)_4 \cdot 3$ NMA	1500	1035	743	1285	725	810	1618	177
$Th(NO_3)_4 \cdot 2.5$ DEA	1515	1028	741	1280	710	808	1590	177
$U(NO_3)_4 \cdot 2.5$ DEA	1522	1040	750	1290	718	812	1608	177
$Th(NO_3)_4 \cdot 2.5$ DMPA	1500	1033	746	1280	722	812	1610	177
$U(NO_3)_4 \cdot 2.5$ DMPA	1525	1035	751	1285	725	815	1610	177
$Th(NO_3)_4 \cdot 2$ DPHA	1495	1035	748	1285	720	814	1608	177
$U(NO_3)_4 \cdot 2.5$ PVA	1520	1035	748	1275	720	813	1583	177
$Th(NO_3)_4 \cdot 2.5$ DIPA [c]	1516	1035	748	1294	680	814	1570	179
$U(NO_3)_4 \cdot 2.5$ DIPA	1525	1039	755	1295	726	815	1585	179
$Pu(NO_3)_4 \cdot 2$ DIPA	1530 1515	1030 1010	738	1273	715	800	1560	179

[a] Abbreviations used for the amides $R^1CONR^2R^3$ are: R^1 = Me, $R^2 = R^3$ = Me (DMA); R^1 = Me, R^2 = H, R^3 = Me (NMA); R^1 = Me, $R^2 = R^3$ = Et (DEA); R^1 = Me, $R^2 = R^3$ = Ph (DPHA); R^1 = Et, $R^2 = R^3$ = Me (DMPA); $R^1 = Me_3C$, $R^2 = R^3$ = Me (PVA); R^1 = Me, $R^2 = R^3$ = i-Pr (DIPA); R^1 = Me, R^2 = H, R^3 = Et (EA). [b] The Raman spectrum of this complex shows the following nitrate bands: ν_1 = 1525, 1450, ν_2 = 1036, ν_3 = 750, ν_4 = 1312, ν_5 = 705. [c] The Raman spectrum of this complex shows the following nitrate bands: ν_1 = 1516, 1480, 1465, ν_2 = 1036, ν_3 = 749, ν_5 = 705, 697.

The pale green complex $U(NO_3)_4 \cdot 2.5$ DMA has been prepared by treating an acetone solution of $UCl_4 \cdot 2.4$ DMA, in the presence of an excess of ligand, with the calculated quantity of $AgNO_3$ in CH_3CN. The complex can also be prepared, but in poor yield, from $Cs_2U(NO_3)_6$ and DMA in hot acetone or cold ethanol [23]. $U(NO_3)_4 \cdot 2.5$ DMA is non-hygroscopic and soluble in acetone, acetonitrile, N,N-dimethylacetamide, dioxan, ethanol, methanol and nitromethane, slightly soluble in ethylacetate and insoluble in benzene, diethylcarbonate, diethylether and diisobutylketone. It is not very stable, the evolution of oxides of nitrogen being detectable at 65°C; it melts to a green liquid at 80—82°C and oxidation to uranium(VI) is complete at 90—95°C. It is

TABLE 14

Raman spectra of some thorium(IV) nitrate complexes with amides (cm^{-1}) [a] [177]

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
$Th(NO_3)_4 \cdot 3$ NMA	1523w	1038vs	750w	1315w	705vw	
$Th(NO_3)_4 \cdot 2.5$ DEA	1490s 1455s	1031vs 1026vs	747m	1290w	714s	
$Th(NO_3)_4 \cdot 2.5$ DMPA	1500w 1460w	1033vs	745w		720w 705vw	815w
$Th(NO_3)_4 \cdot 2.5$ PVA	1509w 1449w	1040vs 1030vs	750w		722m	830w
$Th(NO_3)_4 \cdot 2$ DPHA	1490m 1470m	1029m	745w		712	

[a] Abbreviations used for the amides are: R^1 = Me, R^2 = H, R^3 = Me (NMA); R^1 = Me, R^2 = R^3 = Et (DEA); R^1 = Et, R^2 = R^3 = Me (DMPA); R^1 = Me_3C, R^2 = R^3 = Me (PVA); R^1 = Me, R^2 = R^3 = Ph (DPHA).

slowly oxidized on storage (about 6% in one month). Nitrate bands have been observed in its IR spectrum at 1517, 1277, 1020, 807 and 702 cm^{-1} with a doublet at 743, 739 cm^{-1} indicating covalent nitrate groups [23].

A pale green neptunium(IV) tetranitrate—DMA complex of composition $Np(NO_3)_4 \cdot 2.5$ DMA, is formed by the reaction of tetrachloride complex with $AgNO_3$ in dry CH_3CN as in the case of the uranium analogue [23], but the complex is more conveniently prepared by treating $Np(NO_3)_4 \cdot 2\ H_2O$ with a mixture of DMA and acetone [24]. X-ray power data show it to be isostructural with $U(NO_3)_4 \cdot 2.5$ DMA [24]. $Np(NO_3)_4 \cdot 2.5$ DMA evolves oxides of nitrogen at about 65°C and melts at 85—90°C to a greenish-yellow solution which evolves more brown fumes with frothing at 105°C [24]. Although $Np(NO_3)_4 \cdot 2.5$ DMA appears to show Curie-Weiss dependence at higher temperatures, deviations appear below about 200 K and no accurate assignment of the Weiss constant has been reported [23,24].

The thorium tetranitrate complexes with the amides of the general formula $R^1CONR^2R^3$ (R^1 = Me, R^2 = H, R^3 = Me (NMA); R^1 = Me, R^2 = R^3 = Et (DEA), Ph (DPHA); and R^1 = Et (DMFA), Pr^n (BA), Me_2CH (IBA), Bu^n (VA), Me_2CHCH_2 (IVA), Me_3C (PVA), R^2 = R^3 = Me) have been prepared by treating the hydrated nitrate with the ligands in acetone or ethanol [177]. In some instances (BA, IBA, VA and IVA) the products were oils that could not be solidified. The uranium tetranitrate complexes with DEA and DMPA have been prepared in the same way from $Cs_2[U(NO_3)_6]$, but at 0°C to minimise oxidation to uranium(VI); DPHA does not react with $Cs_2[U(NO_3)_6]$ and PVA reacts only slowly, no pure products being obtained. With NMA the tris complex $Th(NO_3)_4 \cdot 3$ NMA was obtained in contrast to the 1 : 2.5 stoicheiometry of the DEA, DMPA (thorium(IV), uranium(IV)) and PVA (thorium) complexes.

The behaviour of PVA with thorium(IV) tetranitrate is surprising because DPHA forms only the bis-complex with thorium tetranitrate and PVA, a bulky ligand, is known to form only bis-complexes with thorium and uranium tetrachloride [178].

One possible formulation of the complexes of 1 : 2.5 stoicheiometry would be an ionic species of the type $[M(NO_3)_2(L)_5]^{2+}[M(NO_3)_6]^{2-}$; the molar conductivities (Λ_{1000}) of the complexes in nitromethane at 20° C ranged from 25.0 for $U(NO_3)_4 \cdot 2.5$ DEA to 57.5 Ω^{-1} cm^2 mol^{-1} for $Th(NO_3)_4 \cdot 3$ NMA, most of them being below 47 Ω^{-1} cm^2 mol^{-1}. The plots of Λ against $\sqrt{c}$ are moderately linear, but no conclusions as to the ionic species present, if any, could be drawn from the results. The thorium(IV) complexes are not hygroscopic; they are soluble in common organic solvents, such as acetone, ethanol, methyl cyanide and nitromethane and insoluble in hydrocarbons, diethylether and carbon tetrachloride. The monodentate ligands are coordinated to the metal atom via the amide carbonyl oxygen atom, the shifts to lower frequency in the C=O stretching mode ranging from 32 to 77 cm^{-1}. Ionic nitrate groups are absent and although the features of the Raman spectra of the thorium(IV) tetranitrate complexes were badly obscured because of fluorescence, ν_4 usually being too weak to be discerned, ν_2 could be seen easily as a very strong feature. In these complexes the nitrate groups are considered to be bidentate [177]. The uranium(IV) compounds were too thermally unstable for Raman spectra to be obtained [177].

The interaction of thorium(IV), uranium(IV) and plutonium(IV) tetranitrate with N-ethyl and N,N-diisopropylacetamide (EA and DIPA, respectively) has been reported [179]. The thorium(IV) tetranitrate complexes have been prepared from the hydrate nitrates, and uranium and plutonium tetranitrate complexes from $Cs_2[M(NO_3)_6]$ (M = U, Pu) [177]. The attempted preparation of a complex of plutonium tetranitrate with the more bulky ligand N,N-dimethyl-2,2-dimethylpropanoic acid amide (PVA) by this latter method was unsuccessful [179]. The uranium tetranitrate complexes are unstable with respect to oxidative decomposition to uranyl(VI) species; the DIPA complex decomposes above 110°C and the EA complex decomposes at room temperature within 24 h of preparation. $Pu(NO_3)_4 \cdot 2$ EA isolated as an oil, becomes crystalline after grinding under 2-methylbutane for 14 days. All the complexes are soluble in hydrocarbons; they are not noticeably hygroscopic. The molar conductivities (Λ_{1000}) in nitromethane range from 29.3 for $U(NO_3)_4 \cdot 2.5$ EA to 68.1 Ω^{-1} cm^2 mol^{-1} for $U(NO_3)_4 \cdot 2.5$ DIPA but no conclusions as to the ionic species present, if any, have been drawn from the results. Again the ligands are coordinated to the metal atom via the amide carbonyl group oxygen atom, the shift, 40—70 cm^{-1}, to lower frequency in the C=O stretching mode being comparable with those in other amide complexes. All the nitrate groups are covalently bound (Tables 13 and 14).

Q. ACTINIDE(VI) NITRATE COMPLEXES WITH AMIDES

Uranyl(VI) nitrate forms bis complexes with amides of the type $UO_2(NO_3)_2(L)_2$ (Table 15) [177, 179]. They are yellow, non-hygroscopic, soluble in common organic solvents such as acetone, ethanol, methyl cyanide and nitromethane but insoluble in hydrocarbons, diethylether and carbon tetrachloride. The ligands are coordinated to the uranyl(VI) ion through the amide carbonyl oxygen atom, the shift to lower frequency in the C=O stretching mode ranging from 40 to 77 cm^{-1}. From the IR data it may be concluded that the nitrates are bidentate, the uranyl(VI) ion being hexacoordinated in the equatorial plane (Table 15).

TABLE 15

Infrared spectra of uranyl(VI) nitrate complexes with amides (cm^{-1}) [a]

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	νC—O	Ref.
$UO_2(NO_3)_2(DEA)_2$	1515	1030	742	1285	710	810	1600	177
$UO_2(NO_3)_2(DMPA)_2$	1510	1025	743	1270	710	810	1565	177
$UO_2(NO_3)_2(PVA)_2$	1500	1025	740	1275	703	806	1592	177
$UO_2(NO_3)_2(IVA)_2$	1500	1025	740	1270	710	804	1590	177
$UO_2(NO_3)_2(VA)_2$	1500	1025	740	1270	700	808	1596	177
$UO_2(NO_3)_2(DPHA)_2$	1530	1030	742	1280	710	805	1605	177
$UO_2(NO_3)_2(BA)_2$	1515	1028	741	1275	718	804	1595	177
$UO_2(NO_3)_2(IBA)_2$	1505	1028	740	1280	715	808	1584	177
$UO_2(NO_3)_2(DIPA)_2$	1510	1025	740	1274	715	805	1668	179

[a] Abbreviations used for the amides $R^1CONR^2R^3$ are: R^1 = Me, $R^2 = R^3$ = Et (DEA); R^1 = Et, $R^2 = R^3$ = Me (DMPA); $R^1 = Me_3C$, $R^2 = R^3$ = Me (PVA); $R^1 = Me_2CHCH_2$, $R^2 = R^3$ = Me (IVA); R^1 = n-Bu, $R^2 = R^3$ = Me (VA); R^1 = Me, $R^2 = R^3$ = Ph (DPHA); R^1 = n-Pr, $R^2 = R^3$ = Me (BA); $R^1 = Me_2CH$, $R^2 = R^3$ = Me (IBA); R^1 = Me, $R^2 = R^3$ = i-Pr (DIPA).

R. ACTINIDE(IV) NITRATE COMPLEXES WITH AMINE N-OXIDES

The reaction of thorium(IV) tetranitrate with the aromatic amine oxides, pyridine N-oxide (pyO), lutidine N-oxide (lutO), collidine N-oxide (colO), 2-picoline N-oxide (2-picO), 4-picoline N-oxide (4-picO) and quinoline N-oxide (QuO), has been studied [157]. With the exception of pyO, all the ligands form 1 : 3 complexes with $Th(NO_3)_4$ and complexes with higher metal : ligand ratios could not be obtained. Pyridine N-oxide alone forms the 1 : 8 complex, $Th(NO_3)_4 \cdot 8$ pyO, and attempts to form the 1 : 3 complex with this ligand always lead to the 1 : 8 complex even with excess metal present.

The spectrum of $Th(NO_3)_4 \cdot 8$ pyO shows no evidence of coordinated nitrate; a strong band centered at 1352 cm^{-1}, corresponding to the ionic nitrates, is present while the bands corresponding to coordinate nitrate

TABLE 16

Infrared spectra of thorium (IV) nitrate complexes with aromatic amine N-oxides (cm^{-1}) [157][a]

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	νN—O
$[Th(pyO)_8](NO_3)_4$ [b]							1266
$Th(NO_3)_4 \cdot 3$ LutO	1500	1032	744	1301		812	1210
$Th(NO_3)_4 \cdot 3$ ColO	1505	1030	741	1274		809	1209
$Th(NO_3)_4 \cdot 3$(2-PicO)	1499	1030 1028	741	1316 1295	721	811	1215 1225
$Th(NO_3)_4 \cdot 3$(4-PicO)	1494	1029	745	1282	722	809	1217, 1231
$Th(NO_3)_4 \cdot 3$ QuO	1500	1027	743	1295			1231

[a] pyO = pyridine N-oxide; LutO = lutidine N-oxide; ColO = collidine N-oxide; 2-PicO = 2-picoline N-oxide; 4-PicO = 4-picoline N-oxide; QuO = quinoline N-oxide. [b] IR spectrum shows no evidence of coordinated nitrate; a strong band centered at 1352 cm^{-1} occurs, corresponding to ionic nitrate.

groups are absent. The spectra of the remaining complexes are all consistent with coordinated nitrate groups. The spectral data of the fundamental vibrations of the nitrate groups do not allow one to distinguish between unidentate and bidentate bonding of nitrate; however the separation of the combination bands ($\nu_2 + \nu_3$) and ($\nu_2 + \nu_5$) suggests that the nitrate groups are bidentates. The frequencies of the N—O stretching are consistent with oxygen-bonded amine oxides. $Th(NO_3)_4 \cdot 8$ pyO is thus eight coordinated and can be written $[Th(pyO)_8](NO_3)_4$ while the remaining complexes are eleven coordinate (Table 16).

S. ACTINIDE(VI) NITRATE COMPLEXES WITH AMINE N-OXIDES

It is known that in Me_3NO the oxygen is linked to the nitrogen atom by a single bond [158], the lack of π-bonding in the N—O bond as compared with the P—O or As—O bond accounts well for the greater donor properties of Me_3NO compared with the substituted phosphine or arsine oxide [159].

