

PREPARATIVE AND CRYSTALLOGRAPHIC STUDIES
ON ACTINIDE HALIDES

A thesis presented for the
Degree of Doctor of Philosophy

in the
Faculty of Science
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by
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STATEMENT

The experimental work in this thesis has been carried out by the author in the Chemistry Division at A.E.R.E., Harwell, Didcot, Berkshire between October 1965 and October 1968 under the supervision of Professor R. D. Peacock. This work has not been presented and is not being concurrently presented for any other degree.

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Some of the work described has already been published in the open literature and the appropriate reprints are enclosed at the end of the thesis.

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Finally my grateful thanks to my wife for patiently typing this thesis.

Summary

Since the discovery of neptunium in 1940 there has been considerable progress in the chemistry of the actinide elements and the halides and halogen complexes, especially, have received a good deal of attention. The purpose of this work was to further investigate some preparative and structural aspects of certain halogen compounds of the earlier actinides, in particular those of protactinium and neptunium.

The availability and valency states of the actinide elements are outlined in Chapter 1, and in the next chapter, a short review of the actinide halides, oxyhalides and pentavalent fluoro-complexes, is followed by a discussion of the proposed aims of the investigation.

A general method for the preparation of actinide (IV) oxydihalides of the type MOX_2 (M is variously Th, Pa, U and Np with X = Cl, Br and I) has been developed and has also been successfully applied to the preparation of protactinium (V) oxyhalides. The preparation of the new oxyhalides $PaOI_3$, PaO_2I , $NpOF_3$ and ' NpO_2F ' is described together with new methods for obtaining NpO_2F_2 . The attempted preparation of new protactinium (V) oxyfluorides and new neptunium (V) fully fluorinated complexes has led to the characterisation of $PaF \cdot H_2O$ and Na_3NpF_8 respectively. $NpBr_4$ has now been obtained in high yield by a new method. The infrared spectra, x-ray powder diffraction properties and chemical properties of the new compounds and of the actinide (IV) oxydihalides are reported.

X-ray single crystal studies have shown that in Na_3PaF_8 there is an almost perfect cubic arrangement of the fluorine atoms around the protactinium. This is the first reported instance of this type of co-ordination. Cs_2PaF_7 has been shown on the basis of x-ray single crystal studies to be isostructural with K_2PaF_7 , the structure of which is known. Preliminary results of single crystal studies on PaI_5 , TaI_5 and UBr_4 are also discussed.

Finally the proposed aims are compared with the achievements and the review of the actinide halogen compounds is brought up to date.

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Chapter 1

THE ACTINIDE ELEMENTS

The elements with atomic number 89 to 103⁽¹⁾ are now generally known as the 'actinide elements' although perhaps a more correct definition would cover only the f transition series of which actinium is the precursor, namely, elements 90 to 103. Other nomenclatures⁽²⁾ such as 'uranides', 'protactinides' and 'thorides' have been suggested to cover various features of the chemistry of the group but these terms were not generally accepted and are little used.

Availability

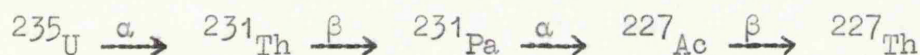
Thorium and uranium occur in the earth's crust with abundances of 12ppm and 4ppm, respectively. Both elements have been known for many years; thorium was discovered by Berzelius in 1828 and uranium by Klaproth in 1789. Up to 1939 some properties and compounds were fairly well established but only thorium had been commercially exploited. Research into the development and production of nuclear reactors and nuclear weapons, which followed the discovery of atomic fission by Hahn and Strassmann⁽³⁾, considerably advanced the knowledge of the properties of thorium, uranium and their compounds.

²³²Th is the naturally occurring long-lived isotope ($t_{\frac{1}{2}} = 1.39 \times 10^{10}$ yr.). One of its decay products, ²²⁸Th ($t_{\frac{1}{2}} = 1.9$ yr.) also occurs naturally.

The two longest-lived, naturally occurring isotopes of uranium are

^{238}U ($t_{\frac{1}{2}} = 4.5 \times 10^9$ yr.) and ^{235}U ($t_{\frac{1}{2}} = 7.1 \times 10^8$ yr.). ^{238}U gives another uranium isotope in its decay chain, ^{234}U ($t_{\frac{1}{2}} = 2.5 \times 10^5$ yr.).

The isotopic composition of naturally occurring uranium is 99.27% ^{238}U , 0.72% ^{235}U and 0.0056% ^{234}U . The decay chain of ^{235}U includes the two longest-lived isotopes of protactinium and actinium, ^{231}Pa ($t_{\frac{1}{2}} = 32,340$ yr.) and ^{227}Ac ($t_{\frac{1}{2}} = 22$ yr.), respectively.



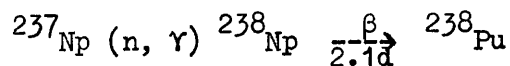
Neither isotope has a long enough half-life for independent occurrence in nature although at equilibrium there is approximately 300mg ^{231}Pa and 0.2mg ^{227}Ac per tonne of uranium ore.

As a consequence of the vast quantities of uranium ores processed for nuclear purposes the amounts of protactinium-231 accumulated in certain residues became sufficiently high (over 100g) to make a large scale separation a worthwhile proposition. By 1960 the U.K.A.E.A. had separated⁽⁴⁾ some 120g ^{231}Pa from 60 tonnes of ethereal sludge residues. The availability of this material has been responsible for most of the impetus given to protactinium chemistry in the last few years.

Isotopes of the synthetic actinide elements Np to Fm are best prepared by successive neutron capture from uranium in a nuclear reactor. Eventually the thermal neutron capture cross-section and the thermal neutron fission cross-section, which compete at each stage, reducing the yields for each successive step, become so biased towards fission

that no further increase in atomic number can be obtained. Each product nucleus invariably undergoes further neutron capture making the product isotopically impure. Neptunium is one of the few elements that can be produced isotopically pure, as ^{237}Np . It is a non-fissionable isotope with a half-life of 2.2×10^6 years and is produced by two different routes. One from ^{235}U , which undergoes slow neutron capture, instead of fission, to produce ^{237}U which decays by β emission with a half-life of 6.75 days. The other route is from fast neutron capture by ^{238}U , which is non-fissile, giving a (n, 2n) reaction to produce ^{237}U .

Thermal neutron capture by ^{238}U gives ^{239}U which decays by β emission with a 23.5 minute half-life to ^{239}Np , which in turn decays with a 2.33 day half-life to ^{239}Pu . Plutonium-239 can undergo further neutron capture to yield the heavier isotopes ^{240}Pu to ^{244}Pu , inclusive. ^{238}Pu is obtained from ^{237}Np by the route:-



Neptunium-237 and plutonium-239 have both been detected in uranium ores at a steady state concentration of about $1\text{g}/10^6$ tonnes. Their presence is due to neutron reactions with ^{238}U . Kilogram amounts of neptunium and plutonium are now available.

Americium-241 ($t_{\frac{1}{2}} = 458$ yr.) is the β decay product of ^{241}Pu . The longer-lived americium isotope ^{243}Am ($t_{\frac{1}{2}} = 7,950$ yr.) is obtained by neutron capture reactions starting with ^{242}Pu . Gram amounts of both

are now available, largely as a result of the transplutonium programmes⁽⁵⁾ mainly undertaken in the U.S.A.

The space programme in the U.S.A. was also indirectly responsible for boosting the amounts of transplutonium elements available. For example, 3 kilograms⁽⁶⁾ of ^{244}Cm was needed to assess its value as a thermoelectric power source for satellites. In one experiment 500g of ^{242}Pu was irradiated in the High Flux Isotope Reactor at Oak Ridge (10^{15} neutrons/cm²/sec.). 215g of ^{244}Cm were obtained after 80% burn-up, together with 10mg of berkelium isotopes, 50mg of californium isotopes and 2mg of einsteinium. It was estimated that if the demand for ^{244}Cm were to continue a recycling process would yield 5 to 10 milligrams of ^{252}Cf at steady state conditions.

The only long-lived isotope of fermium, ^{257}Fm , is best formed under the conditions of a nuclear explosion using targets of ^{238}U , ^{242}Pu or ^{243}Am .

The last three actinides, mendelevium, 102* and lawrencium are produced at the rate of a few atoms per experiment by the reaction of heavy ions such as ^{12}C or ^{11}B with the heavier actinides in a cyclotron.

Valency States

With the exception of actinium and thorium all the actinide elements possess f electrons in the ground state configurations of the neutral gaseous atoms (Table 1). As the thorium atom is progressively ionised the f electrons become more stable⁽⁷⁾ and occur in the ground

*originally named nobelium

states of Th^{2+} and Th^{3+} . The presence of these f electrons supports the assumption that the actinide series parallels the lanthanide series as an f transition group. A comparison of the valency states of the lanthanide and actinide elements (Table 2), however, shows that there is a higher multiplicity of valency states for the earlier actinides. Heptavalent neptunium and plutonium have only recently been reported. Russian workers⁽⁸⁾ claim to have oxidised Np (VI) and Pu (VI) in alkaline solution with ozone. Some insoluble alkaline earth and rare earth compounds have been prepared and it will be interesting to see what physical properties these have.

The underlying reasons for the differences in oxidation states are not yet completely understood. The environment of the 4f and 5f electrons is different. The 4f orbitals do not penetrate the 5s, 5p and 6s orbitals and there is, therefore, considerable shielding from external forces. The magnetic and spectral properties of the lanthanide elements support this. The 5f electrons, however, are thought to penetrate the outer valence regions, since the atomic radii of the corresponding lanthanides and actinides do not differ much, and are, therefore, not shielded as well as the 4f electrons. There is, therefore, the possibility that the 5f electrons can participate in bonding due either to the lower binding energy or to the greater spacial size allowing better orbital overlap. The effect of the 5f electrons will not, however, be as great as that of the 6d in bonding. The stability of the MO_2^+ and MO_2^{++} ions⁽⁹⁾, which are peculiar to the actinide elements,

Table 1

Outer electronic ground state configurations of the
gaseous actinide elements*

Ac	$6d7s^2$	Cm	$5f^76d7s^2$
Th	$6d^27s^2$	Bk	$5f^97s^2$ or $5f^86d7s^2$
Pa	$5f^26d7s^2$ or $5f^16d^27s^2$	Cf	$5f^{10}7s^2$
U	$5f^36d7s^2$	Es	$5f^{11}7s^2$
Np	$5f^46d7s^2$ or $5f^57s^2$	Fm	$5f^{12}7s^2$
Pu	$5f^67s^2$	Md	$5f^{13}7s^2$
Am	$5f^77s^2$	102	$5f^{14}7s^2$
		Lw	$5f^{14}6d7s^2$

*the inner core is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$

Table 2

Oxidation States of the Lanthanide and Actinide Elements

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Atomic Number	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Oxidation State	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	<u>3</u>	3	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>
	<u>4</u>		4						4						
	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	* Lw	
Atomic Number	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Oxidation State	2					2			2				2	2	
	<u>3</u>	3		3	3	3	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>	<u>3</u>
	<u>4</u>	4	4	4	4	<u>4</u>	4	4	4						
		<u>5</u>	5	<u>5</u>	5	5									
			<u>6</u>	6	6	6	6								
				7	7										

*name not internationally recognised.

∅ most stable aqueous oxidation state underlined.

has in fact been attributed to the participation of f orbitals in the bonding.

The ease of oxidation of the actinides is not adequately explained⁽¹⁰⁾ by these factors alone. The major factor is probably the screening of the 5f electrons from the nucleus by the lower lying 4f and 5d electrons which results in the 5f electrons experiencing a relatively smaller nuclear charge than the 4f. A similar type of screening also accounts for the differences in oxidation state in descending the first, second and third row d transition series, although the situation here is also influenced by the increasing atomic radii⁽¹¹⁾. Cunningham⁽⁷⁾ has also discussed the greater ease of obtaining higher oxidation states in terms of variations in ionisation potentials and heats of sublimation of the metals.

Corbett (references 12-16) has suggested that the prime factor determining oxidation in the lanthanide series is the heat of sublimation of the metal and that the electronic structure is not so important. Previously the $4f^0$, $4f^7$ and $4f^{14}$ electronic configurations were thought to be important in explaining the divalency and tetravalency of certain lanthanides.

Divalent lanthanides have recently received a great deal of attention⁽¹⁷⁻¹⁹⁾ and almost all have been prepared in a CaF_2 matrix. Attempts to stabilise divalent neptunium, plutonium and curium⁽²⁰⁾ in

CaF_2 have failed but divalent americium⁽²¹⁾ has been obtained. Under similar conditions it is quite probable that the elements beyond curium will show divalency. Divalent californium⁽²²⁾, mendelevium^(23, 24) and element 102⁽²⁵⁾ have, in fact, recently been reported in aqueous solution. This was predicted for mendelevium by Seaborg⁽²⁶⁾.

The ionic radii of the M^{n+} ions of the actinide elements show a small but significant decrease with increasing atomic number giving an actinide contraction analogous to the lanthanide contraction. The f electrons do not shield one another at all effectively due to the shape of the orbitals so that successive addition of f electrons causes a greater effective nuclear charge on each f electron, reducing the size of the whole shell and hence gives rise to a contraction. This is shown effectively by a comparison of the M^{3+} ions (Table 3). With the contraction of the orbitals the tendency to form higher oxidation states decreases and there is no evidence for oxidation states greater than three for the actinides following berkelium.

The curves of binding energy/atomic number for the 5f and 6d electrons cross between thorium and protactinium and there is only a small difference between these levels for the earlier actinides. As a consequence there may be a tendency in Th, Pa, U and perhaps Np for d orbitals to be filled in preference to f. The electronic structures of very few compounds have been determined and those results that have been interpreted indicate that the f level is

Table 3

Atomic and ionic radii for the actinide elements (Å)

	Atomic	M ³⁺	M ⁴⁺
Ac	1.88	1.11	-
Th	1.79	(1.08)	0.99
Pa	1.63	(1.05)	0.96
U	1.56	1.03	0.93
Np	1.55	1.01	0.92
Pu	1.59	1.00	0.90
Am	1.73	0.99	0.89
Cm	1.74	0.98	0.88

preferentially filled. Examples of the compounds studied are^(27, 28) Cs_2PaCl_6 in Cs_2ZrCl_6 , in which the Pa^{4+} ion was shown to possess the $5f^1$ configuration, and CsUF_6 ⁽²⁹⁾, in which the U^{5+} ion was also shown to be $5f^1$.

Magnetic properties, which are very useful in the determination of electronic configurations in the 4f and the d transition groups, are less useful with the 5f group as it is not possible, as yet, to predict the exact behaviour of specific 5f or 6d configurations. The magnetic moments observed generally lie between those calculated on the basis of a spin only condition and those calculated assuming Russell-Saunders coupling for the $6d^n$ condition. In limited cases electronic configurations have been predicted by comparison with corresponding lanthanide compounds. Thus, the electronic configuration of⁽³⁰⁾ U^{3+} in UCl_3 and⁽³¹⁾ of Pu^{3+} in PuCl_3 have been predicted as $5f^3$ and $5f^5$ respectively by comparison of magnetic properties with those of Nd^{3+} in NdCl_3 and Sm^{3+} in SmCl_3 .

There is some resemblance between the chemistry of the early actinides and the vertical d group elements. For example, zirconium and hafnium have close analogies with thorium, niobium and tantalum with protactinium, and molybdenum and tungsten with

uranium. The greatest differences occur in the vertical groups between molybdenum and tungsten and uranium.

Chapter 2

SURVEY AND AIMS

Actinide halogen compounds can be obtained in almost all of the wide range of valency states shown in Table 2. There are, nevertheless, certain compounds that have not been reported which ought to be capable of existence. Such compounds, together with the lack of reported properties for certain of the known halides and oxyhalides, will be discussed in this Chapter. Some potentially interesting and fruitful areas for further investigation, which existed in 1965, will be highlighted and those chosen for investigation during this study will be discussed later.

Tables 4, 5 and 6 list respectively the then known binary actinide halides, the actinide oxyhalides and the pentavalent actinide fluoro-complexes. Review articles by Haissinsky⁽³²⁾, Katz and Sheft⁽³³⁾, Bagnall^(34, 35), Hodge⁽³⁶⁾ and by Tananaev⁽³⁷⁾ deal in varying detail with the individual preparations and properties. Structural and preparative details are also to be found in the books by Katz and Seaborg⁽³⁸⁾ and by Brown⁽³⁹⁾. Consequently, individual preparative details and properties are not discussed here.

Binary actinide halides

The stability of the hexafluorides decreases rapidly from uranium to plutonium. Plutonium hexafluoride is a powerful fluorinating agent and will, for example, oxidise BrF_3 ⁽⁴⁰⁾ to BrF_5 . It is likely, therefore, that americium hexafluoride will not be prepared. However, most experimental work on americium has been done with ^{241}Am ($t_{1/2} = 457 \text{ yr.}$)

Table 4

The actinide halides

	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
Fluorides	AcF ₃	-	-	UF ₃	NpF ₃	PuF ₃	AmF ₃	CmF ₃		
		ThF ₄	PaF ₄	UF ₄	NpF ₄	PuF ₄	AmF ₄	CmF ₄		
		-	-	U ₄ F ₁₇	-	Pu ₄ F ₁₇				
		Pa ₂ F ₉	PaF ₅	U ₂ F ₉	-	-				
		-	-	UF ₅	-	-				
		-	-	UF ₆	NpF ₆	PuF ₆				
Chlorides	AcCl ₃	-	-	UCl ₃	NpCl ₃	PuCl ₃	AmCl ₃	CmCl ₃		CfCl ₃
		ThCl ₄	PaCl ₄	UCl ₄	NpCl ₄					
		-	PaCl ₅	UCl ₅						
		-	-	UCl ₆						
Bromides	AcBr ₃	-	-	UBr ₃	NpBr ₃	PuBr ₃	AmBr ₃	CmBr ₃		-
		ThBr ₄	PaBr ₄	UBr ₄	NpBr ₄					
		-	PaBr ₅	UBr ₅						
Iodides		ThI ₂								
	AcI ₃	ThI ₃		UI ₃	NpI ₃	PuI ₃	AmI ₃	CmI ₃		-
		ThI ₄	PaI ₄	UI ₄						
		-	PaI ₅							

Table 5
The actinide oxyhalides

	Ac	Th	Pa	U	Np	Pu	Am
Fluorides	AcOF	-	-	-	-	PuOF	-
		ThOF ₂	-	-	-		
			Pa ₂ OF ₈	U ₂ OF ₈	-		
			-	-	-		
				UO ₂ F ₂	-	PuO ₂ F ₂	
Chlorides	AcOCl	-	-	UOCl	-	PuOCl	AmOCl
		ThOCl ₂	PaOCl ₂	UOCl ₂	NpOCl ₂		
			Pa ₂ OCl ₈		-		
			Pa ₂ O ₃ Cl ₄	UOCl ₃	-		
			PaO ₂ Cl	-	-		
				UO ₂ Cl ₂			
Bromides	AcOBr	-	-	-	-	PuOBr	-
		ThOBr ₂	PaOBr ₂	UOBr ₂	-		
			PaOBr ₃	UOBr ₃			
			PaO ₂ Br	UO ₂ Br			
				UO ₂ Br ₂			
Iodides	AcOI	-	-	-	-	PuOI	-
		ThOI ₂	PaOI ₂	-	-		
				(UO ₂ I ₂)			

(): existence not proven.

Table 6

A selection of actinide (V) fluoro complexes (88, 90-93, 96-101)

Type	M ^I	M ^V	M ^I	M ^V
$M^I M^V F_6$			Li	
	Na	Pa	Na	U
	K		K	
	NH ₄		NH ₄	
	Rb		Rb	
	Cs		Cs	
$M_2^I M^V F_6$			Ag	
	K	Pa	K	U
	NH ₄		NH ₄	
	Rb		Rb	
	Cs		Cs	
	$M_3^I M^V F_6$			
Li		Pa		U
Na			Na	
K			K	
Rb			Rb	
Cs			Cs	
			Ag	
		Ti		

and if ^{243}Am ($t_{1/2} = 7,950$ yr.) were used, the resulting reduction in radiation damage might be sufficient to allow formation of americium hexafluoride provided it is chemically stable. This aspect is important with curium tetrafluoride, which^(41, 42) cannot be prepared using ^{242}Cm but has been obtained with ^{244}Cm .