The pale yellow complex $UO_2(NO_3)_2(Me_3NO)_2$ was isolated by concentrating an acetone solution of $UO_2(NO_3)_2 \cdot 6\ H_2O$ and Me_3NO (1 : 2 molar ratio); with a molar ratio of 1 : 5 the green yellow complex $[UO_2(Me_3NO)_4](NO_3)_2$ can be obtained [160]. $UO_2(NO_3)_2(Me_3NO)_2$ is monomeric and on the basis of the IR fundamental and combination bands due to the vibrational modes of the nitrate group, an eight coordinate complex is probable. The resulting configuration of $UO_2(NO_3)_2(Me_3NO)_2$ is expected to be quite similar to those of the Ph_3PO and Ph_3AsO analogues. In the IR spectrum of $[UO_2(Me_3NO)_4](NO_3)_2$ only two fundamental bands have been assigned to the

TABLE 17

Infrared spectra of uranyl(VI) nitrate complexes with urea and trimethylamine N-oxide (cm^{-1})

Compound	ν_1	ν_3	ν_4	ν_3	ν_4	ν_5	ν_2	ν_1	ν_6	ν_2	ν_3O—U—O	Other bands	Ref.
α-$UO_2(NO_3)_2(urea)_2$	1520 1510		1320 1300	757 753			1042 1031		811		938	1640 (C=O)	181
β-$UO_2(NO_3)_2(urea)_2$	1530		1290	746			1032		810		952 934		181
$UO_2(NO_3)_2(Me_3NO)_2$	1500		1306	[a]		[a]	1041		813		875	960, 940 (N—O) [b]	160
$[UO_2(urea)_4(H_2O)](NO_3)_2$ [c]		1390 1310			 765			1058 1021		820 812	910	1640 (C=O)	154, 181
$[UO_2(urea)_5](NO_3)_2$		1370			722					823	917		181
$[UO_2(Me_3NO)_4](NO_3)_2$		1350			[a]					828	913	957, 947 (N—O) [b]	160

[a] Not observed. [b] This band should be due to the C—N and N—O stretching modes respectively; in the complexes such an assignment is uncertain. [c] The anomalous IR behaviour of the nitrate groups is due to the hydrogen bonds which change the D_{3h} symmetry of the NO_3^- ions.

vibration modes of the nitrate ion: ν_2 at 828 cm^{-1} and the ν_3 at 1350 cm^{-1} of the D_{3h} nitrate group. The combination bands at 2385 cm^{-1} and at 1752 cm^{-1} have been interpreted in terms of a likely ionic structure for the solid (Table 17). $[UO_2(Me_3NO)_4](NO_3)_2$ behaves in solution as a bi—univalent electrolyte and the nitrate ion can be substituted by tetraphenylborates indicating the existence of the species $[UO_2(Me_3NO)_4]^{2+}$.

T. ACTINIDE(IV) NITRATE COMPLEXES WITH PHOSPHINE AND ARSINE OXIDES

The thorium tetranitrate phosphine oxide complexes have been prepared by treating $Th(NO_3)_4 \cdot 5\ H_2O$ with the appropriate ligand in a suitable solvent. The uranium(IV) and neptunium(IV) analogues were obtained in a similar manner from the hexanitrato complexes $Cs_2[M(NO_3)_6]$. A serious problem is the ready oxidation of several of the resulting uranium(IV) complexes to the corresponding uranyl(VI) compounds. To date only $Pu(NO_3)_4(Ph_3PO)_2$ has been prepared by reaction of plutonium(IV) nitrate and triphenylphosphine oxide in methanol [130]. The stoicheiometry of the complexes obtained depends to a considerable extent on the size of the ligand. Thus, with the smallest of the ligands, Me_3PO (trimethylphosphine oxide), thorium and uranium tetranitrate form the tetrakis [93] and the pentakis [129] complexes. Although the mother liquor from the recrystallization of the thorium complex $Th(NO_3)_4 \cdot 4\ Me_3PO$ yields a small amount of the corresponding tris complex; the uranium tris complex could not be isolated. In contrast, under similar conditions, neptunium tetranitrate forms only the tris complex. The IR spectra of the tris complexes indicate all the nitrate groups are bonded whereas additional modes, assignable to the ionic nitrate, are present in the spectra of the tetrakis complexes (Tables 18—20) suggesting that they are of the form $[M(NO_3)_3(R_3PO)_4]^+(NO_3)^-$. The molar conductivities in nitromethane are consistent with 1 : 1 electrolyte behaviour. It has been reported, on the basis of Raman spectra, that in the complexes the nitrate groups are bidentate whereas some or all of the nitrato groups appear to be unidentate in $Np(NO_3)_4 \cdot 3\ Me_3PO$. Oxidation of the uranium(IV) complexes occurs in the laser beam.

With the ligand Pr^n_3PO (tris-n-propylphosphine oxide) complexes of composition $M(NO_3)_4 \cdot 2.67\ Pr^n_3PO$ (M = Th, U, Np) have been obtained. IR and Raman spectra indicate all the nitrate groups are bidentate. It is likely that the complexes are ionic but the conductivity results are inconclusive and do not allow one to assign a correct stoicheiometry to the complexes; a structural investigation of these complexes is clearly desirable. Partial X-ray powder diffraction photographs indicate that $Th(NO_3)_4 \cdot 2.67\ Pr^n_3PO$ and $Np(NO_3)_4 \cdot 2.67\ Pr^n_3PO$ are isomorphous [93]. Only the bis complexes $M(NO_3)_4 \cdot 2\ L$ (L = Ph_3PO, Ph_3AsO) have been obtained with the more bulky ligands [93,130,133]. $Th(NO_3)_4 \cdot (Ph_3PO)_2$ has been prepared by treating thorium nitrate hydrate with Ph_3PO in acetone, evaporating to dryness the resulting solution and extracting the crystalline residue with benzene. This

TABLE 18

Infrared spectra of actinide(IV) nitrate complexes with phosphine and arsine oxides

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν(P—O)	Ref.
$Th(NO_3)_4 \cdot 3\ Me_3PO$	1500br	1037	742	1290	710	820	1083	93, 140
$U(NO_3)_4 \cdot 3\ Me_3PO$	1500br	1030	746	1290	705sh	810		140
$Np(NO_3)_4 \cdot 3\ Me_3PO$	1502 1495	1024	760 752	1278		820 805	1073	93
$Th(NO_3)_4 \cdot 4\ Me_3PO$	1512	1035	760	1287		820, 813	1085	93
$U(NO_3)_4 \cdot 4\ Me_3PO$	1510	1035	764 750	1292		820	1087	93
$Th(NO_3)_4 \cdot 5\ Me_3PO$	1390 1470	[a]	740	1300	[b]	827		140
$U(NO_3)_4 \cdot 5\ Me_3PO$	1470 1390	[a]	740	1295	[b]	820		140
$Th(NO_3)_4 \cdot 3.67\ Me_3PO$	1515	1037	743	1295	710	[c]	1084	129.
$Th(NO_3)_4 \cdot 2.67\ Me_3PO$	1515 1495 (1548)	1037	763 750	1300	710	[c]	1091	129
$Th(NO_3)_4 \cdot 2.33\ Me_3PO$	1510	1035	745					
	1485 (1545)	1031	738	1300	705	[c]	1087	129.
$PPh_4Th(NO_3)_5(Me_3PO)_2$	1520	1038 1031	756	[c]	708	[c]	1098	129
$Th(NO_3)_2(Me_3PO)_5[BPh_4]_2$	1510 (1559)	1031		1310	700	[c]	1075	129
$U(NO_3)_2(Me_3PO)_5[BPh_4]_2$	1508 1499	1033	[c]	1310	[c]	[c]	1073	129
$U(NO_3)_4 \cdot 3.33\ Me_3PO$	1515	1036 1028	748 741	1318 1290	706	[c]	1094 1077	129
$Th(NO_3)_4 \cdot 2.67\ Pr^n_3PO$	1520 1496	1042	745	1299 1282		815	1102 1095	93
$U(NO_3)_4 \cdot 2.67\ Pr^n_3PO$	1515 1495	1029	747	1298 1285		809	1092	93
$Np(NO_3)_4 \cdot 2.67\ Pr^n_3PO$	1518 1496	1031	744	1292 1282		805	1086	93
$Th(NO_3)_4 \cdot 4\ Bu^n_3PO$	1509 1504	1032	740	1295		815	1102 1082	93
$Th(NO_3)_4 \cdot 2\ Ph_3PO$	1540 1530	1027		1283		808	1062	93
$U(NO_3)_4 \cdot 2\ Ph_3PO$	1530	[d]	755	1275	700	815		134
$Np(NO_3)_4 \cdot 2\ Ph_3PO$	1546 1528	1020 1014	744	1277 1268		800	1056	93

TABLE 18 (Continued)

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν(P—O)	Ref.
$Pu(NO_3)_4 \cdot 2\ Ph_3PO$	1520	1032		1295		809	1067 1137	130
$U(NO_3)_4 \cdot 2\ Ph_3AsO$	1510	[d]	[e]	1280	[e]	808		134
$Pu(NO_3)_4 \cdot 2\ Ph_3AsO$	1519	1028		1298		809		130
$Th(NO_3)_4 \cdot 2$ HMPA	1528	1027	767	1286		812	1066	93
$U(NO_3)_4 \cdot 2$ HMPA	1545 1525 1510	1024		1293		814	1050	93
$Np(NO_3)_4 \cdot 2$ HMPA	1548 1524 1505	1057 1024	760	1300 1280 1253		805	1052	93
$Th(NO_3)_4 \cdot 3$ HMPA	1510	[b]	[b]	1300	711	820		140
$Th(NO_3)_4 \cdot 4$ HMPA	1500 1480	[b]	[b]	1310	712	818		140
$U(NO_3)_4 \cdot 2$ PTPA	1525	[d]	[e]	1280	[e]	808		134
$U(NO_3)_4 \cdot 4$ HMPA	1490			1308	705	811		134
$U(NO_3)_4 \cdot 4$ HMPA	1540		772 750	1305		842 813		134
$U(NO_3)_3 \cdot 4$ HMPA $\cdot$ BPh_4	1500		765	1312	715	818		134
$Th(NO_3)_4 \cdot 2.5$ OMPA	1510	1029	760	1289		807	1174	93
$Th(NO_3)_4 \cdot 1.5$ OMPA	1513	1028	750	1290		813	1166	93
$U(NO_3)_4 \cdot 1.5$ OMPA	1513	1029	745	1285		808	1155	93
$Np(NO_3)_4 \cdot 1.5$ OMPA	1515	1030	744	1283		805	1154	93
$Th(NO_3)_4 \cdot 1.5$ PPM	1546 1526 1516	1027		1293 1282		810	1160 1150 1140	93
$Th(NO_3)_4 \cdot 2$ PPE	1536 1515	1025		1290 1280		808	1182 1142 1131	93

solution deposits well-formed crystals on standing. Infrared results (Table 11) indicate the presence of covalent nitrate groups, confirmed by an X-ray structure determination carried out on the isostructural cerium(IV) and thorium(IV) complexes $M(NO_3)_4(Ph_3PO)_2$ (M = Ce and Th) [131]. In these complexes cerium(IV) and thorium(IV) are ten-coordinate, two oxygen atoms from each nitrate group being bonded to cerium, together with two oxygen atoms from Ph_3PO molecules. The coordination observed in $Ce(NO_3)_4(Ph_3PO)_2$ (Fig. 28) may be described as a distorted *trans* octahedral arrangement of two phosphoryl oxygen atoms and four nitrate groups, each nitrate group being con-

TABLE 19

Raman spectra of some actinide(IV) nitrate complexes with phosphine oxide [93]

Compound	ν_1	ν_4	ν_2	ν_6	ν_3, ν_5
$Th(NO_3)_4 \cdot 4\ Me_3PO$	1500vw	1300vw	1056s 1045s		775m 728m
$Np(NO_3)_4 \cdot 4\ Me_3PO$		1296ms	1048w, sh	810s	795m, sh
$Th(NO_3)_4 \cdot 2.67\ Pr^n_3PO$	1520w	1216w 1282vw	1040vs		753w
$Np(NO_3)_4 \cdot 2.67\ Pr^n_3PO$	1520w	1300w 1260w		810	
$Th(NO_3)_4 \cdot 4\ Bu^n_3PO$	1510w	1310w 1270w	1040		
$Th(NO_3)_4 \cdot 2$ HMPA	1545m 1539w 1496m	1320vw 1290vw	1034s		762w
$Th(NO_3)_4 \cdot 1.5$ OMPA	1625w 1552m 1520m		1040vs		760w, sh 710w
$Th(NO_3)_4 \cdot 1.5$ PPM	1590w 1530w 1510w		[a]		[a]
$Th(NO_3)_4 \cdot 2\ Ph_3PO$	1540w 1563w		[a]		752w 740w

[a] Obscured by ligand absorptions.

sidered to occupy a single coordination position [14]. The phosphoryl oxygen atoms are not colinear with the cerium atom but subtend 155.0°, while the four nitrate ions have their planes inclined in the approximate shape of a four-bladed propeller. The Ce—O distances are 2.437—2.518 Å for the nitrate group oxygens and significantly shorter 2.216 and 2.222 Å for the phosphoryl Ce—O contacts. The N—O distance r_3, is somewhat shorter than the r_1 and r_2 distances (Table 5).

More recently the crystal structure of $Th(NO_3)_4(Ph_3PO)_2$ has been determined [245]. The crystals are monoclinic, space group $P2_1/n$ and $Z = 4$ with $a = 12.08$, $b = 17.59$ and $c = 16.57$ Å, $\beta = 91.0°$. The structure is obviously identical to that found for the isostructural cerium(IV) analogue. A typical negative IR shift relative to the free P—O stretching frequency (Table 18) is observed for $Th(NO_3)_4(Ph_3PO)_2$ indicating coordination of the ligand via the oxygen atom. The shift to low frequency is much greater in this complex than observed for lanthanide(III) complexes [137,138] and similar to that observed for uranium(IV) [139]. The green $Pu(NO_3)_4(Ph_3PO)_2$ and the pink $Pu(NO_3)_4$-$(Ph_3AsO)_2$ have been obtained by reaction of plutonium nitrate and the

TABLE 20

Vibrations arising from ionic nitrate (cm^{-1}) and molar conductivities of some actinide (IV) nitrate complexes with phosphine oxide in nitromethane at 20°C [93].

Compound		$E'(\nu_3)$	$A_2''(\nu_2)$	Λ_{500} (Ω^{-1} cm^2 mol^{-1})	Λ_{1000} (Ω^{-1} cm^2 mol^{-1})	Electrolyte type
$Th(NO_3)_4 \cdot 4\ Me_3PO$	IR	1365sh	830w	72.4	75.6	1 : 1
	Raman	1365vw				
$U(NO_3)_4 \cdot 4\ Me_3PO$	IR	1350s, 1365m, sh	832vw	63.5	67.7	1 : 1
$Th(NO_3)_4 \cdot 4\ Bu_3^nPO$	IR	1343s	830w, sh	55.5	56.9	1 : 1
	IR [a]	1355m	835w, sh			
	Raman	1360w, 1310m				
$Th(NO_3)_4 \cdot 2.5$ OMPA	IR	1352s, 1334s, 1314s	832w			
$Th(NO_3)_4 \cdot 2$ HMPA				11.2	12.1	Non-electrolyte

[a] Carbon tetrachloride solution.