The only known pentafluorides are PaF_5 and UF_5 . Thermodynamic studies show^(43, 44) that NpF_5 and PuF_5 ought to be capable of existence. However, despite considerable work these compounds have not yet been prepared. UF_5 exists in two crystal modifications^(45, 46), a low temperature β form prepared below 125° and a high temperature α form. PaF_5 ⁽⁴⁷⁾ has only been observed in one crystal form which is isostructural with βUF_5 . This is an interesting fact when one considers that the only direct method of preparing PaF_5 is to react fluorine and PaF_4 at 700° . X-ray powder diffraction data for UF_5 ⁽⁴⁸⁾ have been interpreted by Zachariasen on the basis of a six co-ordinate structure for the α form and a seven co-ordinate one for the β modification. Unfortunately no single crystal studies have been reported and the known 'd' transition metal pentafluorides are not isostructural with either form of UF_5 . It would be interesting to have accurate structural information on UF_5 and PaF_5 .

The instability of UCl_5 , which readily undergoes thermal decomposition and also disproportionates, would seem to preclude the existence of either NpCl_5 or PuCl_5 . The possibility of obtaining pentabromides of elements beyond uranium would also seem remote since even NpBr_4 is

unstable⁽⁴⁹⁾ and, when sublimed, extensive decomposition occurs.

Thermodynamic calculations indicate⁽⁵⁰⁾ that NpBr_4 should be unstable above 430° .

The structures of PaCl_5 ⁽⁵¹⁾, UCl_5 ⁽⁵²⁾ and PaBr_5 ⁽⁵³⁾ have either recently been or are being determined and in view of the dimeric or polymer nature of the pentachlorides structural data for protactinium penta iodide would be of interest. It has in fact been predicted⁽⁵⁴⁾ that PaI_5 will be monomeric. The only actinide penta iodide known is PaI_5 ⁽⁵⁵⁾ and only two d transition metal penta iodides are known, NbI_5 ⁽⁵⁶⁾ and TaI_5 ⁽⁵⁷⁾. Single crystals of PaI_5 ⁽⁵⁸⁾ and TaI_5 ⁽⁵⁹⁾ have been studied and although both possess orthorhombic symmetry the unit cell dimensions indicate that they possess different structures. (Table 7).

Table 7

Unit cell dimensions (in Å) for PaI_5 and TaI_5

	a_o	b_o	c_o	Symmetry
TaI_5	6.65	13.95	20.10	D_{2h}^{16}
PaI_5	7.22	21.20	6.85	

Thermodynamic calculations⁽⁶⁰⁾ for solid PuCl_4 suggest that it is incapable of existence as the equilibrium pressure of chlorine over solid PuCl_4 at room temperature should be about 10^7 atmospheres. The formation of PuCl_4 in the gaseous phase⁽⁶¹⁾ has, however, been

postulated by Abrahams to explain the enhanced volatility of PuCl_3 in a chlorine flow at $600^\circ\text{--}800^\circ$. In view of the instability of NpBr_4 and UCl_4 and the non-existence of PuCl_4 , higher actinide tetrachlorides, tetrabromides and tetraiodides are not anticipated.

There is a structural change in the tetrabromides in going from thorium to neptunium. $\text{PaBr}_4^{(62)}$ and $\beta\text{ThBr}_4^{(63)}$ are isostructural with UCl_4 , possessing tetragonal symmetry, while $\text{UBr}_4^{(64)}$ and $\text{NpBr}_4^{(65, 66)}$, which are monoclinic, are isostructural. The structural properties of NpBr_4 have not been reported. It would be of interest to have details of this structural change.

Both thorium and uranium form triiodides and the absence of trihalides for protactinium is probably due to lack of investigation. Powerful reducing conditions will, of course, be necessary to prepare protactinium trihalides.

The only known dihalide is ThI_2 . Much of the earlier conflicting evidence on the properties of ThI_2 was resolved by the investigations of Clark and Corbett⁽⁶⁷⁾ and Scaife and Wylie⁽⁶⁸⁾. It appears to be a semi-metallic compound and is probably best regarded as, in the case of $\beta\text{ThI}_2^{(67)}$, $\text{Th}^{4+(e)}_2\text{I}_2$ and not as an example of divalent thorium. Americium by analogy with europium, its counterpart in the lanthanide series, might be expected to give stable dihalides but none have been observed.

The actinide oxyhalides

As a group the actinide oxyhalides have been poorly characterised and there are numerous gaps in Table 5, indicative of the lack of

investigation of these compounds.

Of the hexavalent oxyfluorides only UO_2F_2 has been thoroughly studied. NpO_2F_2 has only been prepared⁽⁶⁹⁾ contaminated with sodium fluoride by the reaction between sodium neptunyl acetate and hydrogen fluoride at 325° to 350° . PuO_2F_2 ^(70, 71) has been prepared pure but no thorough study of its properties has been reported. Despite the existence of hexavalent americium in solution, as AmO_2^{2+} , AmO_2F_2 has not been prepared. The only other pure hexavalent oxyhalides reported are UO_2Cl_2 ⁽⁷²⁾, and UO_2Br_2 ⁽⁷³⁾ though it should be possible using the correct preparative conditions to obtain NpO_2Cl_2 , NpO_2Br_2 and PuO_2Cl_2 .

Only two pentavalent oxyfluorides are known, Pa_2OF_8 ⁽⁴⁷⁾ and U_2OF_8 ⁽⁷⁴⁾. In view of the range of oxychlorides and oxybromides given by protactinium^(75, 76) other pentavalent oxyfluorides ought to be obtainable and so should protactinium (V) oxyiodides.

The only tetravalent oxyfluoride known is ThOF_2 ^(77, 78) and certainly analogous compounds for the other actinides from protactinium to plutonium might be expected if a suitable preparative method can be found. The only general method for the preparation of tetravalent oxydihalides is the reaction between a dioxide and a tetrahalide⁽⁷⁹⁻⁸²⁾. This, unfortunately, does not have a general application as it is not always possible to obtain a reactive dioxide. For example, PaO_2 ⁽⁸³⁾ is prepared by hydrogen reduction of Pa_2O_5 at 1600° . Only microgram amounts of NpOCl_2 ⁽⁴⁹⁾ have been obtained as the residue from the sublimation of NpCl_4 and although X-ray powder diffraction data are available for

NpOBr_2 ⁽⁸⁴⁾ no preparative details are known. The preparation of the tetravalent actinide oxydihalides requires further study, particularly if a general preparative method is to be established. The properties of the oxydihalides are also poorly documented. For example, no structural information is available for these compounds. Few infrared studies have so far been reported and those data available are not wholly consistent. For example, Selbin and Schober⁽⁸⁵⁾ have studied UOCl_2 and its various hydrates and for UOCl_2 , obtained by reaction of UCl_4 with UO_2 , assigned a band at 730cm^{-1} to a U-O-U vibrational mode. Scaife et al.⁽⁸¹⁾ have observed no bands above 600cm^{-1} in the spectrum of ThOI_2 and Prigent⁽⁸⁶⁾ reported two bands at 500cm^{-1} and 546cm^{-1} for UOBr_2 .

Trivalent oxyhalides have not been reported for thorium, protactinium or neptunium. The only trivalent uranium compound is the oxymonochloride⁽⁸⁷⁾ but the oxymonobromide and oxymonoiodide of both uranium and neptunium should be obtainable.

Pentavalent actinide fluorocomplexes

A wide range of actinide halogen complexes are known (see references 35, 39 and 88) but it is beyond the scope of this thesis to comprehensively review them all. The preparation of new pentavalent fluorocomplexes was undertaken as one of the topics for the work for this thesis (see Chapters 3 and 4) so only this class of compound will be discussed.

Fluorocomplexes of the types $\text{M}^{\text{I.V.}}\text{F}_6$, $\text{M}_2^{\text{I.V.}}\text{F}_7$ and $\text{M}_3^{\text{I.V.}}\text{F}_8$ are known only for protactinium and uranium (Table 6). Most pairs of

Table 8

Crystallographic properties of some protactinium (V) and uranium (V) hexafluoro complexes (88)

Compound	Colour	Symmetry	Structure- type or space group	Unit cell dimensions (Å) a_0 b_0 c_0
LiUF ₆	Pale blue	Rhombohedral ^a	LiSbF ₆	5.262 - 14.295
NaPaF ₆	White	Tetragonal	-	5.35 - 3.98
NaUF ₆	Pale blue	Rhombohedral ^a	LiSbF ₆	5.596 - 15.526
NaUF ₆	Pale blue	f.c.c. cubic	NaTaF ₆	8.608 - -
KPaF ₆	White	Orthorhombic	D _{2h} ¹⁸ -Cmca	5.64 11.54 7.98
KUF ₆	Yellow-green	Orthorhombic	D _{2h} ¹⁸ -Cmca	5.61 11.46 7.96
NH ₄ PaF ₆	White	Orthorhombic	D _{2h} ¹⁸ -Cmca	5.84 11.90 8.03
NH ₄ UF ₆	Yellow-green	Orthorhombic	D _{2h} ¹⁸ -Cmca	5.83 11.89 8.03
RbPaF ₆	White	Orthorhombic	D _{2h} ¹⁸ -Cmca	5.86 11.97 8.04
RbUF ₆	Yellow-green	Orthorhombic	D _{2h} ¹⁸ -Cmca	5.82 11.89 8.03
CsPaF ₆	White	Orthorhombic	D _{2h} ¹⁸ -Cmca	6.14 12.56 8.06
CsUF ₆	Pale blue	Rhombohedral ^a	KOsF ₆	8.04 - 8.39

^a Hexagonal cell dimensions are quoted for the rhombohedral complexes.

hexafluoro-protactinates (V) and uranates (V) are isostructural (Table 8). The structure of $\text{RbPaF}_6^{(89)}$, which is typical of a number of the hexafluoro complexes, is currently under investigation. $\text{Rb}_2\text{UF}_7^{(90)}$, which has the K_2TaF_7 structure, is not isostructural with $\text{Rb}_2\text{PaF}_7^{(91)}$. However, the preparative methods were completely different so polymorphism could have occurred. K_2PaF_7 , Rb_2PaF_7 and $(\text{NH}_4)_2\text{PaF}_7$ are isostructural⁽⁹¹⁾ and the structure of $\text{K}_2\text{PaF}_7^{(92)}$ has just been determined. The X-ray powder diffraction data for Cs_2PaF_7 , however, suggest there may be a structural change for the caesium compound.

The first method used for the preparation of $\text{Na}_3\text{UF}_8^{(93)}$ was the oxidation of Na_3UF_7 with fluorine. This method may also be useful for obtaining neptunium (V) and plutonium (V) fluoro complexes from mixtures of NpF_4 or PuF_4 with alkali metal fluorides.

Some pentavalent oxyfluoro complexes are known for the elements from neptunium to americium^(94, 95, 99, 100). These have the general formula $\text{M}^{\text{I}}\text{M}^{\text{V}}\text{O}_2\text{F}_2$ ($\text{M}^{\text{I}} = \text{K}, \text{NH}_4$ and Rb , $\text{M}^{\text{V}} = \text{Np}, \text{Pu}$ and Am). These compounds have received less attention than the fully fluorinated complexes and no fluorides analogous to the known pentavalent oxychloro complexes⁽¹⁰²⁾ $\text{M}_2^{\text{I}}\text{M}^{\text{V}}\text{OCl}_5$ ($\text{M}^{\text{I}} = \text{Cs}$ and Ph_4As , $\text{M}^{\text{V}} = \text{Np}$) and $\text{M}_3^{\text{I}}\text{M}^{\text{V}}\text{O}_2\text{Cl}_4$ ($\text{M}^{\text{I}} = \text{Cs}$, $\text{M}^{\text{V}} = \text{Np}$) are known.

Aims

The choice of topics to be studied was influenced by the work being investigated in Professor Bagnall's group at Harwell. At the start of the work it was decided that three main aspects of the actinide

halides should be studied. These would involve the pentavalent fluoro-complexes, pentavalent and tetravalent oxyhalides and certain structural studies.

The preparation of the fully fluorinated protactinium (V) complexes⁽⁹¹⁾⁽¹⁰⁰⁾ and the structure of K_2PaF_7 ⁽⁹²⁾ had just been completed and to further characterise this group of compounds it seemed worthwhile investigating the structures of Cs_2PaF_7 and Na_3PaF_8 . Since both compounds could be prepared from aqueous solution it was likely that suitable single crystals could be obtained. No fully fluorinated complexes were known for neptunium (V) and fluorine oxidation of Np (IV), in the presence of an alkali metal fluoride, seemed a likely method of achieving a series of compounds analogous to those prepared for protactinium (V) and uranium (V).

$NpO_3 \cdot 2H_2O$ and Np_2O_5 ⁽¹⁰³⁾, which had recently been characterised, appeared to be attractive starting materials for an investigation of the preparation and properties of penta- and hexavalent neptunium oxyfluorides and, possibly, NpF_5 . In addition, since Pa_2OF_8 ⁽⁴⁷⁾ was the only protactinium (V) oxyfluoride known and PaF_5 had only been prepared directly by one method (fluorination of PaF_4), it was decided to investigate the possibility of preparing new pentavalent oxyfluorides and also look at alternative routes to PaF_5 . The possibility of obtaining single crystals of the latter, suitable for structural studies, was also considered.

Protactinium (V) oxychlorides⁽⁷⁵⁾ and oxybromides⁽⁷⁶⁾ had just been

prepared and it was anticipated that similar methods might yield protactinium (V) oxyiodides. Improved preparative methods for PaI_5 were being studied and the preparation of single crystals for X-ray studies might be possible.

There was scope for further work on the actinide (IV) oxydihalides, particularly concerning their infrared spectra and structures and a timely review by Dehnicke⁽¹⁰⁴⁾, together with a later publication on the preparation of CsTaOCl_4 ⁽¹⁰⁵⁾, indicated that it might be possible to develop a general method suitable for the preparation of both tetra- and pentavalent actinide oxyhalides.

Apart from these three main areas of investigation there were some relatively minor topics which were worth looking at. For example, the preparation of NpBr_4 needed further study and, if single crystals were obtained, the structure could be investigated. In addition, NpCl_5 might be obtained using reaction conditions analogous to those used for the preparation of PaCl_5 ⁽⁷⁵⁾.

Chapter 3

EXPERIMENTAL

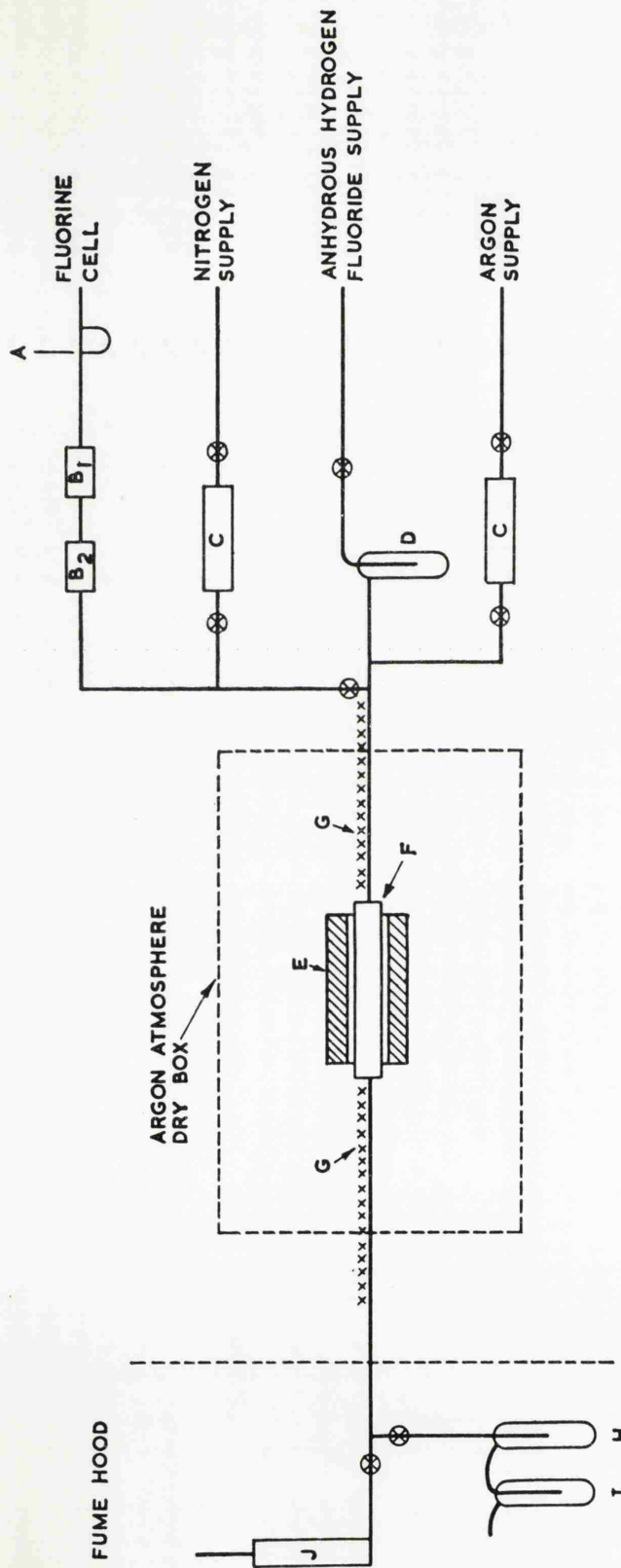
In this chapter the glove box techniques employed during the course of this work are described along with the methods used to collect X-ray and infrared results and the analytical procedures. This is followed by the preparative details for the compounds investigated.

Glove boxes

Most of the experimental work had to be carried out in glove boxes because of the radioactive hazard associated with weighable quantities of protactinium-231 and neptunium-237. Argon atmosphere dry boxes, which were continually flushed with dry argon (3-8 litres/minute when in use and 2 litres at other times) were also used to protect moisture sensitive compounds from atmospheric attack. The box atmospheres were continually monitored for oxygen and water. A small portion of the box atmosphere, removed using a Capex Mk.II diaphragm pump (produced by Charles Austin Pumps Ltd.), was split into two portions, one was bubbled at a constant flow rate (100ml/minute) through a calibrated Hersch cell to determine the oxygen concentration and the other was passed through an Elliot Moisture Meter from which the water content was read directly. Under normal operating conditions the oxygen content was ~ 40 ppm and the water content ~ 50 ppm. The use of phosphorus pentoxide as a dehydrating agent for dry boxes was not satisfactory since a protective film of hydrated oxide prevented further removal of water and, in addition, the disposal of hydrated phosphorus pentoxide from active dry boxes was

Figure 1

Schematic representation of the fluorination and hydrofluorination apparatus



Schematic representation of the fluorination and hydrofluorination apparatus: A, pressure lute; B₁, B₂, sodium fluoride traps; C, molecular sieves; D, Fluorube bubbler; E, furnace; F, nickel furnace tube; G, heating tapes; H, sodium hydroxide bubbler; I, water bubbler; J, fluorine burner

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tedious. Molecular sieves, type 5A, were found to be more effective⁽¹⁰⁶⁾ These were first degassed at 250° in vacuum and then opened up in a dry box and placed in a brass bowl with a gauze base through which the box atmosphere could be circulated using a fan. This method gave quick, efficient desiccation and the molecular sieves were easily regenerated by degassing in a vacuum at 250°.

Two additional special purpose boxes were used for part of the work. One contained a glass vacuum line designed so that controlled amounts of gases could be added to vessels for solid/gas reactions. Moisture or oxygen sensitive compounds were loaded in their reaction vessels in an argon atmosphere dry box and then transferred, joined to a tap with a cone and socket connection, to this box when sealing off was required.

The other box (Figure 1) was used for reactions involving fluorine or hydrogen fluoride. Fluorine, produced from an I.C.I. medium temperature electrolytic cell, was freed from hydrogen fluoride by passing it over a bed of sodium fluoride powder, B₁, then through a tower of sodium fluoride pellets, B₂. A different nickel furnace tube, F, was used for each isotope to prevent cross-contamination. Any unreacted fluorine was converted to carbon fluorides by passing it over a charcoal bed, J, heated to 200°. When the apparatus was used for hydrogen fluoride reactions, the heating tapes, G, on the inlet and outlet pipework were run at 50° to prevent condensation. Unreacted hydrogen fluoride was removed by passing it through water, H, and a sodium hydroxide

solution, I. The apparatus could be flushed with either nitrogen or argon, dried by passing through 5A molecular sieves. Other gas cylinders could be connected to the system so that, for example, reactions with fluorine and oxygen, or, hydrogen and hydrogen fluoride, could be undertaken.

Physical measurements

Infrared spectra The spectra from 4,000 to 600 cm^{-1} were measured using an Infrascan spectrometer and from 660-225 cm^{-1} using a Grubb-Parsons D.M.4 spectrometer.

Either KBr (4,000 to 600 cm^{-1}) or polythene plates (660 to 225 cm^{-1}) were used to contain the mulls, which were 5-10mg of compound in either Nujol or Florube. Alternatively a wax mull⁽¹⁰⁷⁾ pressed between polythene discs was used. A radio frequency heat sealer does not seal polythene but, if P.V.C. is placed either side of two pieces, enough heat is generated to fuse polythene together, without forming a seal with the P.V.C. Radioactive mulls were safely handled by sealing the polythene discs containing wax mulls in outer polythene bags. The wax disc technique had the disadvantage that broad C-H absorption bands, from the wax and polythene, made parts of the spectrum unobtainable. Large interference bands were also observed with the discs mounted flat but these were eliminated by bending the disc to the circumference of a 1cm circle. The advantages of the wax technique are the ability to cover the range from 4,000 to 225 cm^{-1} using one sample and highly moisture sensitive compounds can be examined.

X-ray powder diffraction studies Two techniques were used for the collection of X-ray powder diffraction results. For the Debye-Scherrer 19cm camera finely ground specimens were loaded into silica capillaries, about 100 microns in diameter. If the sample was moisture sensitive the capillary was first flamed out under vacuum to remove traces of moisture.

For the Guinier focusing camera the sample was mounted on a brass ring between two strips of sellotape and a coat of Bostikote applied to the ring to contain the α activity. The sellotape and Bostikote prevent hydrolysis of the sample if it is only slightly moisture sensitive, e.g. PaO_2Br , but this technique cannot be used with very moisture sensitive compounds as the sellotape does contain traces of moisture. An internal standard, such as thoria, was added to the samples. To counteract film shrinkage scales were contact printed on to the films before development. Descriptions of both powder techniques are to be found in the book by Wait and D'Eye⁽¹⁰⁸⁾. All X-ray powder diffraction results were collected using CuK_{α} radiation ($\lambda_{\alpha_1} = 1.54051 \text{ \AA}$).

All cell dimensions were refined, where required, using a computer programme⁽¹⁰⁹⁾ based on the Cohen-Hess method to obtain the best least-squares fit between observed and calculated $\sin^2\theta$ values.

Single crystal studies All the single crystals studied had to be sealed in capillaries since they were either protactinium compounds or were moisture sensitive (or both). The single crystals were obtained

either by sublimation in an evacuated, sealed silica capillary (PaI_5 , TaI_5 and UBr_4) or by crystallisation from aqueous hydrofluoric acid (Na_3PaF_8 and Cs_2PaF_7). The crystals were examined under a polarising microscope, where possible, to determine whether or not they were single.

They were lined up using a Charles Supper Buerger precession camera, model E, following which various layers were examined about two crystallographic axes. The results provided information on the cell dimensions, symmetry and space group. The crystal was transferred to a Unicam single crystal goniometer (S25) and, using either filtered CuK_α or MoK_α radiation, results for intensity measurements were collected using the Weissenberg method. Intensities were visually estimated using scales prepared by photographing a suitable reflection from the crystal being studied.

Analytical procedures

Determination of thorium (IV), protactinium (IV) and (V) and uranium (IV) For this determination 50-200mg of compound was hydrolysed with aqueous ammonia. The gelatinous hydrous oxide was filtered through a weighed, silica filter crucible and washed well with water. Gentle heating to 100° dried the precipitate which was then heated to 700° for 30 minutes. The metal content was determined assuming the composition of the resulting oxide to be ThO_2 , Pa_2O_5 or U_3O_8 .

Determination of neptunium (IV) in the absence of fluoride Neptunium (IV) hydrous oxide, precipitated with aqueous ammonia, was

dissolved in a known volume of molar A.R. nitric acid. Suitable aliquots of this solution were mounted on stainless steel trays and the neptunium content determined by α assay. ^{237}Np , specific activity $1.562 \times 10^6 \alpha$ disintegrations $\text{min}^{-1} \text{mg}^{-1}$ (110), was used throughout this study.

Determination of fluoride Protactinium compounds were hydrolysed using dilute aqueous ammonia and the fluoride was determined, after removal of the protactinium (V) hydrous oxide, using the lead chlorofluoride method⁽¹¹¹⁾.

However, hydrolysis of neptunium (V) fluoro compounds with aqueous ammonia always resulted in some disproportionation and irreproducible results were obtained using the lead chlorofluoride technique. It was found that the colorimetric method of Belcher and West⁽¹¹²⁾ could be used without separation of the neptunium, provided the neptunium was in the hexavalent state.

A suspension of the neptunium (V) compounds (20-50mg) was ozonised in the minimum volume of dilute nitric acid (0.01M) until dissolution was complete. The excess ozone was removed by purging the solution with nitrogen and the solution was made up to a known volume. Neptunium (VI) compounds were soluble and so were dissolved directly in the dilute nitric acid. The fluoride was determined according to the published method⁽¹¹²⁾ taking suitable aliquots of the stock solutions (10-70 μgF^- was the concentration range studied) and using matched 4cm quartz cells. The calibration point used was 620m μ and, for each

solution, the spectrum was scanned from 550 μ to 650 μ using an Optika CF4/DR direct recording spectrometer.

Determination of chloride, bromide and iodide Halide, present in the supernatants from the metal assays, was determined⁽¹¹¹⁾ by direct titration against standard silver nitrate solution or gravimetrically as the silver salt.

To prevent loss of halide during hydrolysis, where the reaction was particularly vigorous, the compounds were cooled momentarily in liquid nitrogen before addition of the aqueous ammonia. The hydrolysis proceeded slowly and smoothly as the mixture warmed to room temperature.

Determination of the oxidation state of the neptunium compounds Neptunium (IV) and (V) give several characteristic peaks between 350 μ and 1000 μ ⁽¹¹³⁾. The two peaks selected for each oxidation state (Table 9) obeyed Beer's Law for the concentration range studied (0.5 to 5mg/ml). Np (VI), however, has only two weak, broad peaks in this region, at 476 μ and 557 μ , and its presence is usually indicated by the tail of its charge transfer band, which extends into the 350 μ -400 μ range. The most satisfactory method of estimating the amount of Np (VI) present⁽¹⁰³⁾ was to quantitatively reduce it to Np (V) with sodium nitrite and measure the increase in height of the Np (V) peak.

Table 9

Some characteristic Np (IV) and Np (V) absorption peaks
(in 1M HClO_4 or 1M HNO_3)

	peak position (m μ)	molar extinction coefficient
Np (IV)	725	145
	960	185
Np (V)	617	20
	970	295

Since it was not always possible to dissolve neptunium compounds in molar perchloric acid, molar nitric acid was also used. Np (VI), Np (V) and Np (IV) are all stable in this solvent provided all traces of NO_2 have been removed by boiling. The neptunium (V) fluorocomplexes and oxyfluorides were only soluble in molar perchloric or nitric acid in the presence of 0.2M boric acid. Fortunately the stability of the various oxidation states was unaffected by the presence of boric acid.

Spectra were measured between 350m μ and 1000m μ using an Optika CF4/DR direct recording spectrometer with matched 1cm quartz cells. The solutions contained approximately 2mg Np per ml.

Reagents

The actinide tetrachlorides^(102, 114, 115) (Th to Np inclusive), tetrabromides^(115, 116) (Th to U inclusive), thorium tetraiodide⁽¹¹⁷⁾, neptunium trioxide monohydrate⁽¹⁰³⁾, neptunium pentoxide⁽¹⁰³⁾,

$\text{Cs}_2\text{NpOCl}_5$ (102), $\text{Cs}_3\text{NpO}_2\text{Cl}_4$ (102), $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ (102), uranyl fluoride (118), uranyl fluoride dihydrate (119), tantalum penta iodide (59), Cs_2PaF_7 (91), Na_3PaF_8 (100), protactinium (V) oxychlorides (75) and oxybromides (76) and protactinium penta iodide (120) were prepared by published methods.

NpO_2 was obtained by thermal decomposition of a sample of NpOCl_2 above 600° . Neptunium and protactinium metals were kindly supplied by Mr. J. A. C. Marples (Ceramics Division, A.E.R.E.).

Fluorine was generated using an I.C.I. medium temperature fluorine cell, 10 amp model. Hydrogen fluoride was removed by passing the fluorine through sodium fluoride pellets. High purity hydrogen fluoride (supplied by I.C.I.), suitable for recharging the fluorine cell, was used for the hydrofluorination experiments.

Other reagents were commercially available and fine or analytical grade materials were used where possible.

Preparative methods

Preparation of the actinide (IV) oxyhalides and halides Two main methods have been used for the preparation of actinide (IV) oxyhalides. The new method involves reaction between antimony sesquioxide, Sb_2O_3 , and an actinide tetrahalide in a sealed evacuated vessel at $\sim 200^\circ$. Compounds of the types ThOX_2 , X = F, Cl, Br and I, UOX_2 , X = Cl and Br, and NpOX_2 , X = Cl and Br, were prepared by this method. The previously known method (79-82) involving the reaction between an actinide dioxide and tetrahalide in a sealed vessel at 500° was also used for the preparation of UOCl_2 , NpOCl_2 and NpOBr_2 so that the infrared and X-ray

results for compounds prepared by the Sb_2O_3 method could be checked. Despite much work the only actinide (IV) oxydifluoride obtained was $ThOF_2$.

Preparation of actinide (IV) oxydihalides using antimony sesquioxide 50 to 200mg of actinide tetrahalide was thoroughly ground, in an argon atmosphere dry box, with the stoichiometric amount of antimony sesquioxide required by the equation:-



The mixture was sealed in a pyrex reaction vessel, evacuated to 10^{-3} torr, and heated at 150° - 200° (300° in the case of the $ThOF_2$ preparation). At this temperature the antimony trihalide so formed sublimed off leaving the non-volatile actinide oxydihalide, which was further heated at 400° for 6 hours to improve crystallinity. The reaction between UF_4 and Sb_2O_3 yielded only UO_2 and UF_4 even at 200° .

The analytical results are listed in Table 10.

Preparation of actinide (IV) oxydihalides from actinide dioxide and tetrahalide 50 to 200mg of actinide tetrahalide was carefully ground, in an argon atmosphere dry box, with the stoichiometric amount of the appropriate actinide dioxide required by the reaction:-

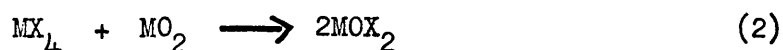


Table 10

Analytical results for the actinide (IV) oxydihalides

	Found %		Required %	
	M	X	M	X
ThOCl ₂	72.61	22.25	72.75	22.23
PaOCl ₂	72.15	22.07	72.66	22.30
UOCl ₂	73.38	21.71	73.25	21.82
NpOCl ₂	72.96	21.62	73.17	21.88
ThOBr ₂	56.81	38.89	56.86	39.22
PaOBr ₂	56.81	39.21	56.76	39.31
UOBr ₂	57.18	38.67	57.49	38.65
NpOBr ₂	56.81	38.69	57.38	38.74
ThOI ₂	46.41	50.41	46.21	50.60

The mixture was sealed in a silica reaction tube, evacuated to 10^{-3} torr and heated for several hours at 500° . Analytical results are listed in Table 10.

$\text{PaF}_4/\text{PaO}_2$ and UF_4/UO_2 mixtures both failed to react under these conditions.

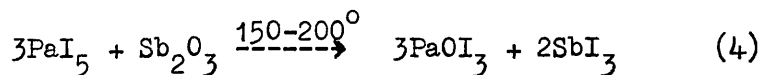
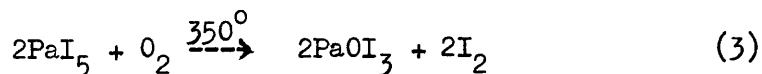
Preparation of neptunium tetrabromide 100mg of neptunium metal, in the form of wire, was placed in a silica reaction vessel with a side-arm similar to that described elsewhere⁽⁷⁶⁾. 1-2ml of bromine was placed in the side-arm and degassed under vacuum using a freezing and melting technique. After several degassings the silica tube was evacuated to 10^{-3} torr with the bromine frozen, sealed off and heated at 400° for several hours. The NpBr_4 sublimed to cooler parts of the apparatus as it formed. When the reaction was complete the remaining bromine was condensed in the side-arm, which was then sealed off.

Preliminary reactions at higher temperatures (up to 600°) resulted in the formation of a mixture of NpBr_3 and NpBr_4 .

Preparation of actinide (V) oxyhalides and PaF_5 hydrates New protactinium (V) oxyiodides, PaOI_3 and PaO_2I , and neptunium (V) oxyfluorides, NpOF_3 and ' NpO_2F ', have been prepared. Attempts to prepare new protactinium (V) oxyfluorides were unsuccessful but new preparative methods have been established for Pa_2OF_8 and the previously unknown monohydrate $\text{PaF}_5 \cdot \text{H}_2\text{O}$ has been characterised.

Protactinium (V) oxytriiodide, PaOI_3 In a typical experiment PaI_5 (50mg) was placed in a pyrex reaction vessel of known volume

and a slight deficiency of oxygen for reaction 3 was admitted. The reaction vessel was sealed and totally enclosed in a furnace at 300-350° for several hours. The temperature was raised to 400° and the tube partially withdrawn to allow the excess protactinium pentaiodide to sublime leaving the non-volatile, dark brown, PaOI₃.



Alternatively, PaI₅ (50mg) was intimately mixed with the stoichiometric amount of Sb₂O₃ required for reaction 4. The mixture was sealed in an evacuated pyrex reaction vessel (10⁻³ torr) and heated at 150-200°. SbI₃ rapidly sublimed leaving the oxytriiodide, which was then heated for several hours at 400° to increase crystallinity. Both preparations gave products with virtually identical analyses (Table 11).

Protactinium (V) dioxyiodide, PaO₂I PaOI₃ (50mg) sealed in an evacuated pyrex vessel (10⁻⁴ torr), was heated at 450°. During the disproportionation (reaction 5) the resulting PaI₅ sublimed to cooler parts of the reaction vessel leaving a residue of the non-volatile, chocolate coloured PaO₂I.

Table 11

Analytical results for actinide (V) and (VI) oxyhalides
and protactinium pentafluoride hydrates

Compound	Colour	Required (%)		Found (%)	
		M	X	M	X
Pa_2OF_8	white	73.33	24.13	72.8	25.0
$\text{PaF}_5 \cdot 2\text{H}_2\text{O}$	white	63.81	26.24	63.2	26.9
$\text{PaF}_5 \cdot \text{H}_2\text{O}$	white	67.15	27.62	66.5	28.4
PaOI_3	dark brown	36.78	60.67	36.8	60.5
PaO_2I	dark brown	61.76	33.96	61.2	34.1
$\text{NpOF}_3 \cdot 1.5\text{H}_2\text{O}$	blue-green	70.4	16.95	70.4	16.3
NpOF_3	blue-green	76.5	18.4	75.9	17.7
' NpO_2F '	light green	82.8	6.6	79.6	6.9 ^a
				77.8	7.4 ^b
				78.8	8.8 ^c
				80.2	9.3 ^d
NpO_2F_2	pink	77.2	12.38	77.0	12.4

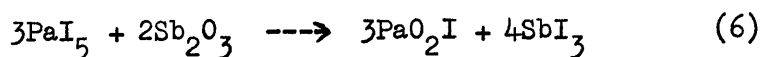
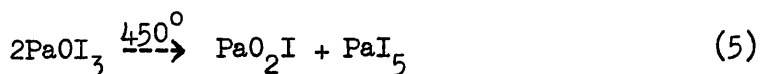
M = metal X = halogen

^a reaction time 5 days temperature 325°C

^b reaction time 5 days temperature 325°C

^c reaction time 2 days temperature 350°C

^d reaction time 2 days temperature 350°C



Reaction between the stoichiometric amounts of PaI_5 and Sb_2O_3 (reaction 6), as described for PaOI_3 , provided an alternative method of preparation. Samples from both preparations gave almost identical analytical results (Table 11).

Neptunium (V) oxytrifluoride hydrate, $\text{NpOF}_3 \cdot 1.5\text{H}_2\text{O}$ Np_2O_5 (0.1g), contained in a platinum boat, was heated at 40° in gaseous, anhydrous hydrogen fluoride. After 3-4 hours the hydrogen fluoride flow was shut off and the apparatus purged with dry, high purity argon. The blue-green product had a composition close to $\text{NpOF}_3 \cdot 1.5\text{H}_2\text{O}$ (Table 11).

Neptunium (V) oxytrifluoride, NpOF_3 The above hydrate, when heated at $150-200^\circ$ in a stream of anhydrous hydrogen fluoride, was converted to the blue-green NpOF_3 . Above 200° some reduction to NpF_4 occurred. Fluorine was not an effective dehydrating agent below 180° and above this temperature oxidation took place. Analytical results are listed in Table 11.

Neptunium (V) dioxydifluoride, NpO_2F_2 In a typical reaction NpO_2F_2 (0.108g) was heated at 325° with the stoichiometric amount of hydrogen to remove one fluorine atom (12.5cm Hg at 25°) in a vessel of known volume (24cc) for 5 to 6 days. During this time the initial pink solid (NpO_2F_2) gradually changed to pale green. Above

350° the product was extensively contaminated with NpO_2 .

UO_2F_2 underwent a similar reaction but the product gave irreproducible analytical results.

Protactinium pentafluoride dihydrate, $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ 0.1g of vacuum dried protactinium (V) hydrous oxide was treated in a platinum boat with anhydrous, gaseous hydrogen fluoride at room temperature. The deliquescent white product was identified analytically as $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ (Table 11).

The previously reported method^(47, 121) for the preparation of $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ was found to yield a mixture of $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$, $\text{PaF}_5 \cdot \text{H}_2\text{O}$ and Pa_2OF_8 .

Protactinium pentafluoride monohydrate, $\text{PaF}_5 \cdot \text{H}_2\text{O}$ 0.1g of $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ was heated in a stream of anhydrous hydrogen fluoride at 40°-60°. The product was identified analytically as $\text{PaF}_5 \cdot \text{H}_2\text{O}$ (Table 11).

Diprotactinium oxyoctafluoride, Pa_2OF_8 The numerous attempts to prepare new protactinium (V) oxyfluorides (discussed later) all resulted in the formation of Pa_2OF_8 . For example, it was obtained when $\text{PaF}_5 \cdot \text{H}_2\text{O}$ (0.1g) was heated in gaseous hydrogen fluoride at 140° for 2 hours or treated with fluorine at room temperature, when the hydrous oxide was heated in hydrogen fluoride at 140°-350° and when PaOBr_3 , or PaO_2Br , was treated with fluorine at room temperature. The vacuum evaporation of a hydrofluoric acid solution of Pa (V) (0.1g in 2ml) initially yielded a mixture of $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$,

$\text{PaF}_5 \cdot \text{H}_2\text{O}$ and Pa_2OF_8 (identified crystallographically). Pumping the solid for 2-3 days produced pure Pa_2OF_8 . Typical analyses are given in Table 11.