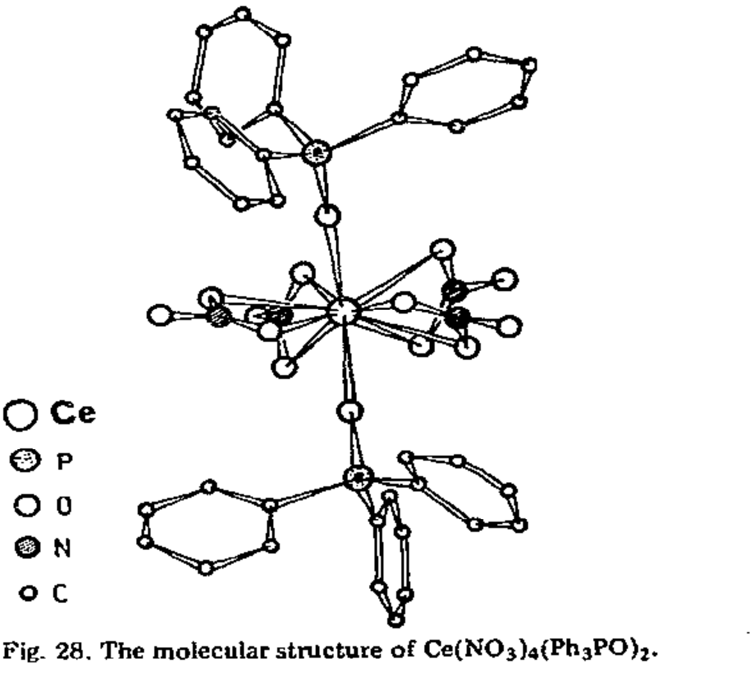


Fig. 28. The molecular structure of $Ce(NO_3)_4(Ph_3PO)_2$.

appropriate ligand in methanol [130]. The IR spectra show the nitrate groups to be bidentate [130]. The P—O stretching vibration is shifted to 1067 cm^{-1} by complex formation (1195 cm^{-1} for the free ligand); for the arsine oxide complex the As—O stretching vibration is lowered by complex formation and a single strong band at 850 cm^{-1} has been observed [130]. A band at 420 cm^{-1} for $Pu(NO_3)_4(Ph_3PO)_2$ has been assigned to the Pu—O stretching of the Pu—O—P group. $Pu(NO_3)_4(Ph_3AsO)_2$ exhibits a band at 377 cm^{-1} assigned to the Pu—O stretching of the Pu—O—As group. Additional bands observed at 224 and 226 cm^{-1} for the Ph_3PO and Ph_3AsO complex respectively have been tentatively assigned to the Pu—O stretching of the Pu—O(nitrate) group [130].

Tributylphosphate (TBP) has been widely employed as an extracting agent for actinide nitrates. If forms with actinide(IV) ion complexes of the type $Th(NO_3)_4(MDPP)_4$ (M = Th [5,132,133], Np [135], Pu [136]). The Raman spectrum of the liquid $Th(NO_3)_4(TBP)_2$ shows all the nitrate ions are bidentate [5].

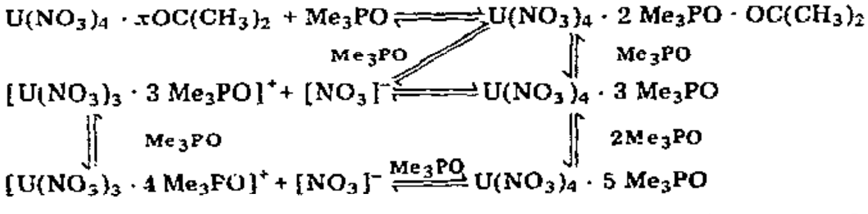
Thorium nitrate forms the complex $Th(NO_3)_4(MDPP)_4$ when a saturated aqueous solution of the actinoid salt is equilibrated with MDPP (MDPP = methyldiphenylphosphate) [220]. The complex is insoluble in mineral acids or bases but some organic solvents such as benzene, methyl isobutyl ketone, dioxan and chlorobenzene decompose it. After the decomposition the organic phase contains MDPP, the solid phase left being $Th(NO_3)_4$. No other physicochemical data have been reported, but very probably the compound has a complex and ionic structure.

$Th(NO_3)_4 \cdot 2$ HMPA and $U(NO_3)_4 \cdot 2$ HMPA (HMPA = hexamethylphosphoramide) are probably similar in structure to $Th(NO_3)_4(Ph_3PO)_2$. The Raman spectrum of $Th(NO_3)_4 \cdot 2$ HMPA, like those of $Th(NO_3)_4(Ph_3PO)_2$ and $Th(NO_3)_4(Ph_3AsO)_2$ (Table 19), is consistent with the presence of bidentate nitrate groups [93] and the molar conductivity is low, indicating non-electrolyte behaviour [93]. Although $U(NO_3)_4(HMPA)_2$ behaves as a non-electrolyte in nitromethane solution, ionisation occurs in the presence of excess ligand. In a conductometric titration of a nitromethane solution of $U(NO_3)_4(HMPA)_2$ containing exactly one mole of excess HMPA with a nitromethane solution of $NaBPh_4$, $NaNO_3$ was precipitated and a sharp endpoint was obtained at a $U(NO_3)_4$ to BPh_4^- ratio of 1 : 1. In an exactly similar titration with no excess HMPA, only a small amount of $NaNO_3$ was precipitated and a weak endpoint was obtained at a $U(NO_3)_4$ to BPh_4^- ratio of 1 : 0.1. The IR spectrum of the $U(NO_3)_4(HMPA)_2 + NaBPh_4$ system indicates a very small amount of free HMPA; in addition all the nitrato groups in the complex seem to be bidentate. It has been suggested that $U(NO_3)_4(HMPA)_2$ reacts in solution with one additional HMPA to form mainly $U(NO_3)_4 \cdot 3$ HMPA which is ionized to some extent into $[U(NO_3)_3 \cdot 3\ HMPA]^+ + NO_3^-$. All efforts to isolate solid $[U(NO_3)_3 \cdot 3\ HMPA]X$ ($X = NO_3^-, ClO_4^-, BPh_4^-$) have failed.

The complex $U(NO_3)_4 \cdot 4$ HMPA has been prepared by dissolving $U(NO_3)_4(HMPA)_2$ in HMPA and acetone and precipitating the light green solid with isopentane. The existence of $[U(NO_3)_4 \cdot 4\ HMPA]^+$ species in solution has been suggested when [$U(NO_3)_3 \cdot 4$ HMPA]BPh_4 was prepared by reacting $NaBPh_4$ with $U(NO_3)_4 \cdot 4$ HMPA. The conductometric titration of $U(NO_3)_4$ with HMPA in acetone solution is in agreement with earlier observations, that an unionized $U(NO_3)_4(HMPA)_2$ complex is formed and that ionization takes place at higher HMPA/uranium ratios [134,140].

In the initial stage of the conductometric titration of HMPA against $Th(NO_3)_4$ the increase in conductivity must be ascribed to enhanced autoionization (formation of $[Th(NO_3)_3 \cdot 2\ HMPA \cdot S]^+$ and $[Th(NO_3)_5S]^-$; S = solvent). After this period the most important reaction will be that of complex formation ($Th(NO_3)_4 \cdot 2\ HMPA \cdot Me_2CO$). Further addition of HMPA leads to a gradual increase in the extent of ionization. The percentage ionization of $Th(NO_3)_4 \cdot 4$ HMPA is greater than that of $Th(NO_3)_4 \cdot 3$ HMPA when an excess of HMPA is present. No solid $Th(NO_3)_4 \cdot 2$ HMPA has been prepared from acetone solution, even when a $Th(NO_3)_4$: HMPA ratio of 1 : 2 was used, only $Th(NO_3)_4 \cdot 3$ HMPA formed. The molar conductivity of $Th(NO_3)_4 \cdot 3$ HMPA in nitromethane indicates it is a weak electrolyte although stronger than $U(NO_3)_4 \cdot 2$ HMPA. $Th(NO_3)_4 \cdot 4$ HMPA is very similar to the corresponding uranium(IV) complex with respect to its molar conductance and IR spectra [134]. When $Th(NO_3)_4 \cdot 4$ HMPA is warmed in vacuo at 50°C $Th(NO_3)_4 \cdot 3$ HMPA is formed, which on heating to 150°C in vacuo gives $Th(NO_3)_4 \cdot 2$ HMPA. Similarly $U(NO_3)_4 \cdot 2$ HMPA can be prepared by warming $U(NO_3)_4 \cdot 4$ HMPA in vacuo at 80°C; oxidation of the former starts only at about 115°C. The minimum at a $Me_3PO : U(NO_3)_4$ molar ratio of 2 : 1 in the conductometric titration of an ice-cold solution of $U(NO_3)_4$ in acetone with Me_3PO suggests that $U(NO_3)_4 \cdot 2\ Me_3PO$ is formed although it was not isolated; even at molar ratio 2 : 1 $U(NO_3)_4 \cdot 3\ Me_3PO$ crystallizes instead. It has therefore been assumed that the species in solution is $U(NO_3)_4 \cdot 2\ Me_3PO \cdot Me_2CO$. $U(NO_3)_4 \cdot 3\ Me_3PO$ is a weak electrolyte in nitromethane solution and when treated conductometrically with Me_3PO in acetone, the conductivity increases until precipitation of $U(NO_3)_4 \cdot 5\ Me_3PO$ occurs at a molar ratio of 1 : 5. The behaviour of the $U(NO_3)_4/Me_3PO$ system has been interpreted according to the scheme. Conductometric titrations of $Th(NO_3)_4$ with Me_3PO in acetone solution show that $Th(NO_3)_4$ reacts differently from $U(NO_3)_4$. The initial increase in conductivity to a maximum at a $Me_3PO : Th(NO_3)_4$ molar ratio 2 : 1 has been interpreted in terms of enhanced autoionization according to

Scheme 2



$$2\ Th(NO_3)_4 + 4\ Me_3PO \rightarrow [Th(NO_3)_3\ 4\ MePO]^+ + [Th(NO_3)_5Me_2CO]^-$$

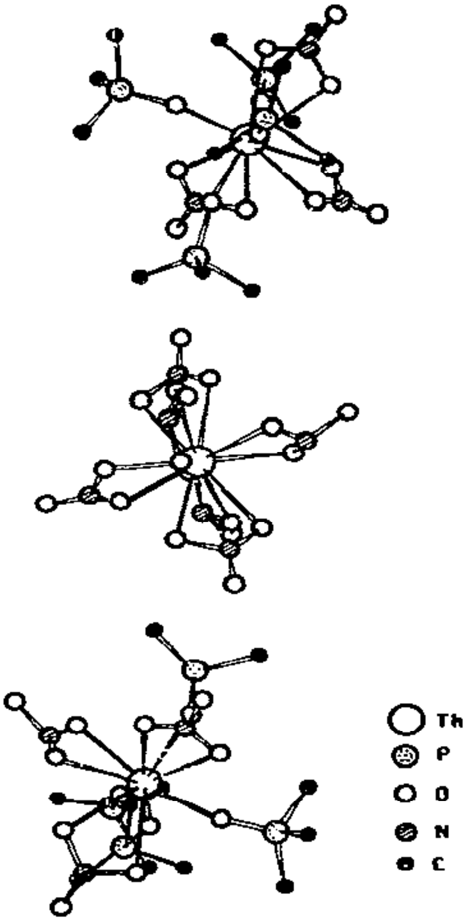
This is followed by a decrease in conductivity and a minimum at a molar ratio of 3 : 1 occurs which suggests that complexes of composition $Th(NO_3)_4 \cdot 3\ Me_3PO$ are formed. The very rapid increase in conductivity in the region 3—4 mol Me_3PO added can only partly be explained in terms of ionization. The formation of the species $[Th(NO_3)_3 \cdot 5\ Me_3PO]^+$ and $[Th(NO_3)_5 \cdot Me_3PO]^-$ must make a significant contribution to the conductivity. When a molar ratio of 4 : 1 is exceeded, ionization again becomes relatively more important.

It has been shown [140] that in these complexes Me_3PO is a stronger ligand than HMPA; this is very probably due to the smaller size of Me_3PO, which can lead to more intense metal—phosphoryl-oxygen donor atom interaction compared with that of HMPA. This effect will lead to greater metal—nitrate bond weakening and, therefore, ionization in complexes with Me_3PO, even where the stoicheiometries of the Me_3PO and HMPA complexes are the same. The higher molar conductivity of $Th(NO_3)_4 \cdot 3\ Me_3PO$ as compared to $Th(NO_3)_4 \cdot 3$ HMPA is in agreement with this. In addition a larger $Me_3PO : M(NO_3)_4$ molar ratio is possible in lattice-stabilised complexes than for HMPA; thus $M(NO_3)_4 \cdot 4$ HMPA but not $M(NO_3)_4 \cdot 5\ Me_3PO$ can be isolated.

Products with non integral M : Me_3PO ratios have been obtained by varying the preparative conditions, including the solvent, or mixture of solvents, used for recrystallisation [129]. With a 1 : 3 molar ratio (metal : ligand) in ethanol (thorium) or dichloromethane (uranium) the products are of composition $Th(NO_3)_4 \cdot 2.67\ Me_3PO$ after recrystallisation from MeCN and $U(NO_3)_4 \cdot 3.33\ Me_3PO$. The former complex is analogous to the previously reported $M(NO_3)_4 \cdot 2.67\ Pr^n_3PO$ (M = Th, U and Np) formulated as $[M(NO_3)_3(Pr^n_3PO)_4]_2$-$[M(NO_3)_6]$ [94]. Additional thorium phases of composition $Th(NO_3)_4 \cdot 2.33\ Me_3PO$ and $Th(NO_3)_4 \cdot 3.67\ Me_3PO$ have also been obtained, the former by slow evaporation of an ethanol solution of the components (Th : Me_3PO = 1 : 3) and the latter from an ethanolic solution of hydrated thorium tetranitrate and a nitromethane solution of the ligand (Th : Me_3PO = 4.3 : 1) followed by recrystallisation from ethanol : nitromethane: n-hexane : diethylether (1 : 1 : 2 : 10), but these products could not be obtained reproducibly and were probably a mixture.

The reaction of sodium tetraphenylborate with the pentakis complexes $M(NO_3)_4 \cdot 5\ Me_3PO$, 3 : 1 molar ratio in ethanol (thorium) or acetone (uranium), yields the complexes $[M(NO_3)_2(Me_3PO)_5][BPh_4]_2$ [129]. The anionic complex $[Th(NO_3)_5(Me_3PO)_2]^-$ has been obtained as the salt from an acetone solution of $Th(NO_3)_4 \cdot 2.33\ Me_3PO$ and $[PPh_4]NO_3$. Direct preparation of $[Th(NO_3)_5(Me_3PO)_2]^-$ from hydrated thorium tetranitrate, Ph_3PO and $[PPh_4]NO_3$ yields precipitates of variable composition and the corresponding uranium(IV) complex could not be isolated. The formation of these two ions may indicate that the tris complexes $M(NO_3)_4 \cdot 3\ Me_3PO$ should be formulated as $[M(NO_3)_2(Me_3PO)_5][M(NO_3)_5(Me_3PO)_2]_2$.

The crystal and molecular structures of $[Th(NO_3)_3(Me_3PO)_4]_2[Th(NO_3)_6]$ and $[PPh_4][Th(NO_3)_5(Me_3PO)_2]$ have been determined by X-ray diffraction [129]. The colourless prismatic crystals of $[Th(NO_3)_3(Me_3PO)_4]_2[Th(NO_3)_6]$



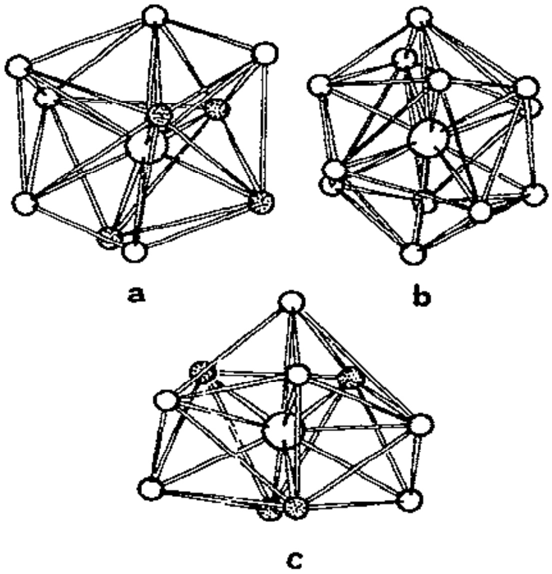


Fig. 29. The coordination around the thorium in the individual ions of the complex [Th-$(NO_3)_3(Me_3PO)_4]_2[Th(NO_3)_6]$.

Fig. 30. The coordination spheres of the three thorium atoms in the complex $[Th(NO_3)_3$-$(Me_3PO)_4]_2[Th(NO_3)_6]$. The cations are represented by the polyhedra (a) and (c) and the anion by (b). The oxygens of the unidentate ligands are stippled.

are monoclinic and the crystal parameters are: space group *Pn*, $a = 9.523$, $b = 14.507$ and $c = 27.302$ Å, $\beta = 95.32°$ and $Z = 2$. The coordination around the thorium in the individual ions is illustrated in Fig. 29. All the nitrate groups are bidentate and the coordination number is therefore 10 for the cations and 12 for both the anions. The packing of the crystals appears to involve only electrostatic interaction between the pseudo-spherical ions. The thorium in the anion $[Th(NO_3)_6]^{2-}$ has the characteristic icosahedral geometry [141] shown in Fig. 30(b), with six bidentate nitrate groups as found in $[Ce(NO_3)_6]^{2-}$. The two ten-coordinate cations are very similar. They can be

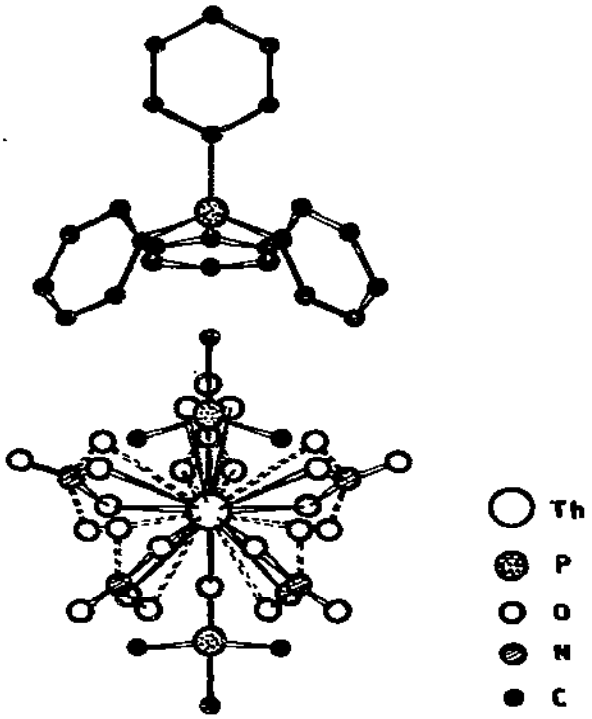


Fig. 31. The molecular structure of $[PPh_4][Th(NO_3)_5(Me_3PO)_2]$. (The disorder in the anion does not allow one to describe its geometry.)

described as 1 : 5 : 4 geometry of the type in Fig. 30(c). This has a closely planar base, but an atom in the 5 layer most nearly opposite one in the base is out of the plane. An alternative description is 1 : 6 : 3 geometry (Fig. 30(a)). This has a puckered 6 layer with the nearly eclipsed atoms close to the apex.

The colourless crystals of $[PPh_4][Th(NO_3)_5(Me_3PO)_2]$ are orthorhombic with space group *Pnma*, $a = 24.626$, $b = 12.922$ and $c = 12.777$ Å, $Z = 4$. The molecular structure is shown in Fig. 31. The thorium atom is 12 coordinate, all the nitrate ions being coordinated but the disorder in the anion means that nothing useful can be said about its geometry. The crystals contain discrete ions and the packing appears to involve only electrostatic interactions between the pseudo-spherical ions. The Th—O coordination distances are in the range 2.24—2.53 Å for Th—O(Me_3PO) and 2.46—2.94 Å (av. 2.61 Å) for Th—O(NO_3) in $[Th(NO_3)_3(Me_3PO)_4][Th(NO_3)_6]$ and 2.34—2.42 Å (av. 2.38 Å) for Th—O(Me_3PO) and 2.52—2.75 Å (av. 2.64 Å) for Th—O(NO_3) in $[Th(NO_3)_2(Me_3PO)_5][BPh_4]_2$. There is a significant difference between the Th—O distance and those found for $La(NO_3)_3 \cdot 4\ Me_2SO$ (La—O(NO_3) 2.65 Å; La—O(Me_2SO) 2.48 Å [142]).

Complexes of stoicheiometry $M(NO_3)_4 \cdot 1.5\ L$ have been obtained with the bidentate phosphine oxides octamethylpyrophosphoramide (OMPA) and bis(diphenylphosphinyl)methane (PPM); a second OMPA complex $Th(NO_3)_4 \cdot 2.5$ OMPA was also obtained [93]. The Raman spectra of $Th(NO_3)_4 \cdot 1.5$ L are consistent with the presence of bidentate nitrato groups and the IR spectrum (Table 18) of $Th(NO_3)_4 \cdot 2.5$ OMPA shows that ionic nitrates are also present in this complex. The two thorium tetranitrate—OMPA complexes behave as electrolytes (Table 20) although there is no ionic nitrate in solid $Th(NO_3)_4 \cdot 1.5$ OMPA. In contrast bis(diphenylphosphinyl)ethane (PPE) forms the bis complex $Th(NO_3)_4 \cdot 2$ PPE in which covalent nitrato groups are probably present (Table 18); there is, however, no evidence to show whether PPE is behaving as a uni- or bidentate ligand in the complex [93].

The shifts in the P=O stretching frequencies in the IR spectrum are shown in Table 18; Me_3PO, Pr_3PO and Bu_3PO all exhibit similar shifts on coordination as might be expected from the similar electronegativities of the substituent groups. The effect of electron withdrawal from the P=O group by the metal atom is felt throughout the small Me_3PO molecule and this is reflected in the IR spectra of its complexes, in which all of the ligand skeletal modes are shifted or split compared with those in the free ligand; this effect is much less marked in the longer chain Pr_3^nPO and Bu_3^nPO. There is very little difference in the magnitudes of the shifts in a set of complexes (Th, U, Np) or between the complexes $M(NO_3)_4 \cdot xL$ and $M(NO_3)_4 \cdot (x + 1)L$. A small splitting of the P=O mode in $Th(NO_3)_4 \cdot 4\ Bu_3^nPO$ was observed both for the solid and for solutions in carbon tetrachloride; this may indicate more than one environment of the ligands. The shifts in the P=O stretching frequencies for the HMPA and Ph_3PO complexes are very much larger than those for the trialkylphosphine oxides, as has been observed for the corresponding complexes of the tetrachlorides [143,144] (Table 18). According to the Raman spectra the covalent nitrato groups in the tetrakis actinide(IV) nitrate complexes are bidentate, whereas some or all the nitrato groups appear to be unidentate in $Np(NO_3)_4 \cdot 3\ Me_3PO$ (Table 19). The vibrations arising from ionic nitrate in some actinide(IV) nitrate complexes and their molar conductivities in nitromethane at 20°C are given in Table 20.

U. ACTINIDE(VI) NITRATE COMPLEXES WITH PHOSPHINE AND ARSINE OXIDES

A range of uranyl(VI) nitrate complexes of the type $UO_2(NO_3)_2(L)_2$ (for example, L = phenacyldimethylphosphine oxide [145], methyldiphenylphosphate [146], triphenylphosphate [147], triphenylphosphine or arsine oxide [148], and trimethyl or triethylphosphine oxide [93]) have been prepared by direct reaction of uranyl(VI) nitrate and the monodentate ligand in solvents such as ethanol.

The phase diagram of the $UO_2(NO_3)_2$—$(EtO)_3PO$—H_2O system has also been studied [149] between 25 and 90°C. Complexes with other actinyl(VI) nitrates do not appear to have been studied. The interaction of triphenylphosphine (Ph_3P) with uranyl(VI) nitrate was previously reported to yield UO_2-

$(NO_3)_2(Ph_3P)_2$ [150] but a subsequent investigation [110] has unequivocally demonstrated that the product is $UO_2(NO_3)_2(Ph_3PO)_2$.

The IR bands at 270 cm^{-1} for $UO_2(NO_3)_2(Ph_3PO)_2$ and at 274 cm^{-1} for $UO_2(NO_3)_2(Ph_3AsO)_2$ have been assigned to the uranyl deformation mode (ν_2) [12,90]. In addition the positions of the Raman active stretching vibration (ν_1) of the uranyl group in these complexes and in the $UO_2(NO_3)_2(EtO)_3PO$ have been reported [11].

$UO_2(NO_3)_2 \cdot 6\ H_2O$ in ethanol reacts with the ligand phenacyldiphenylphosphine oxide (Ph_2POCH_2COPh) in a 1 : 2 ratio to give the anhydrous crystalline complex $UO_2(NO_3)_2(Ph_2POCH_2COPh)_2$ which is soluble in ethanol and acetone and slightly soluble in benzene and toluene. For the ligand the IR spectrum shows the C=O stretch at 1680 cm^{-1} and that for P=O at 1180 cm^{-1}; the uranyl(VI) nitrate complexes give a sharp band at 1680 cm^{-1} indicating that the carbonyl group is not affected while the P=O stretch is shifted to 1160 cm^{-1} so that the UO_2^{2+} ion probably has two nitrate ions and two phosphine oxide ligands coordinated to it, the phosphine oxide coordinating as unidentate ligands. With ratios of uranyl nitrate to ligand 1 : 1, 1 : 3 and 1 : 4, the compound obtained is identical to that obtained using a 1 : 2 ratio [145].

$UO_2(NO_3)_2(MDPP)_2$ has been prepared by equilibrating methyldiphenylphosphate (MDPP) with an aqueous solution of uranyl nitrate. The complex is soluble in $CHCl_3$, dioxan, CH_3OH, C_6H_6, and Bu^iCOCH_3, but almost insoluble in H_2O, dilute mineral acids, Pr^i_2O and hydrocarbons [146]. It probably has the same structure as $UO_2(NO_3)_2(TEP)$ (TEP = triethylphosphate) [63].

The reaction of $UO_2(NO_3)_2 \cdot 6\ H_2O$ in ethyl ether, in dioxan or in ethanol with Ph_3PO gives $UO_2(NO_3)_2(Ph_3PO)_2$ in a 32%, 90% and 5% yield respectively [148]. The same reaction with Ph_3AsO gives $UO_2(NO_3)_2(Ph_3AsO)_2$ in ethyl ether with a 30% yield, and in dioxan with a 99% yield. In ethanol

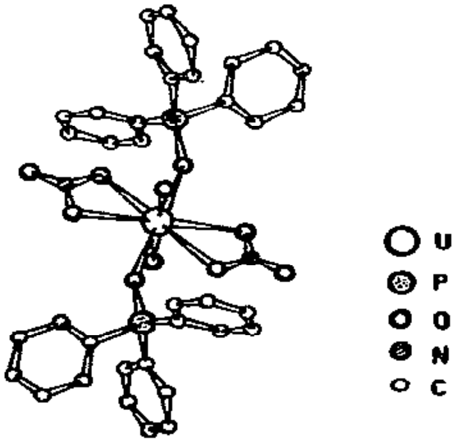


Fig. 32. A perspective view of $UO_2(NO_3)_2(Ph_3PO)_2$.

Ph_3AsO was found to be inert towards uranyl nitrate; in butanol the yield is less than 0.2% and in cyclohexanol is 10% [148]. The crystal and molecular structures of the complexes $UO_2(NO_3)_2(Ph_3PO)_2$, $UO_2(NO_3)_2(Ph_3AsO)_2$ and $UO_2(NO_3)_2(TEP)_2$ have been reported [63,148]. The structures of the Ph_3PO and Ph_3AsO complexes are the same as shown by the similarity in composition, by the IR spectra and by X-ray single crystal diffraction [151]. The uranium atom is eight coordinate and the uranyl ion is surrounded equatorially by an irregular hexagon of six oxygen atoms. A perspective view of the $UO_2(NO_3)_2(Ph_3PO)_2$ molecule is reported in Fig. 32. The two nitrate ions, which are crystallographically equivalent, are coordinated as bidentate groups and are tilted with respect to the equatorial plane. The U—O bond length of the uranyl group, which is symmetrical and linear, is 1.71 Å, the two U—O-(nitrate) distances, 2.56 and 2.60 Å, are slightly longer than in $UO_2(NO_3)_2 \cdot 6\ H_2O$ [68,69]. The U—O bond is 2.36 Å; within the limits of the estimated standard deviations in the bonds and angles, the chromophore UO_8 has D_{2h} symmetry. The very short As—O length (1.65 Å) has been ascribed to the strong character of this bond. Crystals of $UO_2(NO_3)_2(TEP)_2$, grown from $CHCl_3$ have been found to be triclinic with cell dimensions: $a = 9.14$, $b = 8.66$ and $c = 9.06$ Å; $\alpha = 98.2°$, $\beta = 95.9°$, $\gamma = 95.6°$ and $Z = 1$. The structure (Fig. 33) is centrosymmetric and the uranium atom is eight coordinated with bidentate nitrate groups and unidentate phosphate ligands. With uranyl(VI)

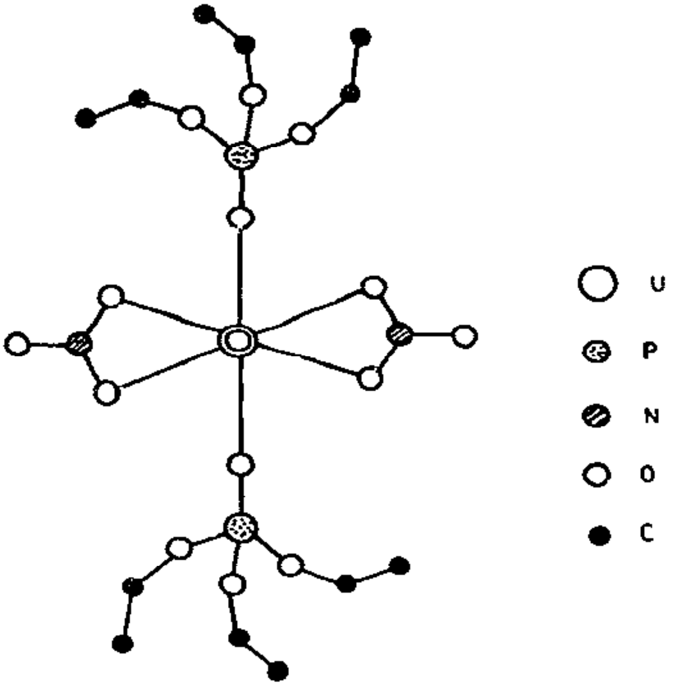


Fig. 33. The molecular structure of $UO_2(NO_3)_2(TEP)_2$.