The preparation of neptunyl fluoride, NpO_2F_2 Pure NpO_2F_2 has been prepared for the first time by a variety of methods. Neptunium pentoxide (0.1g) and neptunium oxytrifluoride hydrate were oxidised to NpO_2F_2 by fluorine at 330° and bromine trifluoride converted $\text{NpO}_3 \cdot \text{H}_2\text{O}$ to NpO_2F_2 at room temperature. The most convenient methods of preparation are the reaction between $\text{NpO}_3 \cdot \text{H}_2\text{O}$ and anhydrous, gaseous hydrogen fluoride or fluorine, and the reaction between $\text{NpO}_3 \cdot \text{H}_2\text{O}$ and aqueous hydrofluoric acid. Typical analyses are given in Table 11.

Anhydrous NpO_2F_2 from aqueous solution $\text{NpO}_3 \cdot \text{H}_2\text{O}$ (0.5g) was dissolved in molar hydrofluoric acid and the resulting grey-green solution evaporated to dryness under vacuum to yield a pink solid. The final traces of water were removed by vacuum drying the product at room temperature for 8-12 hours (10^{-3} torr).

Anhydrous NpO_2F_2 from dry reactions $\text{NpO}_3 \cdot \text{H}_2\text{O}$ (0.5g) was heated at 225° for 4 hours in a flow of either anhydrous hydrogen fluoride or fluorine. In both cases the reaction tube was cooled to room temperature before the fluorinating gases were flushed out with high purity argon.

The preparation of fully fluorinated actinide (V) complexes Only two new neptunium (V) complexes have been prepared pure, these are

Na_3NpF_8 and Rb_3NpF_8 . Identical preparative methods were used.

NpF_4 (50mg) was ground with 3 moles of either NaF or RbF and the mixture, in a nickel boat, was heated at 300° - 400° for 2-8 hours in fluorine.

Alternatively, the required amounts of NpO_2 and alkali metal fluoride were dissolved in nitric acid containing a little hydrofluoric acid and the solution evaporated to dryness. The solid product was heated, in a nickel boat, at 300° - 400° for 2-8 hours in fluorine. In each case the products were identified crystallographically and shown spectrophotometrically to contain only neptunium (V).

Chapter 4

RESULTS AND DISCUSSION

Actinide Oxyhalides

With the exception of the oxyfluorides, antimony sesquioxide has proved useful for preparing actinide (IV) and (V) oxyhalides. Previously the preparation of certain thorium (IV) and uranium (IV) oxydihalides, MOX_2 (M = Th, X = F, Cl, Br and I; M = U, X = Cl and Br) had involved either the reaction between an 'active' dioxide and a tetrahalide^(79, 80) or the thermal decomposition of a tetrahalide hydrate⁽⁷⁷⁾. The reaction between Sb_2O_3 and actinide tetrahalides, however, has the advantages of a low reaction temperature and easy removal of the antimony trihalides from the reaction zone by sublimation. In addition no reactive reagents need to be prepared.

The known protactinium (V) oxyhalides and uranium (V) oxytrichloride have previously been obtained as reaction by-products^(75, 76, 122) during the preparation of the pentahalides. UOCl_3 ⁽¹²³⁾ can be prepared by heating together a 1:1 mixture of UCl_4 and UO_2Cl_2 but this method cannot be applied to the preparation of pentavalent protactinium or neptunium oxyhalides. Protactinium (V) oxychlorides and oxybromides have also previously been prepared directly, by reacting the pentahalides with oxygen. PaOBr_3 and some new protactinium (V) oxyiodides have now been prepared by the reaction between Sb_2O_3 and the appropriate pentahalide. This is a better method since lower reaction temperatures are required and the solid/gas reactions are less convenient.

The Sb_2O_3 /pentahalide reaction was not used for the attempted preparation of protactinium (V) and neptunium (V) oxyfluorides since PaF_5 is difficult to prepare and NpF_5 has yet to be reported. The reactions of Pa_2O_5 and Np_2O_5 with gaseous, anhydrous hydrogen fluoride produced the previously known⁽⁴⁷⁾ Pa_2OF_8 and the new neptunium (V) oxyfluoride, NpOF_3 , respectively. The new protactinium pentafluoride hydrate, $\text{PaF}_5 \cdot \text{H}_2\text{O}$ and the previously reported^(47, 121) $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ have also been prepared by reactions involving protactinium (V) oxide and gaseous hydrogen fluoride. NpO_2F_2 has been prepared pure for the first time by a number of different methods and hydrogen reduction of NpO_2F_2 has produced another new neptunium (V) oxyfluoride, ' NpO_2F '.

Several unsuccessful attempts have been made to prepare new protactinium (V) oxyfluorides by a variety of halogen exchange reactions.

Actinide (IV) oxydichlorides, oxydibromides and oxydiiodides

The tetrahalides, MX_4 , (M = Th with X = F, Cl, Br and I; M = Pa with X = Cl and Br; M = U with X = Cl and Br, and M = Np with X = Cl and Br), react with Sb_2O_3 at 150° - 200° in a vacuum and crystalline samples of the oxydihalides are obtained by heating the non-volatile residue at 450° . A few oxydihalides have also been prepared by the actinide tetrahalide/actinide dioxide reaction, so that crystallographic and infrared results could be checked. Neptunium (IV) oxydichloride has also been obtained from the reaction between thionyl chloride and neptunium (V) hydrous oxide at about 200° (higher temperatures caused further chlorination and neptunium tetrachloride was the major product) in an apparatus similar to that used to prepare

protactinium pentachloride.⁽⁷⁵⁾ This reaction was an unsuccessful attempt to prepare neptunium pentachloride or a neptunium (V) oxychloride.

In order to study the preparation and properties of NpOBr_2 in this general study of the actinide (IV) oxydihalides, it was necessary to improve the preparative method for NpBr_4 . The previous method of preparation⁽⁴⁹⁾, the reaction between neptunium dioxide and aluminium bromide at 350° , resulted in extensive decomposition to NpBr_3 . The search for an improved method of preparing NpBr_4 was greatly aided by the availability of neptunium metal prepared by Mr. J. A. C. Marples, Metallurgy division at Harwell. The reaction between the metal and bromine vapour proceeds smoothly at 400° with complete conversion to NpBr_4 . The partial X-ray powder diffraction results, together with visually estimated intensities, are listed in Table 12. These have been interpreted on the basis of a monoclinic cell, isostructural with UBr_4 , having $a_0 = 10.89 \pm 0.02$, $b_0 = 8.74 \pm 0.02$, $c_0 = 7.06 \pm 0.01 \text{ \AA}$ and $\beta = 94.19^\circ \pm 0.06$. These cell dimensions are almost identical to those for UBr_4 and do not show the expected contraction. This is probably because insufficient high angle lines, which show the effect of small changes in cell dimensions most markedly, were present on the films.

Crystallographic properties The actinide (IV) oxydichlorides form an isostructural series of compounds for which X-ray powder diffraction results have been interpreted on the basis of the orthorhombic unit cell, space group Pbam , reported for PaOCl_2 ⁽¹²⁴⁾ whilst this work

Table 12

Partial X-ray powder diffraction results for NpBr_4

$\text{Sin}^2\theta_{\text{obs}}$	$\text{Sin}^2\theta_{\text{calc}}$	h,k,l	I^*
0.0120	0.0116	0,0,1	s
0.0198	0.0197	2,0,0	m
0.0257	0.0254	1,1,1	m-
0.0293	0.0293	2,0, $\bar{1}$	m+
0.0307	0.0305	0,2,0	s-
0.0503	0.0505	2,2,0	w
0.0628	0.0628	2,0, $\bar{2}$	s-
0.0646	0.0647	2,2,1	m+
0.0675	0.0677	3,1,1	s
0.0739	0.0741	1,3,0	m-
0.0872	0.0871	4,0, $\bar{1}$	m
0.0931	0.0934	3,1, $\bar{2}$	dw+
0.1068	0.1069	3,1,2	m
0.1099	0.1109	4,2,0	w
0.1136	0.1146	3,3,0	w
0.1170	0.1165	1,1, $\bar{3}$	m
0.1199	{0.1197 0.1203}	{1,3, $\bar{2}$ 2,0, $\bar{3}$ }	w
0.1230	{0.1229 0.1232}	{3,3, $\bar{1}$ 1,1, $\bar{3}$ }	dm+
0.1368	0.1366	4,0,2	m
0.1514	0.1513	2,2, $\bar{3}$	dw

*Visually estimated.

was in progress. The cell parameters, which are listed in Table 13, show the effect of the actinide contraction, decreasing with increasing atomic number. Smith et al. used the X-ray powder diffraction data of Brown and Jones⁽¹¹⁵⁾ to confirm that crystals of PaOCl₂ had been obtained during an attempted preparation of PaCl₄ and these crystals were used in the determination of the recently published⁽¹²⁴⁾ structure. The X-ray diffraction results obtained for UOCl₂ are identical, with those reported by

Table 13

Unit cell dimensions for the actinide (IV) oxydichlorides*

	Lattice parameters (Å)		
	a _o	b _o	c _o
ThOCl ₂	15.494	18.095	4.078
PaOCl ₂	15.332	17.903	4.012
UOCl ₂	15.255	17.828	3.992
NpOCl ₂	15.209	17.670	3.948
standard deviation	<u>+0.008</u>	<u>+0.008</u>	<u>+0.002</u>

*All possess orthorhombic symmetry, space group Pbam.

Dunn⁽¹²⁵⁾. The actinide (IV) oxydibromides also form an isostructural series. Their X-ray powder diffraction results suggest that they possess low symmetry and no interpretation has been made. Typical, partial X-ray powder diffraction results, for NpOCl₂ and NpOBr₂, are listed, together with visually estimated intensities, in Tables 14 and 15

Table 14
Partial X-ray powder diffraction results for NpOCl₂

$\text{Sin}^2_{\text{obs}} \theta$	$\text{Sin}^2_{\text{calc}} \theta$	h,k,l	I_a^*	$\text{Sin}^2_{\text{obs}} \theta$	$\text{Sin}^2_{\text{calc}} \theta$	h,k,l	I_a^*
0.0076	0.0077	0,2,0	w	0.0790	0.0793	4,0,1	w+
0.0102	{ 0.0103 0.0104	1,2,0 2,0,0	s	0.0813	{ 0.0812 0.0814	4,1,1 5,3,0	m-
0.0197	0.0198	1,3,0	w	0.0869	0.0869	4,2,1	w
0.0274	0.0275	2,3,0	w	0.0886	{ 0.0883 0.0887	1,5,1 4,5,0	w+
0.0304	0.0306	0,4,0	w+				
0.0383	0.0382	0,0,1	w	0.0918	{ 0.0917 0.0916	3,4,1 3,6,0	w-
0.0402	0.0404	3,3,0	w+				
0.0405	0.0408	2,4,0	w	0.0922	0.0925	6,0,0	w-
0.0425	0.0427	1,1,1	w-	0.0947	{ 0.0944 0.0947	6,1,0 5,4,0	w
0.0455	0.0458	0,2,1	w-				
0.0487	{ 0.0488 0.0485 0.0484	4,2,0 1,2,1 2,0,1	w+	0.0999 0.1037 0.1044	0.1000 0.1035 0.1042	6,2,0 2,7,0 5,1,1	w w w
0.0503	0.0504	1,5,0	m	0.1067	0.1066	0,6,1	w
0.0504	0.0502	2,1,1	m	0.1091	{ 0.1092 0.1088	1,6,1 3,5,1	w
0.0579	{ 0.0579 0.0579 0.0583	2,5,0 1,3,1 4,3,0	w	0.1098	{ 0.1099 0.1096 0.1096	5,2,1 4,4,1 4,6,0	w
0.0633	0.0632	3,1,1	w				
0.0657	0.0656	2,3,1	vw				
0.0685	{ 0.0686 0.0686	0,4,1 0,6,0	w+	0.1194 0.1243	0.1194 0.1243	5,3,1 1,8,0	w- w
0.0692	0.0689	3,2,1	vw	0.1267	0.1267	4,5,1	w-
0.0711	{ 0.0712 0.0711 0.0708	1,4,1 1,6,0 3,5,0	w+	0.1326	{ 0.1324 0.1326 0.1327	6,1,1 5,6,0 5,4,1	vw

I_a^* visually estimated intensities. s, strong; m, medium; w, weak.

Table 15

Partial X-ray powder diffraction results for NpOBr₂

$\text{Sin}^2\theta_{\text{obs}}$	I*	$\text{Sin}^2\theta_{\text{obs}}$	I*
0.0094	s+	0.0858	m
0.0178	w	0.0910	m
0.0247	w	0.0930	m
0.0273	w	0.0971	w
0.0366	s	0.0985	w+
0.0443	w+	0.1010	w
0.0462	w	0.1025	w+
0.0482	m+	0.1049	w-
0.0521	w	0.1116	w+
0.0546	w+	0.1172	w
0.0600	w-	0.1274	w-
0.0614	w-	0.1307	w-
0.0642	w	0.1361	w
0.0665	m+	0.1421	w-
0.0737	m+	0.1482	s-
0.0762	m+	0.1572	w
0.0802	m+	0.1675	w
0.0813	m+		

respectively. The unit cell dimensions (Table 13) for each of the actinide (IV) oxydichlorides were obtained by least squares refinement of over 100 individual reflections.

Infrared spectra Selbin and Schober⁽⁸⁵⁾ have reported the infrared spectra of various hydrated uranium (IV) hydroxychlorides and of the compound, $\text{UO}_{1.15}\text{Cl}_{2.1}$, obtained by thermally decomposing the hydrates. This last compound gave medium intensity bands at 736cm^{-1} and 719cm^{-1} , which were assigned to O-U-O modes, strong bands at 555cm^{-1} and 515cm^{-1} (also present in similar positions in the various hydrates), which were assigned to U-O stretching vibrations and bands showing that traces of OH^- and H_2O were present. Selbin and Schober also prepared UOCl_2 from UO_2 and UCl_4 at 700° and reported a band at 730cm^{-1} . The only other available infrared data for the actinide (IV) oxyhalides have been reported by Prigent⁽⁸⁶⁾, who found two bands for UOBr_2 , one strong and broad at 500cm^{-1} and the other a shoulder at 546cm^{-1} , and by Scaife et al.⁽⁸¹⁾, who found no bands above 600cm^{-1} for ThOI_2 .

In this work no actinide (IV) oxydihalide has been found to give absorption bands in the region of 730cm^{-1} (Table 16) and samples of UOCl_2 and NpOCl_2 prepared from the tetrahalide by both the Sb_2O_3 and the dioxide method give no bands above 600cm^{-1} . The oxydichloride and oxydibromide spectra (Th to Np inclusive) are very similar between 600cm^{-1} and 225cm^{-1} . Small shifts in band positions (to longer wavelength) occur with increasing atomic number and certain oxydichlorides have two extra weak bands around 290cm^{-1} and 280cm^{-1} , which are

Table 16

Metal-oxygen and metal-halogen stretching vibrations in the infrared spectra of actinide (IV) oxydihalides

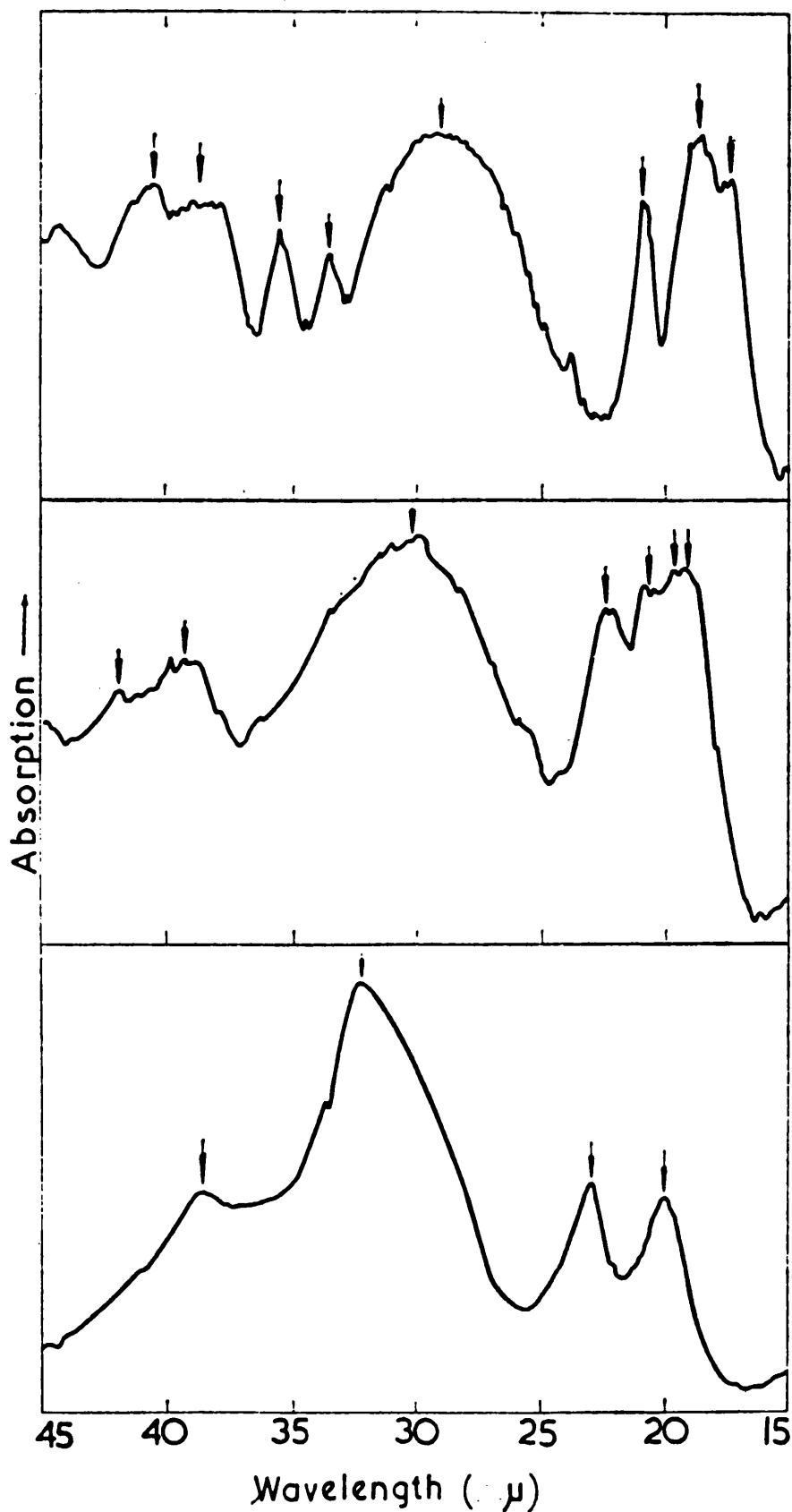
Compound	Colour	$\nu_{\text{M-O}} (\text{cm}^{-1})$	$\nu_{\text{M-X}} (\text{cm}^{-1})$
ThOF ₂ *	White	541m, 377s,b, 330w, 307w	
ThOCl ₂	White	571sh, 540s, 481s, 344s,b, 259m, 246m	298w, 282w
PaOCl ₂	Yellow-green	555sh, 523, 471s, 327s, 256sh, 243m	290w, 278w
UOCl ₂	Green	555sh, 521s, 455m, 300s,b, 259m, 242m	
NpOCl ₂	Light brown	555s, 529s, 460m, 335s,b, 255m, 240m	306w
ThOBr ₂	White	543s, 529s, 495s, 463s, 333s,b, 256m, 243vw	
PaOBr ₂	Orange	546sh, 518s, 495s, 446s, 319s,b, 259m, 240vw	
UOBr ₂	Pale green	538sh, 505s, 429s, 294s,b, 253w	
NpOBr ₂	Orange	540sh, 500s, 424s,b, 315s,b, 258w	
ThOI ₂	White	500m, 444m, 325s,b	
PaOI ₂	Burgundy	459m, 434m, 303s,b	

s-strong; sh-shoulder; m-medium; w-weak; b-broad.

*the stretching vibrations are unassigned.

Figure 2

Infrared spectra of ThOCl_2 , ThOBr_2 and PaOI_2



Infrared spectra of, from top to bottom, ThOCl_2 , ThOBr_2 , and PaOI_2

8

A.E.R.E. HARWELL
PHOTOGRAPHIC GROUP
Neg. No. H63417

tentatively assigned to metal-chlorine stretching vibrations. The absence of these weak bands in the spectrum of UOCl_2 may be due to masking by the strong, broad band at around 300cm^{-1} , which occurs in all the oxydichloride spectra. Certain spectra are illustrated in Figure 2 and band positions are given in Table 16. There is a large difference in the positions of M-Cl and M-Br vibrational frequencies (about 260cm^{-1} and 180cm^{-1} , respectively) in the spectra of the actinide (IV) hexahalogeno-complexes and, therefore, the two weak bands discussed above would seem to be the only ones likely to be associated with metal-halogen vibrations. The close similarity of all the remaining peaks in the spectra of the oxydichlorides, oxydibromides and oxydiiodides (ThOI_2 and PaOI_2) suggests that these bands should be assigned to metal-oxygen vibrations.

The recent structural determination of PaOCl_2 has shown that each protactinium is co-ordinated to either three or four oxygens and, therefore, the above infrared results show that all the actinide (IV) compounds of the type MOX_2 do not contain discrete MO^{2+} groups.

The band observed by Selbin and Schober at 730cm^{-1} for anhydrous UOCl_2 is not compatible with these results. Unfortunately no X-ray powder diffraction data were given by these authors so no direct deductions can be made. It is possible, however, that the UO_2 used by them was contaminated with U_3O_8 and some uranium (V) oxytrichloride was obtained. The spectrum of a sample of UOCl_3 prepared in this laboratory by reacting uranyl chloride with uranium tetrachloride showed a strong

band around 730cm^{-1} . All the compounds described here were perfectly anhydrous, no bands being observed around $3,400\text{cm}^{-1}$ (OH stretching vibration) or around $1,600\text{cm}^{-1}$ (H_2O wagging mode) so that the bands observed around 500cm^{-1} are not due to $(\text{U-O})_{\text{OH}}$ modes.

Chemical properties The oxydihalides are less moisture sensitive than the tetrahalides and are sufficiently stable in contact with sellotape to allow the Guinier method to be used for the collection of X-ray powder diffraction results. Only PaOCl_2 showed signs of slight decomposition. The oxydihalides are rapidly hydrolysed by dilute aqueous ammonia. They are soluble in mineral acids but insoluble in organic solvents such as benzene, isopentane, carbon tetrachloride, chloroform, methyl cyanide, methylene dichloride and nitromethane.

NpOCl_2 is thermally unstable with respect to the tetrahalide and dioxide above 600° . This disproportionation reaction is characteristic of the actinide (IV) oxydihalides apart from ThOF_2 (39).

Actinide (IV) oxydifluorides

A number of different methods have been used in attempts to prepare compounds of the type MOF_2 . However, only the previously known ThOF_2 (77, 78) has been obtained.

ThOF_2 has been prepared by the reaction between ThF_4 and ThO_2 at 900° . UO_2/UF_4 and $\text{PaO}_2/\text{PaF}_4$ mixtures have been heated to 700° and 450° respectively without reaction taking place. The reaction between Sb_2O_3 and the appropriate tetrafluoride has also been tried. Sb_2O_3 and ThF_4 reacted at 300° in a vacuum to produce ThOF_2 , which was

identified crystallographically. The analogous reaction between Sb_2O_3 and UF_4 produced a mixture of UF_4 and UO_2 .

Another possible route to the oxydifluorides which was investigated involved the reaction between antimony trifluoride and one of the other oxydihalides. ThOF_2 was formed by the reaction between ThOCl_2 and SbF_3 at 200° but the product of the $\text{UOCl}_2/\text{SbF}_3$ reaction was shown by X-ray powder diffraction analysis to again be a mixture of UO_2 and UF_4 .

Arsenic trifluoride converted protactinium (V) oxyhalides to Pa_2OF_8 (see later) but it did not react with ThOBr_2 or UOCl_2 at room temperature.

Two reports^(126, 127) on the preparation of UOF_2 have appeared recently. One states that the compound is black, the other states it is green. Neither paper gives sufficient detail for the reliability of the work to be assessed.

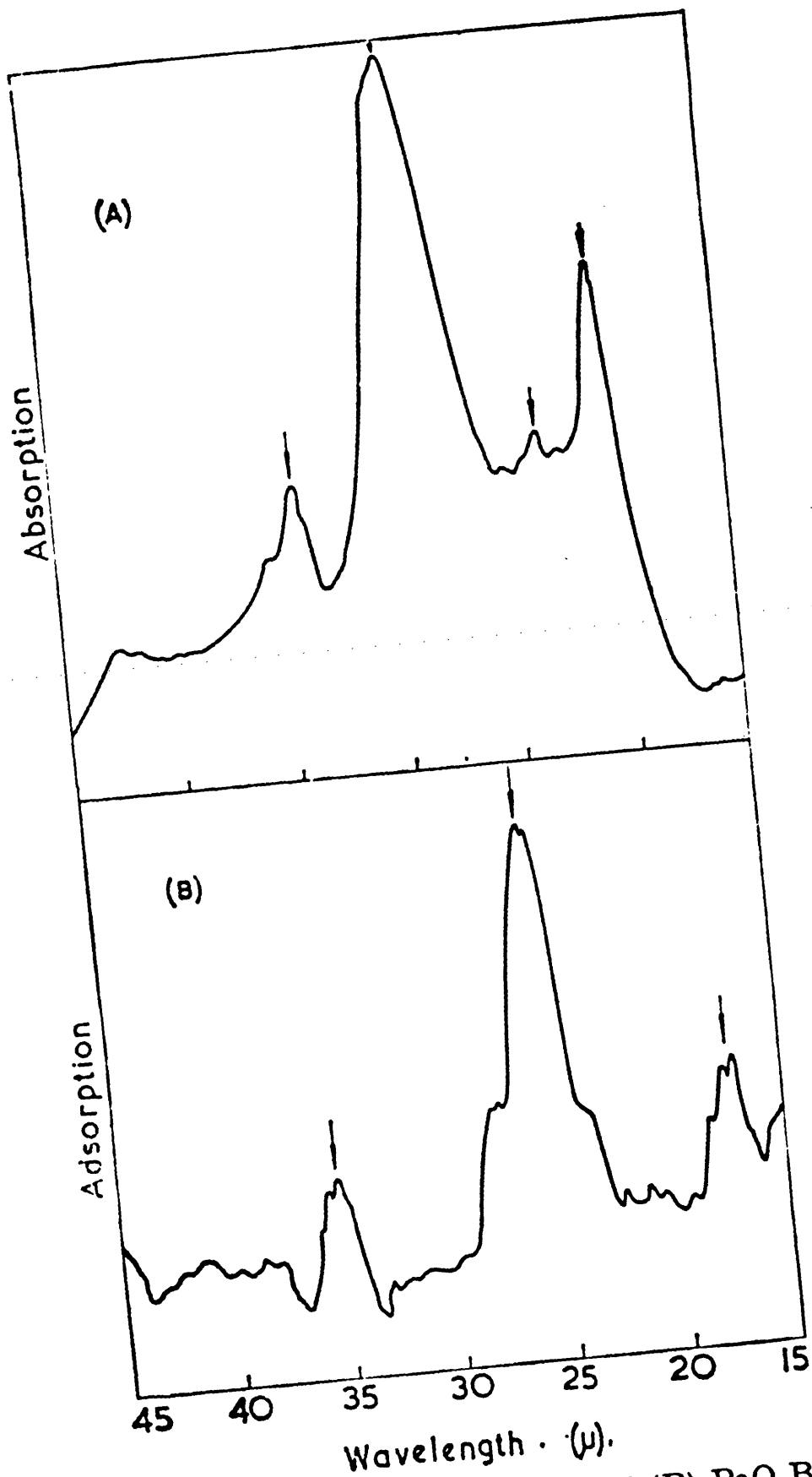
Actinide (V) and (VI) oxyhalides

Protactinium (V) oxyiodides

Several protactinium (V) oxychlorides⁽⁷⁵⁾ and oxybromides⁽⁷⁶⁾ and one oxyfluoride, Pa_2OF_8 ⁽⁴⁷⁾ are known, but no protactinium (V) oxyiodides have previously been prepared. With the improved methods for the preparation of protactinium pentaiodide (developed by Dr. D. Brown and Mr. P. J. Jones in this laboratory) it has been possible to investigate the preparation of protactinium (V) oxyiodides. By reacting PaI_5 with Sb_2O_3 (equations 4 and 6, p.38&40) the two new oxyiodides PaOI_3 and PaO_2I have now been prepared. Oxygen has also been reacted with the pentaiodide but this is a less satisfactory method. The oxyiodides

Figure 3

Infrared spectra of PaOBr_3 and PaO_2Br



Infrared spectra of (A) PaOBr_3 and (B) PaO_2Br

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PHOTOGRAPHIC GROUP

NEG No. *HC 63416*

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have also been observed as by-products during the preparation of PaI_5 by the reaction between protactinium pentoxide and silicon tetraiodide. Protactinium (V) oxytriiodide disproportionates above 450° in vacuo to give protactinium (V) dioxymonoiodide and protactinium pentaiodide (equation 5, p.40). The PaO_2I so obtained is a fluffy, mustard coloured compound in contrast to the dark brown solid obtained from the Sb_2O_3 reaction. Both samples give identical X-ray powder diffraction patterns, infrared and analytical results.

Crystallographic properties The X-ray powder diffraction results for PaOI_3 and PaO_2I are listed in Table 17. Those for PaO_2I have been interpreted on the basis of a hexagonal unit cell with $a_0 = 12.64 \pm 0.01$ and $c_0 = 4.07 \pm 0.01 \text{ \AA}$. Unfortunately no single crystal data are available and the assignments can only be regarded as tentative. PaOI_3 gave poor quality X-ray powder diffraction photographs even after samples had been heated at 400° for a number of hours.

Infrared spectra The absorption bands observed in the spectra of PaOI_3 and PaO_2I are very similar to those of PaOBr_3 and PaO_2Br . (Table 18). The presence of an extra very weak band at 469cm^{-1} in the spectrum of PaO_2I is the only difference from that of PaO_2Br . Improved spectra have been obtained for the oxybromides and these are illustrated in Figure 3. The similarities between the oxybromide and oxyiodide spectra support the assignment of the bands as metal-oxygen vibrations rather than metal halogen. No bands are observed above 600cm^{-1} , which would seem to exclude the presence of discrete PaO^{3+} or

Table 17

Partial X-ray powder diffraction results for PaO₃I and PaO₂I

PaO ₃ I		PaO ₂ I			
Sin ² θ _{obs}	I*	Sin ² θ _{obs}	Sin ² θ _{calc}	h,k,l	I*
0.0414	m-	0.0349	0.0351	0,0,1	s
0.0492	m-	0.0400	0.0400	1,0,1	w-
0.0540	m-	0.0438	0.0439	3,0,0	w-
0.0587	s	0.0546	0.0547	2,0,1	s
0.0647	m-	0.0779	0.0781	4,0,0	m
0.0670	m-	0.0804	0.0796	3,0,1	m
0.0930	w	0.0935	{0.0930	3,2,0	w+
0.0997	w		{0.0941	2,2,1	
0.1142	w	0.0998	0.0992	3,1,1	m-
0.1204	w+	0.1136	0.1138	4,0,1	w-
0.1312	w+	0.1292	0.1288	3,2,1	w-
0.1367	w	0.1327	0.1323	3,3,0	w-
0.1430	m	0.1365	0.1374	4,2,0	w+
0.1493	w+	0.1410	0.1418	0,2,2	w
0.1622	w	0.1766	{0.1767	6,0,0	w+
0.1707	w		{0.1767	2,1,2	
0.2104	w+	0.1915	0.1915	5,2,0	m
		0.2135	0.2129	6,0,1	d,w
		0.2210	0.2205	4,0,2	d,w
		0.2362	{0.2360	3,2,2	d,w
			{0.2360	4,4,0	
		0.2764	0.2768	7,0,1	d,w

w-weak; m-medium; s-strong; d-diffuse.

*Visually estimated.

PaO_2^+ groups in any of these compounds. The structure of PaOBr_3 ⁽¹²⁸⁾ has been reported recently. It is a polymeric oxygen and bromine bridged molecule and in view of the similarities between the infrared spectra of PaOBr_3 and PaOI_3 , the latter would also be expected to be a similar oxygen bridged molecule with the oxygens at least three co-ordinate.

Chemical properties Both oxyiodides are moisture sensitive and immediately hydrolysed by water and dilute aqueous ammonia but they may be safely stored in a dry atmosphere box. They are insoluble in carbon tetrachloride, cyclohexane and isopentane.

Table 18

Protactinium-oxygen stretching vibrations for the pentavalent oxybromides and oxyiodides

Compound	Colour	ν Pa-O (cm^{-1})
PaOBr_3	Green	515m; 476w; 364s; 303w
PaOI_3	Dark brown	480m; -; 339s; 276w
PaO_2Br	Off-white	575m; -; 386s; 286w
PaO_2I	Dark brown	555m; 469vw; 386s; 281w

Neptunium (V) and (VI) oxyfluorides

Although protactinium (V)⁽⁴⁷⁾ and uranium (V)⁽⁷⁴⁾ oxyfluorides of the type M_2OF_8 (M = Pa and U) are known, the only recorded neptunium oxyfluoride⁽⁶⁹⁾ is NpO_2F_2 , and this has only been prepared contaminated

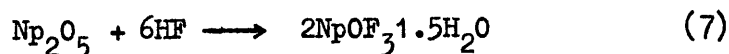
with sodium fluoride by the reaction of sodium neptunyl (VI) acetate and anhydrous hydrogen fluoride at 300-350°. The product was identified by its X-ray powder diffraction pattern which showed it to be isostructural with UO_2F_2 . The recent preparation of neptunium trioxide⁽¹⁰³⁾ hydrate and neptunium pentoxide⁽¹⁰³⁾ has now led to the direct preparation of NpO_2F_2 and some neptunium (V) oxyfluorides.

NpO_2F_2 has been prepared by the reaction between neptunium trioxide hydrate and anhydrous hydrogen fluoride at 225°-250°. Above 250° some reduction takes place. For example, 200mg of NpO_2F_2 yielded a product containing 30% Np (V) when heated at 350° in anhydrous hydrogen fluoride. X-ray powder diffraction patterns of the product suggested that only NpO_2F_2 was present but, should $NpOF_3$ be produced, no extra lines will be observed since, as discussed later, the compounds are isostructural. The pentavalent compound could not be isolated because longer reaction times and higher temperatures caused further reduction to NpF_4 . Between 350° and 450° mixtures of NpO_2F_2 , NpF_4 and the pentavalent compound were obtained in varying ratios. The pale green product obtained at 550° was insoluble in acids and the X-ray powder diffraction pattern showed it to be NpF_4 . Neptunyl fluoride is thus less stable than uranyl fluoride which has been reported⁽¹²⁹⁾ to be stable in anhydrous hydrogen fluoride to 600°. This observation has been confirmed but at 650° some 10% reduction to UF_4 does occur though only in the layer in direct contact with the platinum container. Hydrogen impurity was at first thought to be the

cause of the reduction but gas chromatography indicated that less than 0.1% total impurity was present in the HF and this, coupled with the uranyl fluoride observations suggested that the observations were genuine. As discussed later the hydrogen reduction of NpO_2F_2 and UO_2F_2 in sealed systems starts at 325° and 360° respectively.

Neptunium pentoxide is readily oxidised to NpO_2F_2 by fluorine at 350° but the reaction is slow at lower temperatures. No neptunium (V) fluoride was detected as an intermediate product. NpO_2F_2 is also obtained by the action of either fluorine at 225° or bromine trifluoride at 25° on neptunium trioxide monohydrate. It is conveniently prepared merely by vacuum evaporation of a dilute hydrofluoric acid solution containing neptunium (VI). In addition the evaporation of hydrofluoric acid solutions of neptunium (VI) in air at 50° gives anhydrous NpO_2F_2 whereas under similar conditions a uranium (VI) solution⁽¹¹⁹⁾ deposits crystals of $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$.

Neptunium pentoxide reacts with anhydrous hydrogen fluoride at 40° - 60° to yield the hydrated oxytrifluoride, $\text{NpOF}_3 \cdot x\text{H}_2\text{O}$ ($1 < x < 2$), which is readily dehydrated at 100° - 150° in anhydrous hydrogen fluoride. Above 225° some reduction to NpF_4 occurs. An unusual feature of the reaction is the fact that if the Np_2O_5 is heated to 300° before the hydrogen fluoride is admitted, no reaction occurs. This is strange since Np_2O_5 ⁽¹⁰³⁾ is prepared by vacuum thermal decomposition of $\text{NpO}_3 \cdot \text{H}_2\text{O}$ at 350° - 400° . The lack of reactivity may be due to surface deactivation or possibly the water produced during the reaction,



is necessary as a catalyst and is driven off too rapidly at 300°. The water content of the hydrate appears to be due solely to that produced during the reaction and not to the presence of traces of moisture in the anhydrous hydrogen fluoride since no increase in hydration is detected on prolonged contact with anhydrous hydrogen fluoride at 40°-60°. With relatively small amounts (0.1g) of the compound available for analysis and the water content being inferred from the results for the neptunium and fluorine the compound is referred to as $\text{NpOF}_3 \cdot x\text{H}_2\text{O}$ ($1 < x < 2$).

The products obtained from reactions between hydrogen and NpO_2F_2 have given analytical results dependent on the duration and temperature of the reaction. Thus, the products of reactions done at 325° for five to six days analyse approximately as NpO_2F , the range of composition being $\text{NpO}_{1.96}\text{F}_{1.08}$ to $\text{NpO}_{1.91}\text{F}_{1.18}$, whereas reactions at 340° (two to three days) have given products in the composition range $\text{NpO}_{1.89}\text{F}_{1.22}$ to $\text{NpO}_{1.8}\text{F}_{1.4}$. Above 350° considerable reduction to NpO_2 occurs, but between 325° and 350° the essentially pentavalent produce contains only a little (4-6%) NpO_2 . All the products gave X-ray powder diffraction patterns which were virtually identical with that of $\text{NpO}_{1.96}\text{F}_{1.08}$. Slight changes in unit cell parameters would be expected if the products were single phases of varying composition. There were, however, insufficient high-angle reflections present to obtain the high accuracy in the cell dimensions necessary to prove this point. It is also possible that impure samples of NpO_2F were prepared and the impurity was an amorphous neptunium (V) compound. In view of the uncertainty the

compound is represented as 'NpO₂F'.

Preliminary work on the analogous reaction between UO₂F₂ and hydrogen showed that reduction starts at 360° but after 17 hours at this temperature only a quarter of the UO₂F₂ had been reduced. Reaction periods of six days changed the colour of this initial product from green to dark brown. The resulting solid analysed as UO_{1.92}F_{1.13}. A dark brown product was also obtained from reactions at 480° and although this gave an identical X-ray powder pattern to the product obtained at 360° it contained no fluorine.

Crystallographic properties On the basis of the X-ray powder diffraction results (Table 19) NpOF₃ is isostructural with NpO₂F₂. The close similarity in the unit cell dimensions of NpOF₃ and NpO₂F₂ is not surprising as the sizes of oxygen and fluorine atoms are very similar. The oxytrifluoride hydrate gives an X-ray powder diffraction pattern very similar to that of the anhydrous compound with just a few extra diffuse lines present. The films were of poor quality, however, and the results have not been interpreted.

The X-ray powder diffraction results for 'NpO₂F' have been tentatively interpreted, in the absence of single crystal data, on the basis of a tetragonal cell (Table 19). The close agreement between the observed sin² θ values and those calculated on the basis of the tetragonal cell is shown in Table 20.