TABLE 21

Infrared spectra of uranyl(VI) nitrate complexes with phosphine and arsine oxides

Compound [a]	ν_1	ν_4	ν_2	ν_6	ν_3/ν_5	ν(P—O) or (AsO)	Ref.
$UO_2(NO_3)_2 \cdot 2\ Me_3PO$	1505s, 1495w, sh	1299s, 1290s	1040s	816w	764w	1091s	93
$UO_2(NO_3)_2 \cdot 2\ Pr_3^nPO$	1510s, 1490m, sh	1291s	1036m	805m	750m	1095s, 1080m, sh	93
$UO_2(NO_3)_2 \cdot 2\ Bu_3^nPO$	1513s, 1530w, sh	1283s	1032w	816w		1111s, 1098s	93
$UO_2(NO_3)_2 \cdot 2\ Ph_3PO$	1520s, 1526vw	1283vs	1034s 1030m	812w	762m	1081s 1133s	93
$UO_2(NO_3)_2 \cdot 2\ EtO_3PO$	1530s	1280s	1035	810m		1180s	67
$UO_2(NO_3)_2 \cdot 2$ HMPA	1515s	1293s	1037m	817w	768s	1100s	93
$UO_2(NO_3)_2 \cdot$ OMPA	1518s, br	1293s	1033m	814m	750m	1188s	93
$UO_2(NO_3)_2 \cdot 1.5$ PPM	1521s 1512w, sh	1287s	1035w, 1030w, sh	810vw		1135s, 1160w, sh	93
$UO_2(NO_3)_2 \cdot 2\ Ph_3AsO$	1500s	1288s	1035	811		868	67

[a] Me_3PO = trimethylphosphineoxide; Pr_3^nPO = tri-n-propylphosphineoxide; Bu_3^nPO = tri-n-butylphosphineoxide; Ph_3PO = triphenylphosphineoxide; EtO_3PO = triethylphosphate; HMPA = hexamethylphosphoramide; OMPA = octamethylpyrophosphoramide; PPM = bis(diphenylphosphinyl)methane; Ph_3AsO = triphenylarsineoxide.

nitrate, hexamethylphosphoramide forms the complex $UO_2(NO_3)_2(HMPA)_2$ [152—154]. All the vibration modes due to the nitrate groups of C_{2v} symmetry have been found active. The assignment of the fundamental frequencies are: ν_1 1505, ν_2 1050, ν_4 1285, ν_5 720, ν_6 820—810 cm^{-1}. Because of the broad absorption of the ligand the ν_3 mode of the nitrate was not observed. In addition, the weak absorption at 2530 and 2305 cm^{-1} could be assigned to the combinations $\nu_2 + \nu_1$ and $\nu_2 + \nu_4$, respectively, with a separation of 225 cm^{-1}, comparable to the $\Delta(\nu_1 - \nu_4)$. The bands at 1770 and 1730 cm^{-1}, probably arise from the combinations $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$, respectively. The separation of these bands (40 cm^{-1}) and the difference $(\nu_2 + \nu_1) - (\nu_2 + \nu_4)$ are in agreement with the values found for bidentate nitrato groups [74] (Table 9). Therefore the IR spectrum of $UO_2(NO_3)_2(HMPA)_2$ confirms the nitrate anions are bidentate in the solid state. The P—O bond stretching frequency in the IR spectrum of $UO_2(NO_3)_2(HMPA)_2$ has been reported to be 10—20 cm^{-1} lower than the corresponding frequency in the free ligand [152,153]; shifts of the order 100—120 cm^{-1} toward lower frequencies appears to be more correct. Moreover even larger shifts (160—180 cm^{-1}) have been found in complexes of uranium(IV) with the same ligand [144]. For the uranyl complex with Ph_3PO the shifts are of the order 60—80 cm^{-1}. The larger shift observed for the HMPA complex probably arises from resonance effects induced by the electron releasing dimethylamino groups. The ν_3O—U—O lies at 928 cm^{-1} or 932 cm^{-1} [155], and the ν_1O—U—O at 845 cm^{-1} while a strong band in the region 260—270 cm^{-1} arises from ν_2O—U—O [160]. The Raman spectrum of $UO_2(NO_3)_2(HMPA)_2$ contains a weak line at about 510 cm^{-1} and a stronger one at 480 cm^{-1}, whereas only the latter is present in the spectrum of HMPA; a similar situation has been observed in the IR

TABLE 22

Raman spectra of some actinide (VI) nitrate complexes (cm^{-1}) with phosphine oxide [93]

Compound	ν_1	ν_4	ν_2	ν_3/ν_5
$UO_2(NO_3)_2 \cdot 2\,Me_3PO$	1500vw	1275vw	1040m 1028w	770w
$UO_2(NO_3)_2 \cdot 2\,Pr^n_3PO$	1520w		1041s	
$UO_2(NO_3)_2 \cdot 2\,Bu^n_3PO$	1510w		1030w	
$UO_2(NO_3)_2 \cdot 2$ HMPA	1505w, sh 1490s		1035vs	750w
$UO_2(NO_3)_2 \cdot$ OMPA	1535w	1280vw 1320vw	1033w	755w
$UO_2(NO_3)_2 \cdot 1.5$ PPM	1530w		1034vs (?)[a]	[a]

[a] Obscured by ligand absorptions.

spectrum. It has been suggested that the band at 510 cm^{-1} is due to a U—O·(HMPA) mode [156]. Infrared spectra of the dioxouranium(VI) nitrate complexes with phosphine oxides indicate that all the nitrate groups are covalent (Table 21) and Raman spectra are consistent with the presence of bidentate nitrate groups (Table 22). The molar conductivities in nitromethane are low, indicating non-electrolyte behaviour.

V. ACTINIDE(IV) NITRATE COMPLEXES WITH SULPHOXIDES

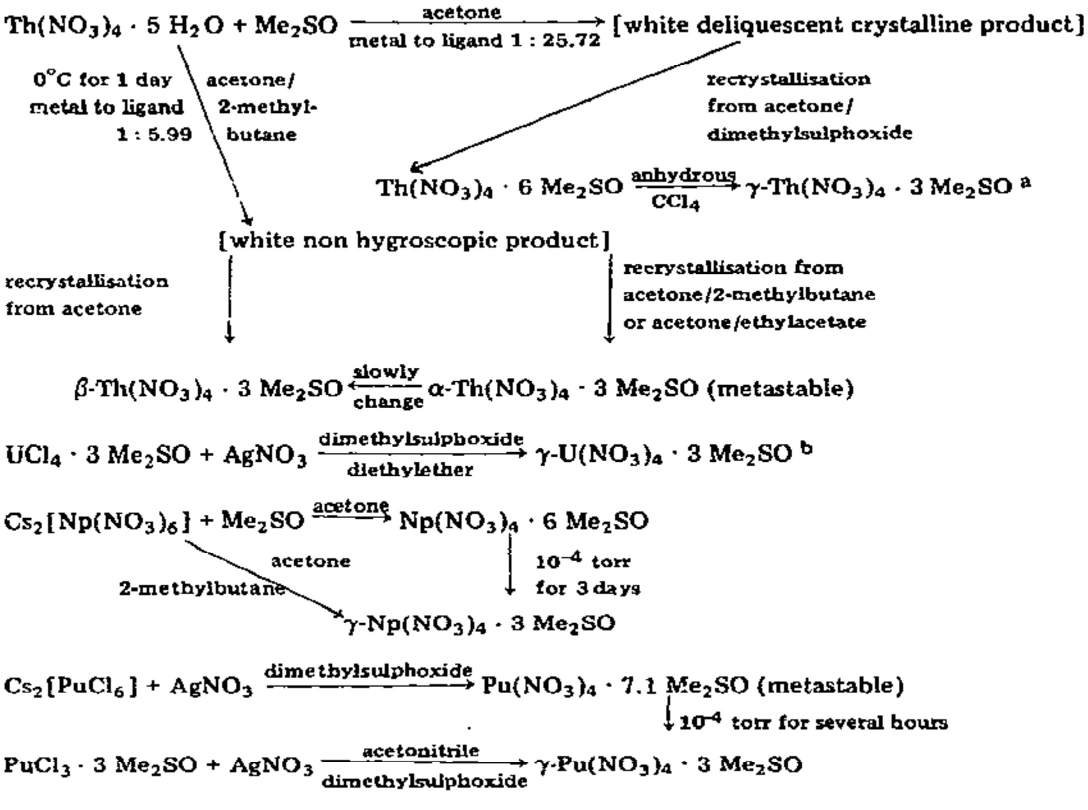
Two series of complexes are formed with dimethylsulphoxide [88], $M(NO_3)_4 \cdot 6\ Me_2SO$ (M = Th, Np and Pu) and $M(NO_3)_4 \cdot 3\ Me_2SO$ (M = Th, U, Np and Pu), the 1 : 6 complexes decreasing in stability along the series from thorium to plutonium (cf. the 1 : 7, 1 : 5 and 1 : 3 complexes formed by actinide tetrachlorides [161]). All the ligand molecules are coordinated in both series of complexes, the shift in S=O frequency (96 to 119 cm^{-1}) relative to the free ligand position increases with the atomic number of the actinide element in each series and is consistently greater for 1 : 6 than 1 : 3 complexes. Infrared results indicate that both ionic and covalent nitrates are present in the 1 : 6 complexes but their structures are unknown.

Reaction between $Th(NO_3)_4 \cdot 5\ H_2O$ and a large excess of dimethylsulphoxide in acetone followed by recrystallization of the precipitate from acetone—dimethylsulphoxide results in the formation of the complex $Th(NO_3)_4 \cdot 6\ Me_2SO$ whereas recrystallization from acetone—2-methylbutane or acetone—ethylacetate mixture yields the tris complex $Th(NO_3)_4 \cdot 3\ Me_2SO$ [88]. This is metastable and slowly changes to a β-form which is also obtained on crystallization from acetone. $Th(NO_3)_4 \cdot 3\ Me_2SO$ is also formed when the hexakis complex is treated with anhydrous CCl_4. Thorium tetranitrate apparently forms other anhydrous and hydrated complexes with dimethylsulphoxide. Thus, $Th(NO_3)_4 \cdot 3\ Me_2SO \cdot 2\ H_2O$, $Th(NO_3)_4 \cdot 7\ Me_2SO \cdot 2\ H_2O$, $Th(NO_3)_4 \cdot 8\ Me_2SO \cdot 2\ H_2O$, $Th(NO_3)_4 \cdot 11\ Me_2SO \cdot H_2O$ and $Th(NO_3)_4 \cdot 9\ Me_2SO$ are obtained [163] by grinding together the tetranitrate hydrate and the ligand, whilst $Th(NO_3)_4 \cdot 12\ Me_2SO$ is reported [164] to form on repeated recrystallization from the ligand. Infrared studies have shown [163] that the 1 : 9 complex and the hydrates apart from $Th(NO_3)_4 \cdot 11\ Me_2SO \cdot H_2O$ contain both ionic and covalent nitrate groups; the latter complex contains only ionic nitrate. The existence of $Th(NO_3)_4 \cdot 4\ Me_2SO$, reported by other workers [165], was not confirmed during the other investigations mentioned above and it would seem likely that this phase was a mixture of the 1 : 3 and 1 : 6 complexes.

An unstable complex, $U(NO_3)_4 \cdot 3\ Me_2SO$, has been prepared by metathesis of $UCl_4 \cdot 3\ Me_2SO$ with $AgNO_3$ in methyl cyanide provided that the product was isolated rapidly by the addition of diethyl ether. Slow crystallisation from acetone—2-methylbutane at ice temperature resulted in oxidation yielding only $UO_2(NO_3)_2 \cdot 2\ Me_2SO$. Attempted preparation of $U(NO_3)_4 \cdot 6\ Me_2SO$ was unsuccessful; the reaction product decomposed, even in a dry atmosphere, before it could be characterized. The preparation of protactinium tetranitrate dimethylsulphoxide complexes was not attempted, since protactinium(IV) is appreciably less stable with respect to oxidation than is uranium(IV). It seems probable that the ligand rather than the nitrate ion is the oxidant in the uranium—tetranitrate—dimethylsulphoxide system when one considers the stability with respect to oxidation of the complex $U(NO_3)_4 \cdot 2.5$ DMA (DMA = dimethylacetamide) [23].

Hexakis and tris complexes of neptunium(IV) tetranitrate were obtained in a similar manner from $Cs_2[Np(NO_3)_6]$ and Me_2SO. The hexakis complex losses DMSO relatively slowly at 10^{-4} torr, three days being required for the

Scheme 3. Actinide(IV) nitrate—dimethylsulphoxide system



[a] Tentatively called γ-$Th(NO_3)_4 \cdot 6\ Me_2SO$ on the basis of the similarity between its X-ray powder pattern and those of the other γ-modifications. The possibility remains, however, that it is a fourth crystal form.

[b] Slow crystallisation from acetone/2-methylbutane at ice temperature results in oxidation with the formation of $UO_2(NO_3)_2 \cdot 2\ Me_2SO$.

complete conversion to the tris complex whilst $Th(NO_3)_4 \cdot 6\ Me_2SO$ appears to be stable under such conditions. Metathesis of $PuCl_4 \cdot 3\ Me_2SO$ with $AgNO_3$ in methylcyanide—Me_2SO yields $Pu(NO_3)_4 \cdot 3\ Me_2SO$ whilst a similar reaction involving $Cs_2[PuCl_6]$, a large excess of Me_2SO and the stoicheiometric quantity of $AgNO_3$ yields a complex of composition $Pu(NO_3)_4 \cdot 7.1\ Me_2SO$ when the initial product is recrystallised from acetone. This complex continuously loses Me_2SO when exposed to a vacuum (10^{-4} torr), the final product after several hours being γ-$Pu(NO_3)_4 \cdot 3\ Me_2SO$. There is no evidence for formation of a stable hexakis complex.

Single crystal studies [162] have shown that the complex β-$Th(NO_3)_4 \cdot 3\ Me_2SO$ possesses monoclinic symmetry, space group $P2_1/c$ with $a = 15.50$, $b = 15.71$ and $c = 16.16$ Å and $\beta = 146.70°$. The four nitrate groups are each bidentate; all three Me_2SO molecules are coordinated via the oxygen atoms, the thorium atom being eleven coordinate. The stoicheiometry around each thorium atom is close to a singly capped pentagonal antiprism (D_{5d}). X-ray powder diffraction measurements show $Th(NO_3)_4 \cdot 6\ Me_2SO$ and the analogue neptunium complex are isostructural [88]. Complexes of the actinoid tetranitrates with other sulphoxides, $M(NO_3)_4 \cdot xR_2SO$ ($R = C_2H_5$, (Et_2SO); Ph, (Ph_2SO); α-$C_{10}H_7$, (Nph_2SO); $x = 3$ or 4 and M = Th, U, Np, Pu) have been prepared [162]. The thorium tetranitrate tris complexes separated as crystals ($Th(NO_3)_4 \cdot 3\ Ph_2SO$) or as oils which ultimately crystallised (Et_2SO or Nph_2SO) when the ligand was added to a solution of $Th(NO_3) \cdot 5\ H_2O$ or when the latter was added to the solid ligand (Nph_2SO). Prolonged exposure of the solvated complex $Th(NO_3)_4 \cdot 3(Nph_2SO) \cdot EtOAc$, obtained in ethylacetate solution, removes the ethylacetate from the solvate.