The UO₂F₂·H₂O products all gave X-ray powder photographs identical with those of UO_{2.9} (Table 19).

Table 19

Crystallographic properties of uranium and neptunium penta- and hexavalent oxyfluorides

Compound	Colour	Symmetry and Space Group	a ₀	b ₀	c ₀
UO ₂ F ₂	Yellow	R $\bar{3}m$ -D _{3d} ⁵	4.198		15.661
NpO ₂ F ₂	Pink	R $\bar{3}m$ -D _{3d} ⁵	4.185±0.01		15.790±0.01
NpOF ₃	Green	R $\bar{3}m$ -D _{3d} ⁵	4.185±0.01		15.799±0.01
'NpO ₂ F'	Green	Tetragonal	8.341±0.005		7.193±0.005
product UO ₂ F ₂ /H ₂	Dark Brown	Orthorhombic	6.888±0.004	3.958±0.003	4.135±0.002

*hexagonal cell parameters are listed.

Table 20

Partial X-ray powder diffraction pattern of NpO_2 $1.96^{\text{F}}-1.08$

$\text{Sin}^2\theta_{\text{obs}}$	$\text{Sin}^2\theta_{\text{calc}}$	h,k,l	I*	$\text{Sin}^2\theta_{\text{obs}}$	$\text{Sin}^2\theta_{\text{calc}}$	h,k,l	I*
0.0084	0.0087	1,0,0	w	0.1718	{0.1712	4,2,0	m
0.0118	0.0116	0,0,1	w		{0.1720	2,2,3	
0.0175	0.0173	1,1,0	w-d	0.1813	0.1806	3,0,3	m-
0.0200	0.0202	1,0,1	w	0.1840	0.1840	0,0,4	m
0.0338	0.0344	2,0,0	m+	0.2177	{0.2171	4,2,2	m-
0.0430	0.0430	2,1,0	w-		{0.2182	2,0,4	
0.0460	{0.0461	0,0,2	s	0.2219	0.2224	5,1,0	vw-
	{0.0459	2,0,1		0.2268	0.2267	2,1,4	w-
0.0544	{0.0547	1,0,2	w-	0.2409	0.2403	4,0,3	vw-
	{0.0545	2,1,1		0.2505	0.2522	2,2,4	vw-
0.0693	0.0687	2,2,0	wd	0.2736	0.2735	4,4,0	m-
0.0798	{0.0801	2,2,1	m+	0.2843	0.2850	4,4,1	vw-
	{0.0805	2,0,2		0.2933	0.2938	5,2,2	vw-
0.0887	0.0887	3,0,1	w-	0.3042	0.3043	1,1,5	w-
0.0896	0.0891	2,1,2	vw-	0.3193	{0.3191	6,0,1	w
0.1030	0.1037	0,0,3	w-		{0.3194	4,4,2	
0.1119	{0.1115	3,2,0	w-	0.3216	0.3214	2,0,5	m
	{0.1122	1,0,3		0.3499	0.3503	5,4,0	
0.1139	0.1147	2,2,2	w-	0.3553	{0.3553	2,2,5	m-
0.1377	{0.1371	4,0,0	m+		{0.3546	4,2,4	
	{0.1376	2,0,3		0.3842	0.3844	6,3,0	w-
0.1462	{0.1456	4,1,0	w	0.4136	0.4134	0,0,6	w+
	{0.1464	2,1,3		0.4216	0.4219	1,0,6	
0.1487	0.1484	4,0,1	w-	0.4426	0.4436	6,4,0	vw-
0.1574	{0.1573	3,2,2	w	0.4476	0.4475	2,0,6	w+
	{0.1570	4,1,1		0.4569	0.4569	4,4,4	

w-weak; m-medium; s-strong; d-diffuse

*Visually estimated.

The X-ray diffraction results for NpO_2F_2 agree with the published data⁽¹³⁰⁾.

Infrared spectra The Np-O stretching vibration for both NpOF_3 and $\text{NpOF}_3 \cdot x\text{H}_2\text{O}$ (Table 21) occurs very close to the ν_3 (asymmetric Np-O stretching vibration) for NpO_2F_2 . It has previously been noted that related compounds containing NpO^{3+} and NpO_2^{2+} groups have very similar Np-O stretching vibrations. For example, the chloro-complexes⁽¹⁰²⁾ $\text{Cs}_2\text{NpOCl}_5$ and $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ ($\sim 920\text{cm}^{-1}$) and the nitrates⁽¹³¹⁾ $\text{NpO}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\sim 960\text{cm}^{-1}$). A sharp band observed at 852cm^{-1} in the spectra of NpOF_3 and $\text{NpOF}_3 \cdot x\text{H}_2\text{O}$ may be associated with a Np-F vibration since no analogous metal oxygen bands have been observed in the spectrum of $\text{Cs}_2\text{NpOCl}_5$ or $\text{NpO}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ and the sharpness rules out a combination mode. Despite NpOF_3 and NpO_2F_2 being isostructural their infrared spectra are quite different below 900cm^{-1} (Table 21).

Samples of NpO_2F_2 prepared by high temperature reactions involving hydrogen fluoride or fluorine have a slightly different ν_3 position from samples prepared from aqueous solution (Table 21). It has previously been reported⁽¹¹⁹⁾ that ν_3 occurs at 1010cm^{-1} for UO_2F_2 prepared by dehydration of $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$ whereas it is observed at 990cm^{-1} in sample of UO_2F_2 prepared by reacting anhydrous hydrogen fluoride with UO_3 . During this study neither the symmetric Np-O stretching vibration, ν_1 , nor the combination band, $\nu_1 + \nu_3$, have been observed, although the latter has been observed⁽¹¹⁹⁾ at 1872cm^{-1} .

Table 21

Infrared spectra (cm^{-1}) of neptunium and uranium pentavalent and hexavalent oxyfluorides

Compound	$\nu_{\text{Np-O}}$	$\nu_{\text{Np-F}}$	Other bands
$\text{UO}_2\text{F}_2^{\text{a}}$	990s.	286s.b.	-
$\text{NpO}_2\text{F}_2^{\text{a}}$	980s.	278s.b.; 255s.b.	-
$\text{NpO}_2\text{F}_2^{\text{b}}$	990s.	278s.b.; 255s.b.	-
NpOF_3	985s.	852w.sh.; 350b.; 300s.b.	1160s.
$\text{NpOF}_3 \cdot x\text{H}_2\text{O}$	985s.	852w.sh.; 300s.b.	3450 (OH st.) 1630 (H_2O rock) 1160w.
' NpO_2F '	825s.; 705s.	274s.b.	1100w.b. ^c ; 955w. ^c ; 400w.
' UO_2F '	800s		1075w.b. ^c ; 990w.b. ^c

^aAnhydrous preparative method

^bPrepared from aqueous hydrofluoric acid

^cOf variable intensity

s-strong; sh.-sharp; m-medium; w-weak; b-broad.

for UO_2F_2 . Neptunium oxygen stretching vibrations for compounds containing the NpO_2^+ group have previously been observed at 759cm^{-1} ($\text{NpO}_2\text{NO}_3 \cdot \text{H}_2\text{O}$)⁽¹³¹⁾ and 800cm^{-1} ($\text{Cs}_3\text{NpO}_2\text{Cl}_4$)⁽¹⁰²⁾. The two bands observed in the spectrum of ' NpO_2F ' at 825cm^{-1} and 705cm^{-1} are tentatively assigned to Np-O vibrations and the strong broad band at 274cm^{-1} to a Np-F stretching vibration. In the absence of complete structural data and a full co-ordinate analysis the remaining bands in the spectra of the pentavalent neptunium compounds are difficult to assign although the weak ones at 1110cm^{-1} and 1160cm^{-1} are possibly overtones.

The spectrum of the $\text{UO}_2\text{F}_2/\text{H}_2$ reaction product contained a strong band at 800cm^{-1} which is comparable with the 825cm^{-1} band in the spectrum of ' NpO_2F '. A strong, broad band between 600cm^{-1} and 300cm^{-1} obscured any weak bands in this region. The 1075cm^{-1} band is probably an overtone and that at 990cm^{-1} is probably due to traces of unreacted UO_2F_2 .

Chemical properties NpO_2F_2 , NpOF_3 , $\text{NpOF}_3 \cdot x\text{H}_2\text{O}$ and ' NpO_2F ' are all non-hygroscopic. 50mg samples do not significantly change in weight when left in air for several days. They are insoluble in organic solvents and the pentavalent compounds only dissolve in dilute mineral acids in the presence of boric acid. However, NpO_2F_2 , like UO_2F_2 , readily dissolves in water and mineral acids.

The reaction between hydrogen fluoride and ' NpO_2F ' at 225° produces NpOF_3 and fluorine oxidises ' NpO_2F ' to NpO_2F_2 at 300° without any observable intermediate fluorides being formed.

Protactinium (V) oxyfluorides and pentafluoride hydrates

Only one protactinium (V) oxyfluoride⁽⁴⁷⁾, Pa_2OF_8 , and one pentafluoride hydrate^(47, 121), $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ have previously been reported. During the present investigations various reactions have been studied in attempts to prepare new pentavalent oxyfluorides and to establish alternative preparative methods for the pentafluoride. In almost all instances the products have either been Pa_2OF_8 or hydrates of protactinium pentafluoride. The work is briefly summarised below and certain reactions which resulted in the formation of Pa_2OF_8 are listed in Table 22.

The reaction between anhydrous hydrogen fluoride and vacuum dried protactinium (V) hydrous oxide yields successively $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$, $\text{PaF}_5 \cdot \text{H}_2\text{O}$ and Pa_2OF_8 at 40° , 60° and 140° respectively. All three phases give characteristic X-ray powder photographs and $\sin^2 \theta$ values for $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ and $\text{PaF}_5 \cdot \text{H}_2\text{O}$ are listed in Table 23. The unit cell constants

Table 22

Reactions producing Pa₂O₈F₈

Reactants	Temperature
Pa (V) hydrous oxide/HF gas	140-350°
PaF ₅ hydrates/HF gas	140-350°
PaCl ₅ /HF gas ^(a)	20°
Pa ₂ O ₅ /20MHF ^(b)	20°
Pa ₂ O ₅ /HF gas ^(c)	325°
PaF ₅ hydrates/F ₂	20°
PaOBr ₃ or PaO ₂ Br/F ₂	20°
PaOI ₂ /H ₂ /HF gas	20°
Pa ₂ O ₈ F ₈ /F ₂	300°
Pa ₂ O ₈ F ₈ /HF	200°
PaOBr ₃ or PaO ₂ Br/AsF ₃ ^(d)	20°

(a) the moisture sensitive PaCl₅ was possibly partially hydrolysed before fluorination.

(b) solution evaporated dry under vacuum and pumped for 2-3 days at 10⁻³ torr.

(c) product contained some PaF₅.

(d) X-ray powder photograph of product indicated the presence of an impurity.

Table 23

Partial X-ray powder diffraction results for $\text{PaF}_5 \cdot \text{H}_2\text{O}$ and $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$

$\text{PaF}_5 \cdot \text{H}_2\text{O}$		$\text{PaF}_5 \cdot 2\text{H}_2\text{O}$	
$\text{Sin}^2\theta_{\text{obs}}$	I*	$\text{Sin}^2\theta_{\text{obs}}$	I*
0.0092	s-	0.0180	s-
0.0164	w-	0.0248	w
0.0216	w-	0.0355	w
0.0293	m+	0.0471	s
0.0445	s	0.0500	w
0.0477	s	0.0515	w
0.0588	w-	0.0554	s
0.0662	w+	0.0602	m
0.0803	w	0.0671	m
0.0930	w	0.0950	w
0.1093	w+	0.1014	w-
0.1245	w+	0.1047	w
0.1301	m	0.1204	w-
0.1396	w+	0.1380	w+
0.1428	w	0.1404	s
0.1540	w	0.1464	m-
0.1685	w+	0.1532	m
0.1760	w+	0.1648	m
		0.1694	m
		0.1740	m-

I* visually estimated.

s-strong; m-medium; w-weak.

obtained for Pa_2OF_8 are in agreement with those reported by Stein⁽⁴⁷⁾. The reaction between Pa_2O_5 (obtained by heating protactinium (V) hydroxide in air at 467°) and anhydrous hydrogen fluoride at 325° yields a mixture of PaF_5 and Pa_2OF_8 . Increasing the temperature to 375° does not convert all the Pa_2OF_8 to PaF_5 . At 500° Pa_2F_9 , a black solid, is produced. Pa_2F_9 and Pa_2OF_8 are isostructural⁽⁴⁷⁾ with almost identical unit cell dimensions so it is not possible to determine from the X-ray powder diffraction patterns at exactly what temperature Pa_2F_9 is first formed. However, from the colour of the products it would seem that this temperature is around 370° .

A number of other possible routes to PaF_5 have also been studied. The reactions involved only a few milligrams of material and the products were identified by X-ray powder diffraction analysis. The reaction between PaCl_5 and fluorine at room temperature has produced either $\text{PaF}_5 \cdot \text{H}_2\text{O}$ or an X-ray amorphous compound. It is possible that the latter was PaF_5 and only minute amounts of water would be necessary to produce the monohydrate. At 200° fluorine and PaCl_5 reacted to form Pa_2OF_8 . An attempt to dehydrate $\text{PaF}_5 \cdot \text{H}_2\text{O}$ with fluorine at 225° produced Pa_2OF_8 (at 100° the product was amorphous). Here too the initial product might have been PaF_5 since the presence of only small amounts of oxygen in the fluorine would result in the formation of Pa_2OF_8 at higher temperatures. Fluorine and Pa_2OF_8 do not appear to react at 300° though this too could be due to the presence of small amounts of oxygen. Stein⁽⁴⁷⁾ had to rigorously purify the fluorine he used for converting PaF_4 to

PaF_5 in order to prevent the formation of Pa_2OF_8 . The reaction between PaCl_5 and hydrogen fluoride at room temperature has yielded Pa_2OF_8 but this was probably due to initial hydrolysis of the PaCl_5 by traces of moisture. All these results emphasise that pure reagents and rigorously dry conditions are essential for the preparation of PaF_5 .

The reported^(47, 121) preparative method for $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ was investigated to see whether pure $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ was indeed produced under the stated conditions. 0.1g of Pa_2O_5 was dissolved to 20M hydrofluoric acid and the solution evaporated dry at 110° . X-ray powder diffraction results indicated that the product was a mixture of $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$, $\text{PaF}_5 \cdot \text{H}_2\text{O}$ and Pa_2OF_8 . A similar solution was evaporated to dryness in vacuo at room temperature and again a mixture of the two pentafluoride hydrates and Pa_2OF_8 was obtained. When this mixture was left for 48 hours under a pumping vacuum (10^{-4} torr) at room temperature the final product was pure Pa_2OF_8 .

The reactions of some of the known protactinium (V) oxyhalides with gaseous hydrogen fluoride and with fluorine were studied in an attempt to prepare new protactinium (V) oxyfluorides. In general either $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ or $\text{PaF}_5 \cdot \text{H}_2\text{O}$ was obtained by reacting anhydrous, gaseous hydrogen fluoride with PaOBr_3 , PaO_2Br or $\text{Pa}_2\text{O}_3\text{Cl}_4$. Hydration could occur either as a result of traces of moisture in the box atmosphere or water produced during reaction. Both PaOBr_3 and PaO_2Br are converted by fluorine or arsenic trifluoride at room temperature to Pa_2OF_8 . In the AsF_3 reaction an unidentified impurity is produced together with the

Pa_2OF_8 . This same impurity 'grows into' Pa_2OF_8 samples which have been allowed to stand in stoppered glass vessels for 3 to 4 months and it may be due to interaction between Pa_2OF_8 and the glass. Preliminary results indicate that the interaction of Pa_2OF_8 and Sb_2O_3 produces a new crystallographic phase but this has not yet been characterised.

Apart from peaks due to water at $\sim 3400\text{cm}^{-1}$ and $\sim 1600\text{cm}^{-1}$ neither $\text{PaF}_5 \cdot \text{H}_2\text{O}$ nor $\text{PaF}_5 \cdot 2\text{H}_2\text{O}$ show infrared absorption bands above 600cm^{-1} . Pa_2OF_8 has a strong peak at 745cm^{-1} with a shoulder at 800cm^{-1} . Pa-O stretching vibrations have been observed in this region in the spectra of certain protactinium nitrates⁽¹³²⁾ such as $\text{PaO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (773cm^{-1}) and $\text{Pa}_2\text{O}(\text{NO}_3)_8 \cdot 2\text{CH}_3\text{CN}$ (721cm^{-1}).

Fully fluorinated neptunium (V) complexes

In recent years a number of fully fluorinated U (V)^(90, 93) and Pa (V)^(90, 91, 100) complexes have been reported. This work stimulated interest in whether neptunium (V) fully fluorinated complexes were capable of existence. Fluorine oxidation of neptunium (IV) fluoro-complexes, analogous to the method of Rudorff and Leutner⁽⁹³⁾ for preparing Na_3UF_8 from Na_3UF_7 , seemed a possible route to the neptunium (V) compounds.

Mixtures of Np (IV) and potassium fluoride in the correct ratios for producing KNpF_6 and K_2NpF_7 on oxidation, were prepared either by evaporating to dryness a solution of NpO_2 and KF in nitric and hydrofluoric acids, or by grinding together NpF_4 and KF . The mixtures were

loaded into nickel boats and heated in fluorine at 350° - 375° for 8 hours. When the fluorinated solids were dissolved in a mixture of $1M HNO_3$ and 0.2M boric acid and their visible spectra studied variable amounts of Np (V) and Np (VI) were found. In addition, irreproducible X-ray powder diffraction results were obtained.

At that time details of the preparation of Rb_2NpF_7 , $CsNpF_6$ and the analogous plutonium compounds were published^(133, 134). These were isostructural with Rb_2UF_7 and $CsUF_6$ respectively. The colours of these neptunium (V) complexes corresponded with those of the fluorinated products obtained during the present study. The work of Asprey et al. was repeated without success; mixtures of Np (V) and Np (VI) were still obtained. No mention had been made as to whether or not the oxidation states of their compounds had been determined. It was thought that perhaps the neptunium (V) complexes were being further oxidised by fluorine or traces of oxygen in the fluorine. The products were found to be unstable even in an argon atmosphere dry box, the initial purple colour changing to green in 1 to 2 days. There were no peaks in the infrared spectrum around $800-1000cm^{-1}$ for either the oxidised compound or its decomposition product so fluorine was probably causing the oxidation to Np (VI) and the instability was probably not due to reaction between the compound and moisture or oxygen.

The preparation of 3:1 complexes of the type $M^1_3NpF_8$ was therefore investigated to see whether these would be more resistant to further oxidation. At temperatures as low as 250° 3:1 mixtures of NaF and

Np (IV) gave pure Na_3NpF_8 . This compound was isostructural with Na_3PaF_8 ⁽⁹¹⁾ and Na_3UF_8 ⁽⁹³⁾ and solutions in 1M HClO_4 /0.4M boric acid and 1M HNO_3 /0.2M boric acid gave pure Np (V) spectra. 3:1 mixtures of RbF and Np (IV), fluorinated at 250°, yielded a product which was almost isostructural with Rb_3PaF_8 ⁽⁹⁶⁾ but there were also a few extra lines in the X-ray powder diffraction patterns. At 350° a mixture of Rb_3NpF_8 and Rb_2NpF_7 (X-ray diffraction analysis) was obtained. Both preparative methods (p.43) produced compounds, which when dissolved in 1M HNO_3 /0.2M boric acid, showed 90% Np (V), 5% Np (IV) and 5% Np (VI) in the solution spectra. The Np (IV) and (VI) were thought to be produced by slight disproportionation of the Np (V).

Despite the successful preparation of Na_3NpF_8 and Rb_3NpF_8 it was still not understood why the compounds reported by Asprey et al. were not obtained. The only difference between the preparative methods that was apparent was their use of a sapphire boat whereas a nickel boat was used for the present work. Therefore nickel boats containing NaF, KF and RbF were heated at 350° in fluorine. The NaF did not react but KF and RbF produced purple and lilac compounds respectively. It would appear, therefore, that the failure to obtain 1:1 and 2:1 compounds was due to the lack of sufficient alkali metal fluoride to stabilise all the neptunium as Np (V). The Np (VI) observed was probably present as a complex with the rubidium-nickel fluoro-complex. The presence of Rb_2NpF_7 in the Rb_3NpF_8 preparation done at 350° was probably due to reaction of some rubidium fluoride with the nickel boat at this temperature. The

Table 24
Partial X-ray powder diffraction results for Na₃NpF₈

Sin ² _{obs} θ	Na ₃ NpF ₈		I*
	Sin ² _{calc} θ	h,k,l	
0.0201	0.0212	0,0,2	m
0.0249	0.0250	1,0,1	s
0.0399	0.0400	1,1,0	m
0.0600	0.0602	1,1,2	s
0.0653	0.0654	1,0,3	m
0.0800	0.0800	2,0,0	d,w
0.1000	0.1002	2,0,2	w+
0.1050	0.1051	2,1,1	m
0.1208	0.1208	1,1,4	w
0.1458	0.1462	2,1,3	m+
0.1606	0.1608	2,0,4	s-
0.1806	0.1803	2,2,2	w
0.1845	0.1851	3,0,1	w
0.1995	0.2001	3,1,0	w
0.2203	0.2203	3,1,2	m
0.2224	0.2218	1,1,6	m
0.2261	0.2263	2,1,5	w+
0.2620	0.2618	2,0,6	w
0.2648	0.2652	3,2,1	w
0.2815	0.2809	3,1,4	w-
0.3054	0.3056	3,2,3	w-
0.3204	0.3203	4,0,0	w-
0.3404	0.3405	4,0,2	w-

I* visually estimated intensities. s-strong; m-medium; w-weak; d-diffuse

extra lines observed in the X-ray powder diffraction pattern of Rb_3NpF_8 were not those given by the $\text{RbF}/\text{Ni}/\text{F}_2$ compound but nevertheless they are probably due to some impurity given by reaction with the nickel boat. Further work is obviously necessary but this will hinge on the availability of a sapphire boat.

Properties Na_3NpF_8 possesses tetragonal symmetry, space group $\text{I}4/\text{mmm}-\text{D}_{4h}^{17}$, being isostructural with Na_3PaF_8 for which structural results are presented in the next section. Unit cell dimensions are $a_0 = 5.443 \pm 0.001$, $c_0 = 10.838 \pm 0.006 \text{ \AA}$ and with $Z = 2$ the calculated density is 4.577 g.cm^{-3} . Partial X-ray powder diffraction results are listed in Table 24.

Neptunium-fluorine stretching vibrations are observed at 415 cm^{-1} and 410 cm^{-1} for Na_3NpF_8 and Rb_3NpF_8 respectively. The band observed for Na_3NpF_8 was broad and extended from $\sim 500 \text{ cm}^{-1}$ to $\sim 350 \text{ cm}^{-1}$.

Crystal Structures

Trisodium octafluoroprotactinate (V), Na_3PaF_8

Na_3PaF_8 , prepared by the reported method⁽¹⁰⁰⁾, was recrystallised from aqueous hydrofluoric acid. After a suitable crystal had been obtained Guinier powder photographs from the rest of the sample were taken to determine the unit cell constants and standard deviations (Table 25). The crystal was orientated on a precession camera with a_0 parallel to the spindle axis. Multifilm photographs were taken for layers $0kl$ to $4kl$ using the equi-inclination Weissenberg technique with Zr filtered Mo K_α radiation. Lorentz and polarisation corrections were

Table 25

Cell dimensions (\AA) and standard deviations for Na_3PaF_8

a_0	c_0
5.493 ± 0.003	10.970 ± 0.010

applied to the visually estimated intensities (using a computer programme written by Dr. C. E. F. Rickard) and the results were placed on a common scale by comparison of common festoons. No absorption corrections were applied because the crystal was an irregular shaped chunk (maximum dimensions 0.15 x 0.115 x 0.115mm).

The space group $I4/mmm-D_{4h}^{17}$ (No 139) was satisfied by the systematic absences, hkl , $h+k+l = 2n+1$, $hk0$, $h+k = 2n+1$, $Ok1$, $k+l = 2n+1$, hhl , $l = 2n+1$. With two molecules per unit cell the two protactinium atoms could lie in either the 2a or 2b special positions: the former were chosen (choosing the latter would have only shifted the origin). The six sodium atoms could also be placed, two in the 2b positions with the remaining four atoms in the 4d special positions, on the basis of packing considerations. A difference fourier based on the protactinium positions clearly placed the sodium and fluorine atoms. Peaks occurred at $0, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$ (Na in 2b), $0, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{2}, 0, \frac{1}{4}$ (Na in 4d) and approximately $\frac{1}{4}, \frac{1}{4}, \frac{1}{8}$ and $\frac{1}{4}, \frac{1}{4}, \frac{3}{8}$ (F in 16m). No other peaks occurred which were not related to the above co-ordinates.

A structure factor calculation confirmed the assignments and the

Figure 4

Co-ordination of the fluorine atoms around
protactinium in Na_3PaF_8

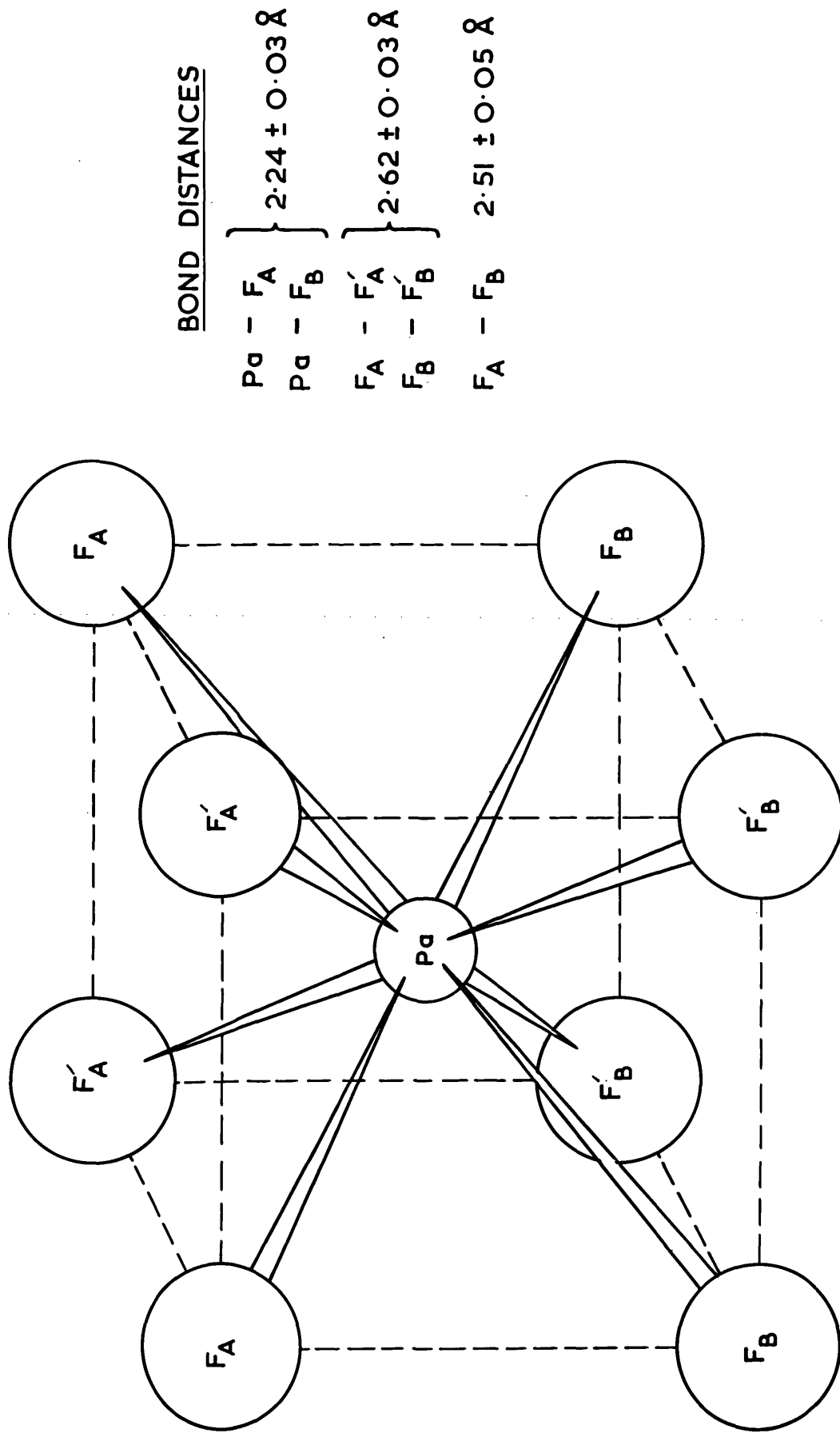


FIGURE 4.

various positional and anisotropic thermal parameters were refined by a full matrix least squares procedure⁽¹³⁵⁾. Sodium and fluorine atoms were treated as unipositive and uninegative ions respectively and the protactinium as a neutral atom. The scattering curves listed in the International Tables⁽¹³⁶⁾ were used. The refinement converged to a final residual of 0.085. The positional and vibrational shifts in the final least squares cycle were all much less than the respective standard deviations. The final atomic parameters and their standard deviations are listed in Table 26 and the values of $|F_o|$ and $|F_c|$ in Appendix A.

Each protactinium atom is surrounded by eight fluorine atoms at the vertices of a cube which has a slight tetragonal distortion (Figure 4). The distortion is very slight, the height being shortened by 0.11 Å, and the results are only just significant within the standard deviations. The sodium atoms are located between the PaF_8^{3-} cubes. The Pa-F distance is 2.24 Å which, assuming 0.64 Å for the covalent radius of a fluorine atom, yields 1.60 Å for the covalent radius of protactinium. This can be compared with the mean values of 1.44 Å found for six coordinate β PaBr_5 ⁽⁵³⁾, 1.45 Å for the seven co-ordinate PaCl_5 ⁽⁵¹⁾ and 1.52 Å for the nine co-ordinate heptafluorocomplex, K_2PaF_7 ⁽⁹²⁾.

The analogous uranium compound, Na_3UF_8 , is isostructural with Na_3PaF_8 and it is of interest to compare the co-ordinates of the fluorine atoms obtained by Rudorff and Leutner⁽⁹³⁾ from their X-ray powder diffraction results. They placed the fluorines in the 16m

Table 26

(a) Final atomic positions and thermal parameters for Na₂PaF₈

Atom	Position	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pa	2a	0.0	0.0	0.0	0.00243	0.00243	0.00010	0.0	0.0	0.0
	standard deviations				0.00049	0.00049	0.00011			
Na	2b	0.0	0.0	0.5	0.01151	0.01151	0.00302	0.0	0.0	0.0
	standard deviations				0.00611	0.00611	0.00217			
Na	4d	0.0	0.5	0.25	0.01400	0.01400	0.00369	0.0	0.0	0.0
	standard deviations				0.00479	0.00479	0.00175			
F	16m	0.23881	0.23881	0.11418	0.03148	0.03148	0.01091	-0.01088	-0.02065	-0.02065
	standard deviations	0.00454	0.00454	0.00317	0.0072	0.0072	0.00325	0.01831	0.00719	0.00719

(b) Bond angles

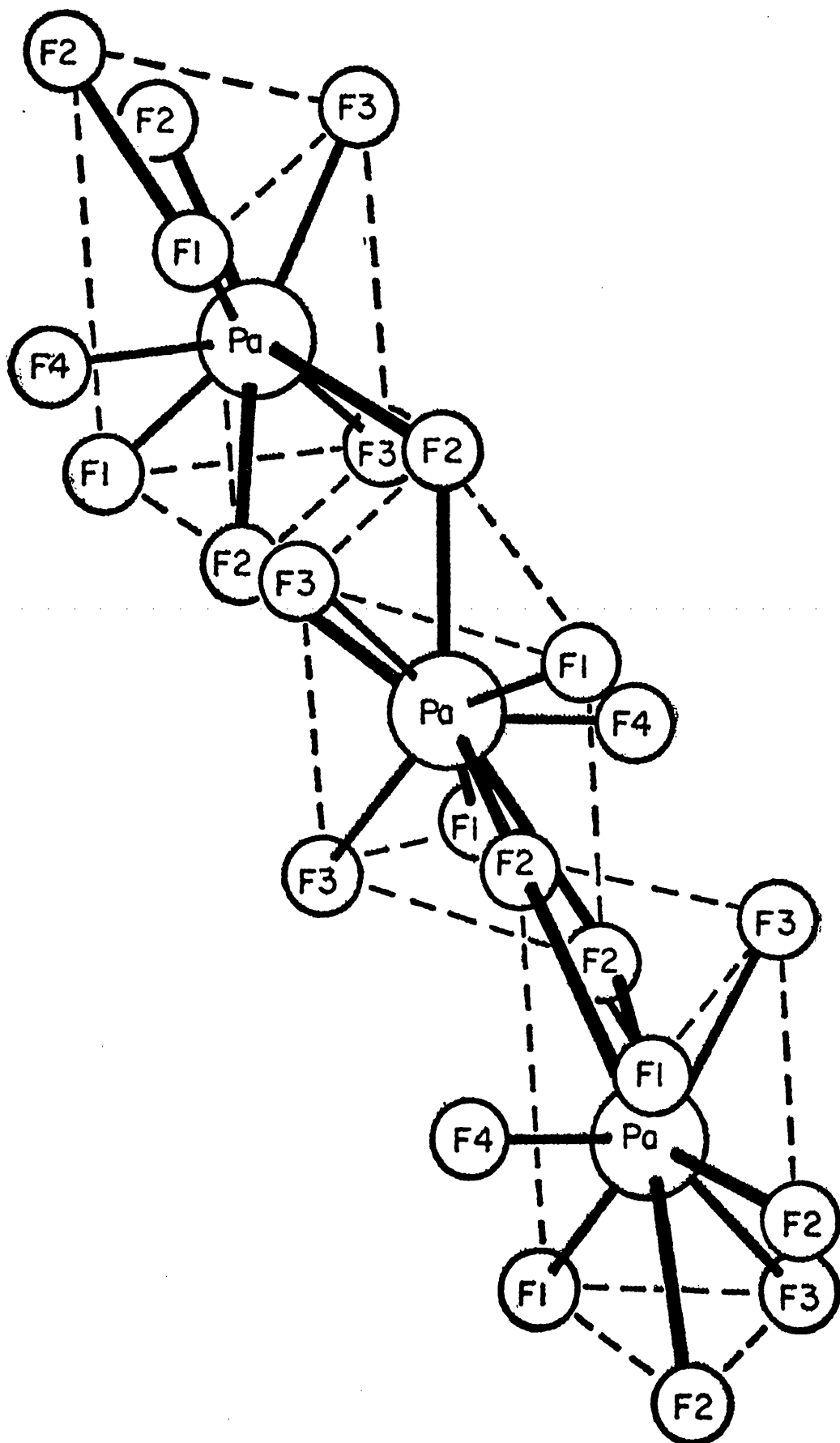
$F'_A - Pa - F'_A$	111.9°	$F'_B - Pa - F'_B$	71.7°
$F'_B - Pa - F'_B$		$F'_A - Pa - F'_A$	
$F'_A - Pa - F'_B$	68.1°	$F'_A - Pa - F'_B$	108.3°

position with $x = \frac{1}{4}$ and $z = \frac{1}{8}$ which are just the positions obtained from the difference fourier for Na_3PaF_8 . They postulated a UF_8^{3-} group on the basis of their results and the present results support their assignments. Zachariassen⁽¹³⁷⁾ had earlier interpreted the structure of Na_3UF_7 , which is apparently isostructural with Na_3UF_8 , with the fluorine co-ordinates $x = \frac{1}{4}$ and $z = \frac{1}{8}$ but the 16m positions were only partially occupied in this case. It has been suggested that cubic coordination will be rare and only possible through the participation of f-orbitals⁽¹³⁸⁾. The heptafluoro-complexes of zirconium and hafnium⁽¹³⁹⁾ are isostructural with Na_3UF_7 and these structures, because of the absence of readily available f orbitals, should be regarded as the average of a large number of seven co-ordinate ions.

Potassium, rubidium and caesium octafluoroprotactinates (V) are reported⁽⁹¹⁾ to possess face centred cubic cells containing four molecules. If they do possess $\text{Fm}\bar{3}\text{m}$ symmetry the protactinium atoms must be located in the 4a special positions and the fluorine atoms in the 32f positions, giving a cubic arrangement about the protactinium. Packing considerations suggest that $x = \frac{1}{8}$ for the fluorines in the 32f positions which leads to Pa-F approaches of $\sim 2.0 \overset{\circ}{\text{A}}$ and, for a potassium atom in 8c, the K-F approach is also $\sim 2.0 \overset{\circ}{\text{A}}$. This latter value is about $0.6\text{-}0.7 \overset{\circ}{\text{A}}$ smaller than expected. It is possible that the cell observed is a supercell and work on the preparation of a single crystal of Rb_3PaF_8 has now started.

Figure 5

Co-ordination of the fluorine atoms around
protactinium in K_2PaF_7



A.E.R.E. HARWELL
PHOTOGRAPHIC GROUP

Neg. No. *H762099*

Dicaesium heptafluoroprotactinate (V)

The crystal structure of K_2PaF_7 ⁽⁹²⁾ has been reported and the X-ray powder diffraction data⁽⁹¹⁾ for $(NH_4)_2PaF_7$ and Rb_2PaF_7 suggest all three compounds are isostructural. The analogous caesium compound, Cs_2PaF_7 , has a different X-ray powder diffraction pattern^(91, 96) suggesting a different structure.

A single crystal of Cs_2PaF_7 was obtained from aqueous hydrofluoric acid, as a well formed needle (0.35 x 0.09 x 0.3mm). The crystal, with its longest edge parallel to the spindle axis, was orientated on a precession camera and eight layers h0l to h3l and Okl to 3kl were photographed using Zr filtered MoK_{α} radiation. Four layers hk0 to hk3 were photographed using the Weissenberg method with Zr filtered MoK_{α} and Ni filtered CuK_{α} radiations. From these results it was concluded that the symmetry of the unit cell was monoclinic with $a_0 = 14.937 \pm 0.005$, $b_0 = 7.270 \pm 0.002$, $c_0 = 8.266 \pm 0.003 \text{ \AA}$ and $\beta = 125.32 \pm 0.02^\circ$. The systematic absences for hkl ($h + k = 2n + 1$), h0l ($h = 2n + 1$, $l = 2n + 1$) and Ok0 ($k = 2n + 1$) suggested the space group observed for K_2PaF_7 whose cell dimensions are $a_0 = 13.84$, $b = 6.76$, $c = 8.24 \text{ \AA}$ and $\beta = 125.5^\circ$. These a_0 and b_0 values are appreciably smaller than the corresponding values observed for Cs_2PaF_7 but c_0 and β are virtually identical. This is extremely significant since the PaF_9 units in K_2PaF_7 lie linked in infinite chains parallel to (001) by bridging fluorines (Figure 5). This suggests the same structure is present in Cs_2PaF_7 .