The uranium(IV) and neptunium(IV) tris-Et_2SO complexes were prepared by treating $Cs_2M(NO_3)_6$ with the ligand in acetone; the reaction is very slow with diaryl sulphoxides, even under reflux, resulting in extensive oxidation to dioxoactinoid(V) or (VI) species. Thus, $Np(NO_3)_4 \cdot 3\ Ph_2SO$ was obtained in only 16% yield by this procedure. The tris complex $U(NO_3)_4 \cdot 3\ Ph_2SO$ and the tetrakis $M(NO_3)_4 \cdot 4\ Ph_2SO$ (M = Th, U, Np, Pu) complexes were prepared by metathesis of the corresponding actinoid tetrachloride complex with silver nitrate in methyl cyanide. This preparative method fails in the case of the $U(NO_3)_4$—Nph_2SO system owing to the spontaneous decomposition of the green primary product, with oxidation to uranium(VI), and the only product obtained by this route in the $Pu(NO_3)_4$—Et_2SO system could not be induced to crystallise. The tris complex $U(NO_3)_4 \cdot 3\ Ph_2SO$ can also be obtained by addition of the ligand to uranium(IV) in 8M HNO_3 containing sulphamic acid to prevent oxidation.

Similarly, the neptunium analogue and $Pu(NO_3)_4 \cdot 4\ Ph_2SO$ were prepared by addition of 2—6 M HNO_3 to stoicheiometric mixtures of the ligand and the appropriate hexanitrato complex, the initial oily product being dissolved in dichloromethane and reprecipitated by the addition of 2-methylbutane. All the complexes obtained were non-hygroscopic. The uranium tetranitrate DESO and DPSO complexes are more stable with respect to oxidation than

TABLE 23

Infrared spectra (cm^{-1}) for actinide(IV) nitrate complexes with sulphoxides

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	νS—O	Ref.
β-$Th(NO_3)_4 \cdot 3\ Me_2SO$ [a]	1502	1037	756 748	1316 1289	728	818 812	956	88
$U(NO_3)_4 \cdot 3\ Me_2SO$	1515	1037	753	1287	726	812	937	88
$Np(NO_3)_4 \cdot 3\ Me_2SO$	1510	1026	742	1283	715	802	939	88
$Pu(NO_3)_4 \cdot 3\ Me_2SO$	1515	1031	747	1284	718	805	937	88
$Th(NO_3)_4 \cdot 6\ Me_2SO$ [b]	1490	1032	739	1315 1295 1280	722	814	960	88
$Np(NO_3)_4 \cdot 6\ Me_2SO$ [b]	1487	1026	732	1308 1297 1276	715	805	950	88
$Pu(NO_3)_4 \cdot xMe_2SO$ [b,c]	1510	1029	737	1313 1278	722	808	950	88
$Th(NO_3)_4 \cdot 3\ Et_2SO$	1497	1030	741	1307	722	811	951	162
$U(NO_3)_4 \cdot 3\ Et_2SO$	1520	1040	750	1287		812	960	162
$Th(NO_3)_4 \cdot 4\ Ph_2SO$	1505	1025	d	1315 1290	d	809	967	162
$Th(NO_3)_4 \cdot 3\ Ph_2SO$	1512	1025	d	1300 1290	d	805	960 935	162

TABLE 23 (Continued)

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	νS—O	Ref.
$U(NO_3)_4 \cdot 4\ Ph_2SO$	1510	1030	d	1300 1290	d	810	945	162
$U(NO_3)_4 \cdot 3\ Ph_2SO$	1520	1030	d	1290	d	810	958 935	162
$Np(NO_3)_4 \cdot 4\ Ph_2SO$	1510	1015	d	1277	d	800	940	162
$Np(NO_3)_4 \cdot 3\ Ph_2SO$	1512	1028	d	1280	d	802	942	162
$Pu(NO_3)_4 \cdot 4\ Ph_2SO$	1510	1028	d	1282	d	802	945	162
$Pu(NO_3)_4 \cdot 3\ Ph_2SO$ [e]	1515	1020	d	1280	d	805	962	162
$Th(NO_3)_4 \cdot 3\ Nph_2SO$	1535 1515 1505	1026	d	1300 1285	d	806	977 946	162
$Th(NO_3)_4 \cdot 3\ Nph_2SO \cdot EtOH$	1535 1515 1505	1026	d	1300 1285	d	806	979 949	162
$Np(NO_3)_4 \cdot 3\ Nph_2SO$ [f]	1530	1021	d	1288 1275 1265	d		977 945	162

[a] Virtually identical band positions were observed for the α- and γ-modifications although $\Delta\nu(S{=}O)$ increased to 105 cm^{-1}. [b] Ionic nitrate vibrations were observed at 1350 and 833, 1345 and 827, and 1350 and 831 cm^{-1}, respectively, for the Th, Np and Pu complexes. [c] X = ca. 7.1. [d] Obscured by ligand vibrations. [e] Product not obtained pure; results refer to composition $Pu(NO_3)_4 \cdot 2.8\ Ph_2SO$. [f] Product not obtained pure; results refer to composition $Np(NO_3)_4 \cdot 2.7\ Nph_2SO$.

TABLE 24

Raman spectra (cm^{-1}) of some thorium(IV) nitrate complexes with sulphoxide ligands [162]

Compound	ν_1	ν_4	ν_2	ν_6	ν_3/ν_5
$Th(NO_3)_4 \cdot 3\ Et_2SO$	1528w 1468w 1408w		1036s		755w 745w 720w
$Th(NO_3)_4 \cdot 3\ Ph_2SO$	1546vw 1529vw		1035m		744w
$Th(NO_3)_4 \cdot 3\ Nph_2SO$	[a]	[a]	1038m	820w	

[a] Obscured by fluorescence.

the DMSO complexes and although they decompose slowly at room temperature they remain unchanged when stored at ice temperature for several weeks. The sulphoxide ligands are coordinated to the central metal via the oxygen atom, the S—O stretching vibrations shifting to lower frequency on coordination [88,162]. On the basis of the IR results [88,162], it has been concluded that the nitrate groups are covalently bound and features assignable to ionic nitrate have not been observed in any of the spectra except for the hexakis dimethylsulphoxide complexes which contain both ionic and covalent nitrate groups (Table 23). Raman spectra (Table 24) show that the relative intensities of the three highest nitrate frequencies agree with a bidentate coordination of the nitrate ions.

W. ACTINIDE(VI) NITRATE COMPLEXES WITH SULPHOXIDES

$UO_2(NO_3)_2(Me_2SO)_2$ [213], $UO_2(NO_3)_2(Ph_2SO)_2$ [147,221], and $UO_2(NO_3)_2(Bu^n_2SO)_2$ [222] appear to be the only hexavalent complexes to have been studied. They have been prepared by reaction of $UO_2(NO_3)_2 \cdot 6\ H_2O$ with an excess of the appropriate ligand in ethanol, acetonitrile or acetone solution. From the IR data (Table 25) the sulphoxides appear to be coordinated through oxygen since the S—O stretching frequencies are lowered by about 60—70 cm^{-1} on coordination. The nitrate groups with C_{2v} symmetry are bidentate. Thus these complexes have the common ring of six ligand atoms around the O—U—O axis which is linear. The U—O (ligand) stretching for $UO_2(NO_3)_2(Ph_2SO)_2$ at 430 and 405 cm^{-1} [221] must be considered tentative. The molar conductance of $UO_2(NO_3)_2(Ph_2SO)_2$ in 10^{-3} M solution of nitrobenzene, acetonitrile, dimethylformamide and dimethylsulphoxide has been studied [221]. In nitrobenzene and acetonitrile (5.3 and 8.6 Ω^{-1} cm^2 mole^{-1}, respectively) it is too low to account for any dissociation of the complex; in dimethylformamide and dimethylsulphoxide (119.7 and 74.6 Ω^{-1} cm^2 mole^{-1}) the complex dissociates almost completely.

TABLE 25

Infrared spectra of uranyl(VI) nitrate complexes with sulphoxides (cm^{-1})

Compound	ν_1	ν_2	ν_3	ν_4	ν_6	νS—O	νO—U—O	Ref.
$UO_2(NO_3)_2(Me_2SO)_2$	1515			1282		985	922	213
$UO_2(NO_3)_2(Ph_2SO)_2$	1535	1038		1284	816	963	940	147, 221
$UO_2(NO_3)_2(Bu_2^nSO)_2$	1530	1030	750	1275	810	955	930	222

X. CONCLUSIONS

No solid compounds are known for the trivalent actinide elements due to the ease with which this valence state is oxidised for the earlier members of the series and the lack of research on the transplutonium elements for which the trivalent state is appreciably were stable. It is readily apparent that much remains to be done with these latter elements.

Much of the work published relates to two of the earlier actinide elements, thorium and uranium but protactinium, neptunium and plutonium nitrates have been studied to some extent.

Simple actinide nitrates have been well characterized by physicochemical measurements, expecially IR and Raman and also by good structural determinations with both X-ray and neutron diffraction.

In the simple actinide nitrates, the NO_3^- group is always bidentate and only under particular conditions does the nitrate coordinate as monodentate; for instance in $[UO_2(NO_3)_4]^{2-}$ there are two bidentate and two monodentate nitrate groups. This is due to the geometry of the uranyl(VI) complexes: a maximum of six oxygen atoms can be accommodated in the equatorial plane of the uranyl ion; this forces some nitrate ions to act as monodentate. For the same reason monodentate nitrate groups have been found in the uranyl

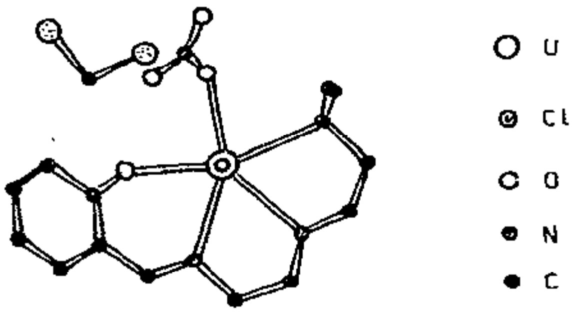


Fig. 34. Projection of the complex $[UO_2(o\text{-}O{-}C_6H_5{-}CH{=}NCH_2CH_2{-}NH{-}CH_2CH_2N(CH_3)_2)NO_3] \cdot CH_2Cl_2$.

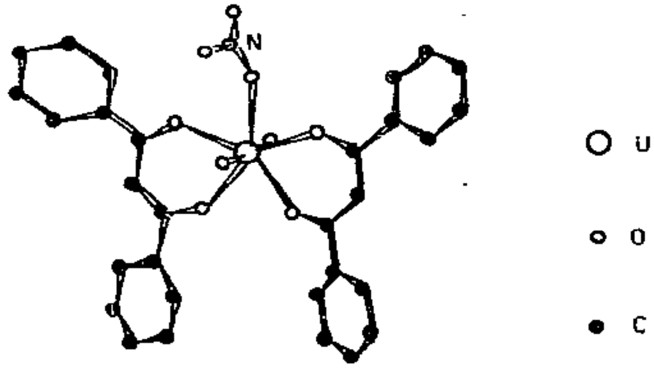


Fig. 35. The molecular structure of $[UO_2(DBM)_2(NO_3)]^-$ (HDBM = dibenzoylmethane).

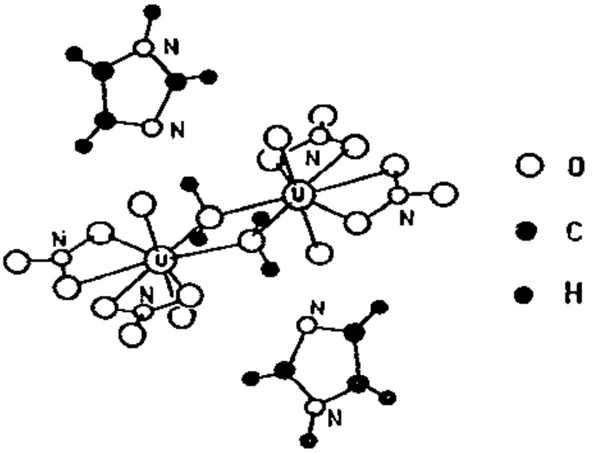
complexes shown in Figs. 34 and 35 [224—226]. In these complexes the nitrate ion occupies the fifth equatorial coordination position; the large bite of the organic ligands (2.6—2.9 Å) prevents the formation of uranyl(VI) complexes six coordinated in the equatorial plane.

Actinide(IV) nitrate complexes have been studied very recently using monodentate ligands containing C=O, P=O, S=O and N—O groups. It has been shown that very often complicated systems exist and that different complexes may be obtained on changing the experimental conditions only slightly. The recent X-ray determinations of the two thorium(IV) complexes with phosphine oxides $[Th(NO_3)_3(Me_3PO)_4]_2[Th(NO_3)_6]$ and $(PPh_4)[Th(NO_3)_5(Me_3PO)_2]$ indicate that further investigation of this oxidation state will prove very interesting. In this context an increase in X-ray studies and a correlation with the data in the solid state (IR and Raman) and in solution (conductivity and NMR) will be very useful.

The pentavalent state has been studied only for protactinium and neptunium and it is obvious that further attention should be given to this field. For the hexavalent elements only the uranyl(VI) nitrate complexes with monodentate oxygen and nitrogen donor ligands appear at the present to be well characterized; those known are of the type $UO_2(NO_3)_2(L)_2$ and are stable and nonconducting in solution. With bidentate ligands complexes of the type $UO_2(NO_3)_2(LL)$ have been obtained. Infrared and Raman spectroscopy and more recent X-ray structural investigations have shown the various complexes to be eight coordinate.

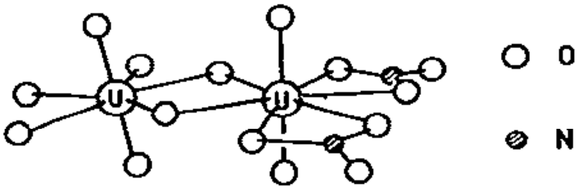
Y. ADDENDUM

Very recently the structure of di-μ-aquo-bis(dioxobis(nitrato) uranium(VI))-diimidazole $[UO_2(NO_3)_2(H_2O)]_2 \cdot C_3H_4N_2$, a water-bridged dimer of uranyl(VI) nitrate, has been published [246]. Greenish-yellow crystals of this compound have been prepared by evaporating very slowly a 1 : 1 millimolar ratio of uranyl(VI) nitrate hexahydrate and imidazole in 500 ml of water; they have a space group $P2_1/c$ with $Z = 4$ and the cell parameters: $a = 9.314(4)$, $b = 16.230(16)$ and $c = 7.053(3)$ Å, $\beta = 100.72(4)°$. The structure is a dimer of two formula units related to each other by a centre of symmetry.



Two $UO_2(NO_3)_2$ units are bridge bonded via the oxygen atoms of two water molecules. Uranium is eight coordinate at the centre of a distorted hexagonal bipyramid which has the uranyl oxygen atoms at the apices.

The geometry and bond distances of this compound are remarkably similar to the hydroxy-bridged uranyl(VI) dimer found in $[(NO_3)_2UO_2(OH)_2UO_2(H_2O)_3] \cdot H_2O$ [247] in which hydroxide instead of water is the bridging



group and three waters occupy one end of the dimer rather than two nitrate groups. The uranium—uranium distance is 3.939 Å in $[UO_2(NO_3)_2(H_2O)]_2 \cdot 2\ C_3H_4N_2$ and 3.944 Å in $[(NO_3)_2UO_2(OH)_2UO_2(H_2O)_3] \cdot H_2O$.

REFERENCES

1 G. Topping, Spectrochim. Acta, 21 (1965) 1743.
2 R.H. Nuttal and D.W. Taylor, Chem. Commun., (1968) 1417.
3 M.F. Curtis and Y.M. Curtis, Inorg. Chem., 4 (1965) 804.
4 B.O. Field and C.J. Hardy, Quart. Rev. (London), 18 (1964) 361.
5 J.R. Ferraro, A. Walker and C. Cristallini, Inorg. Nucl. Chem. Lett., 1 (1965) 25.
6 C.C. Addison, D.W. Amos, D. Sutton and W.H.H. Hoyle, J. Chem. Soc. A, (1967) 808.
7 C.C. Addison, N. Logan, S.C. Wallwork and C.D. Garner, Quart. Rev. (London), 25 (1971) 289.

8 J.I. Bullock and F.W. Parrett, Chem. Commun., (1969) 157.
9 I.R. Beattie and F.W. Parrett, J. Chem. Soc. A, (1966) 1784.
10 R.E. Hester and W.E.L. Grossman, Inorg. Chem., 5 (1966) 1308.
11 J.I. Bullock, J. Chem. Soc. A, (1969) 781.
12 J.I. Bullock and F.W. Parrett, Can. J. Chem., 48 (1970) 3095.
13 H. Brintzinger and R.E. Hester, Inorg. Chem., 5 (1966) 980.
14 F.A. Cotton, D.M.L. Goodgame and R.H. Soderberg, Inorg. Chem., 2 (1963) 1162.
15 K.W. Bagnall, The Actinide Elements. Elsevier, Amsterdam, 1972.
16 J.R. Ferraro, L.I. Katzin and G. Gibson, J. Am. Chem. Soc., 76 (1954) 909.
17 J.L. Drummond and G.A. Welch, J. Chem. Soc., (1956) 2565.
18 G.R. Waterburg, R.M. Douglass and C.F. Metz, Anal. Chem., 33 (1961) 1018.
19 E. Spath, Monatsh. Chem., 33 (1912) 853.
20 Aloy and Rodier, Bull. Soc. Chim. Fr., 31 (1922) 246.
21 Benrath, Z. Wiss. Photogr. Photophys. Photochem., 16 (1917) 259.
22 B. Sahoo and D. Patnaik, Curr. Sci., 29 (1960) 16.
23 K.W. Bagnall, P.S. Robinson and M.A.A. Stewart, J. Chem. Soc., (1961) 4060.
24 J.B. Laidler, J. Chem. Soc. A, (1966) 780.
25 V.M. Vdovenko, V.P. Statesvich and D.M. Suglobov, Sov. Radiochem., 8 (1966) 194.
26 J.S. Cho and M.E. Wadsworth, U.S. Rep., TID-16465 (1962).
27 J.R. Ferraro and A. Walker, J. Chem. Phys., 45 (1966) 550.
28 J.R. Ferraro, L.I. Katzin and G. Gibson, J. Am. Chem. Soc., 77 (1955) 327.
29 M. Schweisser and G. Koehler, Angew. Chem., 77 (1965) 456.
30 T. Veki, A. Zalkin and D.H. Templeton, Acta Crystallogr., 20 (1966) 836.
31 J.C. Taylor, M.H. Mueller and R.L. Hitterman, Acta Crystallogr., 20 (1966) 842.
32 C.C. Addison and B.M. Gathehouse, J. Chem. Soc., (1960) 613.
33 J.R. Ferraro, J. Mol. Spectrosc., 4 (1960) 99.
34 K.I. Petrov, A.K. Molodkin, O.D. Saralidze and Z.V. Belyakova, Russ. J. Inorg. Chem., 12 (1967) 1573.
35 J.R. Ferraro, J.S. Ziomek and G. Mack, Spectrochim. Acta, 17 (1961) 802.
36 J.P. Mathieu and M. Lounsbury, Discuss. Faraday Soc., 9 (1950) 196.
37 B.G. Oliver and A.R. Davis, J. Inorg. Nucl. Chem., 34 (1972) 2851.
38 G.L. Johnson, M.L. Kelly and D.R. Cunco, J. Inorg. Nucl. Chem., 27 (1965) 1787.
39 C.F. Baes Jr., N.J. Meyer and C.E. Roberts, Inorg. Chem., 4 (1965) 518.
40 F.C. Hentz Jr. and S.Y. Tyree Jr., Inorg. Chem., 4 (1965) 875.
41 G. Johansson, Acta Chem. Scand., 22 (1968) 389.
42 D. Brown and P.J. Jones, J. Chem. Soc. A, (1966) 733.
43 G. Gibson and J.J. Katz, J. Am. Chem. Soc., 73 (1951) 5436.
44 C.C. Addison, H.A.J. Champ, N. Hodge and A.H. Norbury, J. Chem. Soc., (1964) 2354.
45 V.M. Vdovenko, D.N. Siglobova and G.A. Romanov, Dokl. Akad. Nauk. SSSR, 146 (1962) 1078.
46 G. Gibson, C.D. Beintema and J.J. Katz, J. Inorg. Nucl. Chem., 15 (1960) 110.
47 W.W. Wendlandt, Anal. Chim. Acta, 15 (1956) 435.
48 R.S. Ondrejein and T.P. Garret, J. Phys. Chem., 65 (1961) 470.
49 W. Lodding and L. Ojamina, J. Inorg. Nucl. Chem., 27 (1965) 1261.
50 W.H. Smith, J. Inorg. Nucl. Chem., 30 (1968) 1761.
51 I.I. Cherneyaev, Complex Compounds of Uranium, Israel Program for Scientific Translations, Cat. No. 2173, Jerusalem, 1966.
52 L.I. Katzin, D.M. Simon and J.R. Ferraro, J. Am. Chem. Soc., 74 (1952) 1191.
53 C. Chottard, J. Fraissard and B. Imelik, Bull. Soc. Chim. Fr., (1967) 433.
54 B. Kedzia and B.J. Trzebiatowska, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 12 (1964) 243.
55 M.E. Krevinskaya, V.D. Nikol'skii, B.G. Pozharskii and E.E. Zastenker, Radiochemistry, 1 (1960) 238.

56 V.M. Vdovenko and A.P. Sokolov, Radiokhimiya, 1 (1959) 118.
57 M.L. Franklin and T.B. Flanagan, J. Phys. Chem., 75 (1971) 1272.
58 M.L. Franklin and T.B. Flanagan, J. Chem. Soc. Dalton Trans., (1972) 192.
59 P.T. Moseley and C.J. Seabrook, J. Chem. Soc. Dalton Trans., (1973) 1115.
60 J.H. Brand and J.W. Cobble, Inorg. Chem., 9 (1970) 912.
61 B.M. Gatehouse and A.E. Comyns, J. Chem. Soc., (1958) 3965.
62 V.M. Vdovenko, E.V. Stroganov, A.P. Sokolov and V.N. Zaudin, Radiokhimiya, 2 (1960) 24.
63 J.E. Fleming and H. Lynton, Chem. Ind., 79 (1960) 1416.
64 J.G. Allpress and A.N. Hambly, Aust. J. Chem., 12 (1959) 569.
65 V.M. Vdovenko, D.N. Suglobov and A.P. Taranov, Sov. Radiochem., 6 (1964) 539.
66 A.M. Deane, E.W.T. Richards and I.G. Stephen, Spectrochim. Acta, 22 (1966) 1253.
67 J.I. Bullock, J. Inorg. Nucl. Chem., 29 (1967) 2257.
68 D.A. Hall, A.D. Rae and T.N. Waters, Acta Crystallogr., 19 (1965) 389.
69 J.C. Taylor and M.H. Mueller, Acta Crystallogr., 19 (1965) 536.
70 V.M. Vdovenko, E.V. Stroganov and A.P. Sokolov, Sov. Radiochem., 5 (1963) 83.
71 V.M. Vdovenko, E.V. Stroganov, A.P. Sokolov and G. Lungu, Radiokhimiya, 4 (1962) 52.
72 N.K. Dalley, M.H. Mueller and S.H. Simonsen, Inorg. Chem., 10 (1971) 323.
73 B.J. Trzebiatowska and B. Kedzia, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 12 (1964) 251.
74 J.I. Bullock, J. Inorg. Nucl. Chem., 29 (1967) 2257.
75 V.M. Vdovenko, I.N. Ladygin and D.N. Suglobov, Russ. J. Inorg. Chem., 13 (1968) 154.
76 S.C. Wallwork and W.E. Addison, J. Chem. Soc., (1965) 2925.
77 C.C. Addison and D. Sutton, in F.A. Cotton (Ed.), Progress in Inorganic Chemistry, Vol. 8, Interscience, 1967, p. 195.
78 G. Norwitz and D.E. Chasan, J. Inorg. Nucl. Chem., 31 (1969) 2267.
79 B.A. Whitehouse, J.D. Ray and D.T. Roger, J. Magn. Resonance, 1 (1969) 311.
80 L.I. Katzin, J. Inorg. Nucl. Chem., 24 (1962) 245.
81 J.M.P.J. Verstegen, J. Inorg. Nucl. Chem., 26 (1964) 25.
82 J. Flahaut, in P. Pascal (Ed.), Nouveau Traite de Chemie Minerale, Vol. IX, 1963, pp. 1124 and 1141.
83 J.R. Ryan, J. Phys. Chem., 64 (1960) 1375.
84 B.P. Nikol'skii, M.V. Posvol'skii and G.S. Markov, Sov. Radiochem., 8 (1966) 105.
85 B.P. Nikol'skii, M.V. Posvol'skii and G.S. Markov, Sov. Radiochem., 9 (1967) 671.
86 W.E. Keder, J.L. Ryan and A.S. Wilson, J. Inorg. Nucl. Chem., 20 (1961) 131.
87 A.D. Gel'man, H.N. Krot and N.P. Ermolaev, Russ. J. Inorg. Chem., 7 (1962) 1051.
88 P.J. Alvey, K.W. Bagnall and D. Brown, J. Chem. Soc. Dalton Trans., (1973) 2326.
89 D. Brown, in A.F. Trotman-Dickenson (Ed.), Comprehensive Inorganic Chemistry, Vol. 5, Pergamon Press, Oxford, p. 277.
90 F.A. Hart and J.E. Newberry, J. Inorg. Nucl. Chem., 30 (1968) 318.
91 E. Staritzky and A.L. Truitt, in G.T. Seaborg and J.J. Katz (Eds.), The Actinide Elements, Nat. Nucl. Energy Series IV, Vol. 14A, McGraw-Hill, NY, 1954, Chap. 19.
92 S. Scavnicar and B. Prodic, Acta Crystallogr., 18 (1965) 698.
93 K.W. Bagnall and M.W. Wakerley, J. Chem. Soc. Dalton Trans., (1974) 889.
94 H.H. Anderson, Atomic Energy Commission Research and Development Report, ANL-064, Argonne National Laboratories, Oct. 23, 1947.
95 H.H. Anderson, in G.T. Seaborg, J.J. Katz and W.M. Manning (Ed.). The Transuranium Elements, Nat. Nucl. Energy Series, IV, Vol. 14B, McGraw-Hill, New York, 1949, pp. 964—967.
96 J.M. Cleveland, in O.J. Wick (Ed.), Plutonium Handbook, Gordon and Breach, New York, 1967, p. 378.

97 T.A. Beineke and J. Delgaudio, Inorg. Chem., 7 (1968) 715.
98 R.D. Larson and G.H. Brown, J. Phys. Chem., 68 (1964) 3060.
99 H.A.C. McKay and J.L. Woodhlad, J. Chem. Soc., (1964) 717.
100 C.A. Addison and N. Hodge, J. Chem. Soc., (1963) 2987.
101 U.A. Yakimonov, N.F. Nosova and A.Ya. Deytyarev, Sov. Radiochem., 5 (1963) 60.
102 J.L. Ryan, J. Phys. Chem., 65 (1961) 1099.
103 A.A. Lipovskii and M.G. Kuzina, Sov. Radiochem., 5 (1963) 628.
104 V.M. Vdovenko, A.A. Lipovskii and M.G. Kuzina, Zh. Neorg. Khim., 2 (1957) 970.
105 E. Staritzky and D.I. Walker, Anal. Chem., 29 (1957) 164.
106 C.C. Waggener, J. Am. Chem. Soc., 80 (1958) 3167.
107 G.A. Barclay, T.M. Sabine and J.C. Taylor, Acta Crystallogr., 19 (1965) 205.
108 M.S. Zavidinovic, Bull. Boris Kidric Inst. Nucl. Sci., Phys., 18 (1967) 1.
109 S.S. Malcic and L.M. Manojlovic, Bull. Boris Kidric Inst. Nucl. Sci., 11 (1961) 135.
110 F.A. Hart and J.E. Newberry, J. Inorg. Nucl. Chem., 28 (1966) 1334.
111 L.V. Volod'ko, A.I. Komyak and M.R. Posledvich, Zh. Prikl. Spektrosk., 11 (1969) 1097, according to Chem. Abstr., 72 (1970) 94796c.
112 I.I. Kapshukov, Yu.F. Volkov, E.P. Moskvichev, I.A. Lebedev and G.N. Yakovlev, J. Struct. Chem. (USSR), 12 (1971) 77.
113 K. Ohwada, J. Coord. Chem., 6 (1976) 75.
114 K. Ohwada, J. Coord. Chem., 8 (1978) 35.
115 L.V. Volod'ko, A.I. Komyak and M.R. Posledovich, Zh. Prikl. Spektrosk., 2 (1969) 436, according to Chem. Abstr., 70 (1969) 52611a.
116 I.J. Kvapil, J. Kvapil and T. Tethal, J. Cryst. Growth, 10 (1971) 279.
117 E. Rabinowitch and R.L. Belford, Spectroscopy and Photochemistry of Uranyl Compounds, Pergamon Press, New York, 1964.
118 A.I. Koruyak and L.V. Volod'ko, Vesti Akad. Navuk Belarus. SSR, Ser. Fiz-Mat. Navuk, (1969) 111, according to Chem. Abstr., 71 (1969) 17311r.
119 B. Bleaneg, P.M. Lleevellyng, M.H. Price and G.R. Hall, Phil. Mag., 48 (1954) 992.
120 A.I. Komyek, A.N. Serchenko and E.V. Ditsh, Dokl. Akad. Nauk. Belorusskoi SSR, 12 (1968) 769.
121 A.F. Leung and E.Y. Wong, Phys. Rev., 187 (1969) 504.
122 J.G. Reynolds, A. Zalkin and D.H. Templeton, Inorg. Chem., 16 (1977) 3357.
123 H.H. Feder, L.E. Ross and R.C. Vogel, U.S. Atomic Energy Commission, Report ANL-4868, March, 1952.
124 P.G. Ganis, G. Avitabile, W. Mechlinski and C.P. Schaffner, J. Am. Chem. Soc., 93 (1971) 4560.
125 K.O. Hodgson and K.N. Raymond, Inorg. Chem., 11 (1972) 171.
126 R.S. Call and W.P. Schaefer, Inorg. Chem., 15 (1976) 2758.
127 S.R. Ely, T.E. Hopkins and C.W. Dekock, J. Am. Chem. Soc., 98 (1976) 1624.
128 J.E. Kilpatrik, K.S. Pitzer and R. Spitzer, J. Am. Chem. Soc., 69 (1947) 2483.
129 N.W. Alcock, S. Esperas, K.W. Bagnall and W. Hsian-Yun, J. Chem. Soc. Dalton Trans., (1978) 638.
130 D.L. Plymale, J. Inorg. Nucl. Chem., 31 (1969) 236.
131 Mazhar-Ul-Haque, C.N. Caughlan, F.A. Hart and R. VanNice, Inorg. Chem., 10 (1971) 115.
132 T.V. Halaley and H.A.C. McKay, Trans. Faraday Soc., 52 (1956) 633.
133 L.I. Katzin, J. Ferraro, W.W. Wendlandt and R.L. McBeth, J. Am. Chem. Soc., 78 (1956) 5139.
134 J.G.H. Du Preez and C.P.J. Van Vuuren, J. Inorg. Nucl. Chem., 36 (1974) 81.
135 K. Alcock, G.F. Best, E. Hesford and H.A.C. McKay, J. Inorg. Nucl. Chem., 6 (1958) 328.
136 G.F. Best, H.A.C. McKay and P.R. Woodgate, J. Inorg. Nucl. Chem., 4 (1957) 315.
137 D.R. Cousins and F.A. Hart, J. Inorg. Nucl. Chem., 30 (1968) 3009.

138 D.R. Cousius and F.A. Hart, J. Inorg. Nucl. Chem., 29 (1967) 1745.
139 P. Gaus and B.C. Smith, J. Chem. Soc., (1964) 4172.
140 J.G.H. Du Preez and C.P.J. Van Vuuren, J. Chem. Soc. Dalton Trans., (1975) 1548.
141 A. Zalkin, J.D. Forester and D.H. Templeton, J. Chem. Phys., 39 (1963) 2881.
142 K.K. Bhandary and H. Manohar, Acta Crystallogr., Sect. B, 29 (1973) 1093.
143 J.P. Day and L.M. Venanzi, J. Chem. Soc. A, (1966) 197.
144 K.W. Bagnall, D. Brown, P.J. Jones and J.G.H. Du Preez, J. Chem. Soc. A, (1966) 737.
145 C.N. Lestas and M.R. Truter, J. Chem. Soc. A, (1971) 738.
146 A. Apelblat and R. Levin, Chem. Commun., (1970) 514.
148 C. Panattoni, R. Graziani, U. Croatto, B. Zarli and G. Bombieri, Inorg. Chim. Acta, 2 (1968) 43.
149 Yu.A. Dyadin, I.I. Yakovlev and I.V. Bandaryak, Izv. Sib. Otd. Acad. Nauk. SSSR, Ser. Khim. Nauk., 3 (1970) 14, according to Chem. Abstr., 74 (1971) 68330r.
150 A.K. Majumdar, A.R. Mukherjee and R.G. Bhattacharya, J. Inorg. Nucl. Chem., 26 (1964) 386.
151 R. Graziani, B. Zarli and G. Bandoli, Ric. Sci., 37 (1967) 986.
152 M. Ziegler, H. Winkler and L. Ziegler, Naturwissenschaften, 52 (1965) 302.
153 A.K. Majumdar, R.G. Bhattacharya and D.C. Bera, Chem. Ind. (London), 26 (1971) 730.
154 B. Zarli, G. Dall'Olio and L. Sindellari, J. Inorg. Nucl. Chem., 38 (1976) 491.
155 F.A. Cotton, R.D. Barnes and E. Bannister, J. Chem. Soc., (1960) 2199.
156 R.N. Shchelokov, A.Yu. Tsivadze, I.M. Orlova and G.V. Podnebesnova, Inorg. Nucl. Chem. Lett., 13 (1977) 375.
157 C.E.F. Rickard and D.C. Woollard, Inorg. Nucl. Chem. Lett., 14 (1978) 207.
158 Y. Kuroda and M. Kimura, Spectrochim. Acta, 22 (1966) 47.
159 S.H. Hunter, V.M. Laugford, G.A. Rodley and C.J. Wilkins, J. Chem. Soc. A, (1968) 305.
160 B. Zarli, L. Volponi, L. Sindellari and G. Depaoli, J. Inorg. Nucl. Chem., 35 (1973) 231.
161 K.W. Bagnall, D. Brown, D.G. Holah and F. Lux, J. Chem. Soc. A, (1968) 465.
162 P.J. Alvey, K.W. Bagnall and D. Brown, J. Chem. Soc. Dalton Trans., (1975) 1277.
163 A.K. Molodkin, O.M. Ivanova, Z.V. Belyakova and L.E. Kolesvikova, Russ. J. Inorg. Chem., 15 (1970) 1692.
164 N. Grundüz, B.C. Smith and M.A. Wassof, Commun. Fac. Sci. Univ. Ankara, Ser. B, 31.
165 G. Gritzner, V. Gutmann and M. Michlmayr, Z. Anal. Chem., 224 (1967) 245.
166 L. Cattalini, L. Baracco, S. Degetto, C. Marangoni, L. Maresca and L. Sindellari, Gazz. Chim. Ital., 104 (1974) 915.
167 R. Graziani, G. Bombieri, E. Forsellini, S. Degetto and G. Marangoni, J. Chem. Soc. Dalton Trans., (1973) 451.
168 G. Faraglia, B. Zarli, L. Sindellari and G. Dall'Olio, Inorg. Chim. Acta, 19 (1976) 39
169 B. Zarli, G. Casotto, L. Sindellari and G. Faraglia, Inorg. Chim. Acta, 31 (1978) 5.
170 J.P. Day and L.M. Venanzi, J. Chem. Soc. A, (1966) 1363.
171 E. Forsellini, G. Bombieri, R. Graziani and B. Zarli, Inorg. Nucl. Chem. Lett., 8 (1972) 461.
172 N.T. Rogers and J.C. Woodbrey, J. Phys. Chem., 66 (1962) 540.
173 T.M. Valega, J. Org. Chem., 31 (1966) 1150.
174 E. Lustig, W.R. Benson and M. Duy, J. Org. Chem., 32 (1967) 851.
175 K.W. Bagnall, D. Brown, P.J. Jones and P.S. Robinson, J. Chem. Soc., (1964) 2531.
176 W.E. Bull, S.K. Madan and J.E. Willis, Inorg. Chem., 2 (1963) 303.
177 K.W. Bagnall and O. Valasquez-Lopez, J. Chem. Soc. Dalton Trans., (1975) 1409.
178 K.W. Bagnall, J.G.H. du Preez, J. Bajorek, L. Bonner, H. Cooper and G. Segal, J. Chem. Soc. Dalton Trans., (1973) 2682.

179 K.W. Bagnall, O. Velasquez-Lopez and D. Brown, J. Inorg. Nucl. Chem., 38 (1976) 1997.
180 K.I. Petrov, A.K. Molodkin, O.M. Ivanova and O.D. Saralidze, Russ. J. Inorg. Chem., 14 (1969) 215.
181 P.S. Gentile and L.S. Campisi, J. Inorg. Nucl. Chem., 27 (1965) 2291.
182 Ref. 2 quoted in N.K. Dalley, M.H. Mueller and S.H. Simonsen, Inorg. Chem., 11 (1972) 1840.
183 Ref. 3 quoted in N.K. Dalley, M.H. Mueller and S.H. Simonsen, Inorg. Chem., 11 (1972) 1840.
184 N.K. Dalley, M.H. Mueller and S.H. Simonsen, Inorg. Chem., 11 (1972) 1840.
185 J.R. Ferraro and A. Walker, J. Chem. Phys., 42 (1965) 1278.
186 G.V. Ellert, I.V. Tsapkina and L.P. Baranova, Russ. J. Inorg. Chem., 15 (1970) 971.
187 V.G. Kuznetzov, G.V. Ellert, I.V. Tsapkina and Yu.N. Mikhailov, Russ. J. Inorg. Chem., 15 (1970) 1280.
188 G.V. Ellert, I.V. Tsapkina, O.M. Erstaf'eva, V.F. Zolin and P.S. Fisher, Russ. J. Inorg. Chem., 16 (1971) 1640.
189 A. Seminara, A. Musumeci and A. Chiarizia, J. Inorg. Nucl. Chem., 40 (1978) 269.
190 R.M. Costes, G. Folcher, P. Plurien and P. Rigny, Inorg. Nucl. Chem. Lett., 12 (1976) 13.
191 D.L. Williams and L.E. Deacon, J. Inorg. Nucl. Chem., 39 (1977) 1079.
192 P.G. Eller and R.A. Penneman, Inorg. Chem., 15 (1976) 2439.
193 G. Bombieri, G. De Paoli, A. Cassol and A. Immirzi, Inorg. Chim. Acta, 18 (1976) L23–L24.
194 G. Bombieri, G. De Paoli and A. Immirzi, J. Inorg. Nucl. Chem., 40 (1978) 799.
195 R.M. Costes, G. Folcher, P. Plurien and P. Rigny, Inorg. Nucl. Chem. Lett., 11 (1975) 469.
196 A. Knochel, J. Klimes, J. Oehler and G. Rudolph, Inorg. Nucl. Chem. Lett., 11 (1975) 787.
197 N. Armagan, Acta Crystallogr., Sect. B, 33 (1977) 2281.
198 J. Klimes, A. Knochel and G. Rudolph, Inorg. Nucl. Chem. Lett., 13 (1977) 45.
199 J.J. Cristensen, D.J. Eatough and R.M. Izatt, Chem. Rev., 74 (1974) 351.
200 M.R. Truter, Struct. Bonding (Berlin), 16 (1973) 71.
201 B.E. Jepson and R. DeWitt, J. Inorg. Nucl. Chem., 38 (1976) 1175.
202 C.J. Pedersen, J. Am. Chem. Soc., 89 (1967) 7017.
203 C.J. Pedersen, J. Am. Chem. Soc., 92 (1970) 386.
204 J.D. Dunitz and P. Seiler, Acta Crystallogr., Sect. B, 30 (1974) 2739.
205 P. Seiler, M. Dobler and I.J. Dunitz, Acta Crystallogr., Sect. B, 30 (1974) 2744.
206 M. Dobler and R.P. Phizackerley, Acta Crystallogr., Sect. B, 30 (1974) 2746.
207 M. Dobler and R.P. Phizackerley, Acta Crystallogr., Sect. B, 30 (1974) 2748.
208 R.M. Costes, G. Folcher, P. Plurien and P. Rigny, Inorg. Nucl. Chem. Lett., 12 (1976) 491.
209 A. Seminara, G. Siracusa and A. Cassol, Inorg. Chim. Acta, 20 (1976) 105.
210 B. Spiess, F. Arnaud-Neu and M.J. Schwing-Weill, Inorg. Nucl. Chem. Lett., 15 (1979) 13.
211 K.C. Dash and H. Mohanta, J. Inorg. Nucl. Chem., 40 (1978) 499.
212 V.P. Markov and V.V. Tsapkin, Russ. J. Inorg. Chem., 7 (1962) 250.
213 P.V. Balakrishnam, S.K. Patil, H.D. Sharma and H.V. Venkatasetty, Can. J. Chem., 43 (1965) 2052.
214 I.M. Koposhova, I.K. Skutov, D.S. Umreiko and R.I. Shamanovskaya, Russ. J. Inorg. Chem., 12 (1967) 1748.
215 V.M. Vdovenko, D.M. Suglobov and V.A. Kraril'nikov, Sov. Radiochem., 5 (1963) 281.
216 M.P. Sahakari and A.J. Mukledkar, J. Inorg. Nucl. Chem., 33 (1971) 888.

217 E. Staritzky, Anal. Chem., 28 (1956) 2021.
218 G. Johansson, Sven. Kem. Tidskr., 78 (1966) 486.
219 G. Chottard, C.R. Acad. Sci., Ser. C, 267 (1968) 147.
220 A. Apelblat and R. Levin, J. Inorg. Nucl. Chem., 41 (1976) 115.
221 V.V. Savant and C.C. Patil, J. Inorg. Nucl. Chem., 31 (1969) 2319.
222 G. Laurence and TM.T. Chaieb, Bull. Soc. Chim. Fr., (1970) 2481.
223 V.M. Vdovenko, I.G. Suglobova and M. Mezei, Sov. Radiochem., (1962) 342.
224 G. Bandoli, D.A. Clemente and M. Biagini Cingi, J. Inorg. Nucl. Chem., 37 (1975) 1709.
225 M. Vidali, P.A. Vigato and U. Casellato, J. Inorg. Nucl. Chem., 37 (1975) 955.
226 R. Graziani, G. Marangoni, G. Paolucci and E. Forsellini, J. Chem. Soc. Dalton Trans., (1978) 818.
227 B.C. Smith and M.A. Wassef, J. Chem. Soc. A, (1968) 1817.
228 J.T. Barr and C.A. Horton, J. Am. Chem. Soc., 74 (1952) 4430.
229 S.P. McGlynn, J.K. Smith and W.C. Neely, J. Chem. Phys., 35 (1961) 105.
230 A. Zalkin, H. Ruben and D.H. Templeton, Inorg. Chem., 18 (1979) 519.
231 J.M. Cleveland, Coord. Chem. Rev., 5 (1970) 101.
232 A.D. Jones and G.R. Choppin, Actinides Rev., 1 (1969) 311.
233 C. Keller, The Chemistry of the Transuranium Elements, Verlag Chemie GmbH, Weinheim Bergstr., Germany, 1971.
234 L. Cattalini, U. Croatto, S. Degetto and E. Tondello, Inorg. Chim. Acta, Rev., 5 (1971) 19.
235 D. Brown, in K.W. Bagnall (Ed.), Inorganic Chemistry, Series I, Vol. 7, Butterworths, London, 1972, p. 87.
236 D. Brown, Adv. Inorg. Chem. Radiochem., 12 (1969) 1.
237 J.J. Katz and J. Sheft, Adv. Inorg. Chem. Radiochem., 2 (1960) 195.
238 H. Gysling and M. Tsutsui, Adv. Organomet. Chem., 9 (1970) 361.
239 R.G. Hayes and J.L. Thomas, Organomet. Chem. Rev., SA, 7 (1971) 1.
240 B. Kanellakopulos and K.W. Bagnall, in K.W. Bagnall (Ed.), Inorganic Chemistry, Series I, Vol. 7, Butterworths, London, 1972, p. 299.
241 J.L. Ryan, in K.W. Bagnall (Ed.), Inorganic Chemistry, Series I, Vol. 7, Butterworths, London, 1972, p. 323.
242 U. Casellato, M. Vidali and P.A. Vigato, Coord. Chem. Rev., 26 (1978) 85.
243 U. Casellato, M. Vidali and P.A. Vigato, Inorg. Chim. Acta, 18 (1976) 77.
244 U. Casellato, M. Vidali and P.A. Vigato, Coord. Chem. Rev., 28 (1979) 231.
245 K.M.A. Malik and J.W. Jeffery, Acta Crystallogr., Sect. B, 29 (1973) 2687.
246 D.L. Perry, H. Ruben, D.H. Templeton and A. Zalkin, Inorg. Chem., 19 (1980) 1067.
247 A. Perrin, Acta Crystallogr., Sect. B, 32 (1976) 1658.