Table 27

Partial X-ray powder diffraction results for Cs₂PaF₇

$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	h, k, l	$I_{\text{est.}}$	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	h, k, l	$I_{\text{est.}}$
0-0154	0-0154	1,1,0	M	0-1896	0-1893	6,2,0	M-
0-0162	0-0162	2,0,0	M-	0-1911	0-1911	1,1,1	W+
0-0200	0-0202	1,1,1	W-	0-1935	0-1937	5,3,3	W
0-0453	0-0453	0,2,0	S-	0-1977	0-1977	6,2,1	M-
0-0474	0-0475	3,1,0	S	0-2091	0-1979	8,0,4	W+
0-0495	0-0496	3,1,2	S	0-2297	0-2093	0,0,4	W-
0-0511	0-0511	4,0,2	M-	0-2297	0-2292	5,1,5	W-
0-0525	0-0526	1,1,2	M+	0-2328	0-2296	4,4,2	W-
0-0582	0-0584	0,0,2	W	0-2377	0-2327	7,3,2	M-
0-0612	0-0613	0,2,1	W-	0-2404	0-2374	9,1,2	M-
0-0828	0-0829	2,2,0	W-	0-2435	0-2399	3,3,2	M-
0-0853	0-0857	5,1,1	W-	0-2462	0-2403	3,1,3	M-
0-0948	0-0947	3,1,1	W	0-2544	0-2437	9,1,1	M-
0-0963	0-0963	4,2,2	W	0-2722	0-2441	4,4,0	M-
0-0976	0-0976	6,0,2	M	0-2761	0-2462	3,3,4	M
0-1015	0-1020	0,2,2	M+	0-2812	0-2542	0,2,4	M
0-1080	0-1081	2,0,2	W-	0-2919	0-2734	7,3,1	W
0-1092	0-1094	1,1,3	W	0-2973	0-2761	6,4,2	W+
0-1104	0-1103	4,2,0	W	0-3169	0-2810	1,3,4	W+
0-1257	0-1255	1,3,1	W+	0-3207	0-2817	2,4,2	W
0-1375	0-1376	3,3,1	W	0-3236	0-2912	6,4,3	W
0-1397	0-1396	3,3,0	M+	0-3274	0-2921	2,0,4	W+
0-1414	0-1411	3,3,2	M	0-3341	0-2974	7,3,0	W+
0-1427	0-1413	6,2,2	M	0-3354	0-2976	0,4,3	W
0-1445	0-1428	7,1,2	W+	0-3372	0-3173	3,5,0	W
0-1469	0-1444	6,0,0	M-	0-3372	0-3173	9,3,5	W
0-1502	0-1470	2,2,2	W	0-3372	0-3208	1,5,2	M-
0-1529	0-1500	3,1,2	M	0-3416	0-3240	6,4,0	M-
0-1563	0-1522	6,2,1	M	0-3416	0-3272	9,3,2	M-
0-1803	0-1528	6,0,4	M	0-3416	0-3270	4,2,3	W
0-1828	0-1558	4,2,1	M+	0-3416	0-3335	9,3,4	W
0-1847	0-1563	3,1,4	W+	0-3416	0-3338	4,0,6	W
	0-1565	6,2,3	W+	0-3416	0-3354	9,1,0	W
	0-1799	3,3,5	W+	0-3416	0-3372	11,1,3	W
	0-1802	0,4,0	W+	0-3416	0-3370	2,2,4	W
	0-1826	7,1,4	W+	0-3416	0-3372	5,3,2	W
	0-1846	4,2,4	W+	0-3416	0-3417	6,2,2	W+

The observed and calculated $\sin^2 \theta$ values for reflections observed on the X-ray powder diffraction pattern and the visually estimated intensities are shown in Table 27. The new preparation of Cs_2PaF_7 did, in fact, produce a compound with the same powder pattern as observed previously⁽⁹¹⁾. The differences between these patterns and that of K_2PaF_7 , which led to the conclusion that the compounds were not isostructural, are obviously due to the appreciable differences between the respective values of a_0 and b_0 .

Protactinium and tantalum pentaiodide

The only known transition metal pentaiodides are NbI_5 ⁽⁵⁶⁾, TaI_5 ⁽⁵⁹⁾ and PaI_5 ⁽⁵⁵⁾ of which only the latter two can be sublimed in a vacuum without decomposition. X-ray powder diffraction data for TaI_5 and PaI_5 was too poor for any comparison to be made but the unit cell constants (58, 59), obtained from single crystals, indicated that they possessed different structures.

The structures of a number of protactinium halides^(51,53) and oxyhalides^(53,124) have been investigated recently and from the results obtained for PaCl_5 and $\beta\text{-PaBr}_5$ it was predicted⁽⁵⁴⁾ that PaI_5 might be monomeric.

A suitable crystal of PaI_5 (a plate 0.115 x 0.07 x 0.04mm) was obtained by vacuum sublimation and this was orientated using a Buerger precession camera with the c_0 axis (6.85 Å) parallel to the spindle. Precession photographs taken of the h0l to h2l layers and the 0kl to 2kl layers inclusive indicated that the unit cell size was 21.6 Å x 21.3 Å x 6.98 Å as compared with the published size of 7.22 Å x 21.2 Å x 6.85 Å. There were many absent reflections (Table 28). Zero level precession

photographs taken at 60° to either axis were, with the exception of two weak streaks, identical with the zero level photographs of the axes. Timed exposure Weissenberg photographs were taken for seven layers (hk0 to hk6 inclusive) using zirconium filtered MoK_α radiation ($\lambda_\alpha = 0.7107$), hk0 to hk2 were also taken with nickel filtered CuK_α radiation to compare the photographs with those from the previous determination of the unit cell⁽⁵⁸⁾. The zero level films were identical but there were minor

Table 28

Conditions governing observed PaI_5 reflections

hk1	$h+k = 2n$	if $h/2$ odd no condition for l if $h/2$ even only l even observed
h0l	if $l = 2n+1$	$h = 2n$
	if $l = 2n$	$h = 6n$
0kl	$k = 2n, l = 2n$	
h0l	$h = 6n$	
0k0	$k = 2n$	
00l	$l = 2n$	

differences between the hk1 layers and these caused the a axis to be split giving a 21.6 \AA as compared to a 7.22 \AA length. The films from the previous work also showed a number of disorder streaks.

Improved X-ray powder diffraction photographs were obtained for TaI_5 and PaI_5 using well flamed out capillaries and these indicated that the compounds were isostructural. The large number of absent reflections in the PaI_5 results coupled with the dissimilarity between the a_0 dimensions which would be expected to be about 14 \AA (based on published data for TaI_5) if TaI_5 and PaI_5 are isostructural, suggested that the PaI_5 crystal was twinned. Other PaI_5 crystals which were examined gave identical precession photographs.

It was therefore decided to prepare and examine crystals of TaI_5 in the hope that non-twinned crystals would be obtained.

A suitably sized crystal of TaI_5 , well separated from other crystals, was obtained by sublimation in vacuo. The crystal, a plate $0.110 \times 0.070 \times 0.230 \text{ mm}$ was orientated using a precession camera with the shortest axis (a_0 in Rolsten's data⁽⁵⁹⁾) parallel to the spindle axis and six layers (h0l to h2l and hk0 to hk2) were photographed. Multi-film equi-inclination Weissenberg photographs were obtained for seven layers (0kl to 6kl) and a total of 579 independent reflections were observed. Timed exposure precession photographs were used to obtain h0l and hk0 results in order to place the Weissenberg results on a common scale. The visually estimated intensities were corrected for Lorentz and polarisation factors (using a computer programme written by Dr. C. E. F. Rickard for the I.B.M. 360/65 computer) and placed on a common scale.

The unit cell dimensions and space group results agree with

Rolsten's data⁽⁵⁹⁾ (Table 29).

Table 29

Comparison of published and observed crystal data for TaI₅

	Lattice parameters			Density (g cc ⁻¹)		Z	Space group
	a _o	b _o	c _o	cal- culated	observed		
Rolsten	6.65	13.95	20.10	5.809	5.798	8	P _b ² ₁ ² _n ² _m ² ₁ -D _{2h} ¹⁶
This work	6.518	13.990	20.126	5.923		8	P _b ² ₁ ² _n ² _m ² ₁ -D _{2h} ¹⁶

The Weissenberg and precession photographs showed the pronounced hexagonal character observed with the PaI₅ crystals. There were a large number of systematically absent reflections (Table 30).

From conditions 1-4 inclusive (Table 30) the space groups Pn₂m or Pn₂1₁ were tentatively deduced (these space groups are the non-standard settings of Pn₂m-D_{2h}¹⁶ (No 62) and Pn₂1₁-C_{2v}⁹ (No 33) respectively). There were still a large number of systematic absences that could not be accounted for using either space group and it was thought that these could be explained if there happened to be special positional relationships between the atoms. The observed intensities and hkl values are listed in Appendix A.

There were no observable intensity differences between the centrosymmetrically related reflections in accordance with Friedel's Law. Intensity differences do occur for a non-centrosymmetric⁽¹⁴⁰⁾ structure

Table 30

Conditions observed for TaI_5 results

1.	h,k,l	h odd k odd no conditions h odd k even, only even $(k/2 + 1)$ observed h even k odd all absent h even k even, only even $(k/2 + 1)$ observed
2.	$0,k,l$	k even only observed
3.	$h,0,l$	h even l even only observed
4.	$h,k,0$	no condition
5.	$h,0,0$	$h = 2n$
6.	$0,k,0$	$k = 4n$
7.	$0,0,l$	$l = 2n$

with some atoms scattering X-rays anomalously. The atomic scattering factor, f , can be represented by a complex number,

$$f = f_0 + \Delta f' + i\Delta f'' \quad (8)$$

where $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of the dispersion correction. Friedel's Law breaks down when some atoms scatter the incident X-rays anomalously because the phase of $\Delta f''$ leads $(f_0 + \Delta f')$ by $\pi/2$. The effects become most significant when the wavelength of the incident X-ray beam is close to the absorption edge of the scattering atom. f'' terms for tantalum are listed in Table 31. Tantalum has a

Table 31

$\Delta f''$ dispersion correction term for Ta with MoK $_{\alpha}$ radiation

$\sin\theta/\lambda$	0.0	0.6	0.9	1.3
$\Delta f''$	7.6	7.2	6.7	6.2

large $\Delta f''$ term so that a non-centrosymmetric system should produce intensity differences between centrosymmetrically related pairs of reflections⁽¹⁴⁰⁾ and in the absence of these effects the crystal is assumed to be centric (Pnbn space group).

A positional parameter was deduced which would explain a number of non-space group absences. The expressions⁽¹⁴¹⁾ for the various structure amplitudes using the space group Pnma-D $_{2h}^{16}$ (No 62) are:-

$$h + l = 2n \quad A = 8\cos 2\pi h x \cos 2\pi k y \cos 2\pi l z$$

$$k = 2n$$

$$h + l = 2n \quad A = 8\sin 2\pi h x \sin 2\pi k y \cos 2\pi l z$$

$$k = 2n + 1$$

$$h + l = 2n + 1 \quad A = 8\sin 2\pi h x \cos 2\pi k y \sin 2\pi l z$$

$$k = 2n$$

$$h + l = 2n + 1 \quad A = 8\cos 2\pi h x \sin 2\pi k y \sin 2\pi l z$$

$$k = 2n$$

Transforming the observed indices to the standard form for Pnma, absences occur for $(h/2 + k + l)$ even, when h is even, and for $(h/2 + k + l)$ odd, when l is odd. Substitution of these results into the appropriate equations above gives the x values of $1/8$, $3/8$, $5/8$ and $7/8$ as possible general solutions.

A three dimensional Patterson projection map was calculated using a set of crystallographic programmes written by Ahmed⁽¹⁴²⁾. No peak positions in the Patterson (Table 32) could be assigned to either single Ta-Ta vectors or single I-I vectors. Assuming no atoms were at 0,0,0 the expected height for the single weight Ta-Ta vector was ~ 140 and that for the single weight I-I was ~ 80 . A number of co-ordinates were chosen, which were compatible with the Patterson map, and also gave reasonable interatomic distances, (3.5 to 4.21 Å)^(106, 143) for I-I and 3 to 3.5 Å for Ta-I. The number of possible co-ordinates was limited since placing iodine atoms on the twofold screw axis ($x = 1/4, y = 0$) or between $y = \pm 0.16$ and ± 0.25 (due to the mirror plane at $y = \pm 1/4$) gave iodine-iodine contacts below 3.5 Å. Unfortunately

Table 32

Peak positions and heights observed in TaI₅ Patterson

x	y	Peak height		
		z=0	z= $\frac{1}{2}$	z= $\frac{1}{4}$
0.0	0.0	5000	595	709
0.16	0.0	296	974	632
0.35	0.0	144	1098	533
0.5	0.0	282	2707	605
0.07	0.1	213	1129	548
0.25	0.1	1581	-	115
0.42	0.1	94	-	481
0.48	0.1	71	1276	
0.0	0.12	78	-	293
0.16	0.20	2308	-	783
0.34	0.20	210	921	744
0.5	0.20	183	990	
0.38	0.24	1996	993	
0.12	0.26	123	-	
0.09	0.30	95	97	722
0.25	0.30	150	1099	216
0.41	0.30	1880	116	722
0.0	0.40	133	1093	122
0.18	0.40	1749	59	430
0.32	0.40	129	1161	445
0.50	0.40	143	1152	120
0.10	0.50	1778	-	528
0.25	0.50	192	1076	566
0.40	0.50	3403	1402	522

when the co-ordinates were used to calculate structure factors using either Ahmed programmes or one written by Bratcher⁽¹³⁵⁾ the residual, R, ($R = (\sum(|F_o| - |F_c|) / \sum|F_o|) \times 100$) was rarely below 80%. It has been shown⁽¹⁴⁴⁾ that random co-ordinates produce residuals of 82.8% for a centrosymmetric and 58.6% for non-centrosymmetric systems.

An attempt was made to solve the Patterson map using an image seeking function⁽¹⁴⁵⁾. A computer programme was written by Dr. A.C. Macdonald and S. Sikka to apply the "minimum function" to the Patterson map. It is normal to use a single weight peak as an origin, but this is not always necessary⁽¹⁴⁶⁾. Several attempts were made to solve the structure this way but no chemically sensible image was produced. The only information obtained about the structure using this technique was that a chain structure was probably involved. Lines parallel to the y axis and 4 Å apart were obtained in many instances.

Statistical methods were used to determine the overall temperature factor, B, and the scale factor, K, necessary to bring the observed structure factors onto an absolute scale. The general value for a structure factor, F, from a system containing N different atoms is,

$$F = \sum_{j=1}^N f_j e^{i2\pi(hx_j + ky_j + lz_j)} \quad (9)$$

where f is the atomic scattering factor and x, y and z the fractional co-ordinates of the atom. The absolute value of $|F|^2$ is obtained by multiplying F by its complex conjugate and the average value, $\overline{|F|^2}$,

for all values of hkl is,

$$\overline{|F|^2} = \frac{1}{N} \sum_{j=1}^N f_j^2 \quad (10)$$

Thus it follows that:

$$\overline{|F_{\text{obs}}|^2} = K \sum_{j=1}^N f_j^2 \quad (11)$$

but for any observed structure factor the atoms are in motion (thermal) and a simple case relates the atomic scattering factor, f , to one at 0°K , f_0 , assuming Debye-Waller temperature correction, i.e.,

$$f^2 = f_0^2 e^{-(2B \sin^2 \theta) / \lambda^2} \quad (12)$$

From equations (11) and (12) it follows that if $\log_e \left\{ \frac{|F_{\text{obs}}|^2}{\sum f_j^2} \right\}$ is

plotted against $\sin^2 \theta / \lambda^2$ a straight line graph is obtained of slope $2B$ and intercept at $\sin^2 \theta / \lambda^2 = 0$ equal to $\log_e K$. This is known as Wilson's method⁽¹⁴⁴⁾.

An alternative method of obtaining values for K and B is to plot a graph of $\log_e \left\{ \frac{\overline{|F_{\text{obs}}|^2}}{\sigma_2^2} \right\}$ against $\sin^2 \theta / \lambda^2$, where σ_2^2 is the value of $\sum_{j=1}^N f_j^2$ at $\sin^2 \theta / \lambda^2$ is zero or in other words $\sigma_2^2 = \sum_{j=1}^N Z_j^2$ where Z is the

atomic number. This is known as the 'auxiliary plot'⁽¹⁴⁷⁾. This method

is supposed to have the advantage of avoiding the oscillation often observed in the Wilson plot, due to uneven numbers of reciprocal lattice points produced when a large number of atoms are in special arrays, for example large densely populated parallel sheets. The average value for K was 14.5 and for B, 1.57.

The normalised structure factors (E values) are defined by,

$$E = \frac{1}{\sqrt{e \sum_{j=1}^N f_j^2}} F \quad (13)$$

where e is a number to correct for multiplicity when F comes from sites of special symmetry.

E values were computed for the 579 observed reflections. Certain average values of E and functions of E indicate the presence or absence of a centre of symmetry⁽¹⁴⁸⁾ (Table 33) and for TaI₅ the average values

Table 33

Symmetry tests using E values

Average value	Centrosymmetric	Asymmetric	This work
E^2	1.0	1.0	1.69
E^2-1	0.968	0.886	0.992
E	0.798	0.736	0.803

of (E^2-1) and E would seem to indicate a centrosymmetric structure.

When the scale factor was altered to make the average value of $E^2=1.0$

the results for (E^2-1) and E had no meaning.

The statistical distribution of the E values is also of interest (147). Theoretically, randomly placed atoms should produce data in which there are 32.0% with E values greater than 1, 5.0% greater than 2 and 0.3% greater than 3. In this work 20.1% were greater than 1, 7.3% greater than 2 and 3.0% greater than 3.

In order to phase the E values, three strong reflections, which were linearly independent and had a large number of interactions⁽¹⁴⁹⁾, were chosen. In a centrosymmetric orthorhombic space group there are eight possible origins and the selection of the phases for the three reflections defines the origin. Even, even, even terms are determined solely by the structure and are independent of the origin chosen. The three reflections chosen were (6,5,4), (14,5,3) and (8,20,1) and all were given a positive sign. Using Karle and Karle's Σ_2 formula⁽¹⁴⁹⁾,

$$sE_h \sim s \sum_k E_k E_{h-k} \quad (14)$$

which states that the sign of a reflection (hkl) is probably the sum of the product of the signs of the reflections (h',k',l') and (h'',k'',l'') where h''-h'=h, k''-k'=k and l''-l'=l the variation in sign of the structure amplitude (which is the same as the E value) for a particular reflection can be obtained by reference to the space group tables⁽¹⁴¹⁾. The probability that a sign will be positive ($P_+(h)$) is given by⁽¹⁴⁹⁾,

$$P_+(h) \approx \frac{1}{2} + \frac{1}{2} \tanh \sigma_3 \sigma_2^{-3/2} |E_h| \sum_k E_k E_{h-k} \quad (15)$$

To allow for scale errors a computer programme was used, which sorted the possible contacts between E_h , E_k and E_{h-k} to find if all three were observed and which only accepted those contacts whose probability was greater than 0.999. In order to produce an E map ten to fifteen independent E_h values are required for each atom in the asymmetric unit. 93 reflections have been phased but no chemically sensible structure has been obtained. Various co-ordinates have been used to calculate structure factors but no R value below 60% (using all the atoms) has been obtained.

Difference fourier maps are being calculated using certain atom co-ordinates shown in the E maps in an attempt to locate the other atoms.

It is apparent that this problem is more complex than originally envisaged. There remains the possibility that the crystal is twinned and also there is some doubt as to the space group. Another crystal of TaI_5 or PaI_5 could be grown in an attempt to obtain an untwinned crystal. However, a more satisfactory procedure might be to grow crystals of $PaBr_3I_2$, which has been reported to be isostructural with PaI_5 ⁽⁵⁸⁾, since the metal atom should be more readily discernible in the Patterson vector map.

The reported structure of NbI_5 ⁽¹⁶⁸⁾, which was overlooked until this thesis was being written, may clarify some of the results obtained with PaI_5 and TaI_5 . Littke and Brauer have reported unit cell

dimensions of $a_0 = 10.58$, $b_0 = 6.58$, $c_0 = 13.88 \text{ \AA}$ and $\beta = 109.14^\circ$ for a monoclinic form of NbI_5 space group $P2_1/c$, with four molecules/unit cell. The crystal used was twinned and so no calculations of Patterson or Fourier syntheses or structure factors were possible. The structure was, however, inferred by assuming the atomic radius of iodine to be 2.0 \AA (the ionic radius of I^- is only slightly larger at 2.19 \AA) and the ionic radius of Nb^{5+} to be 0.69 \AA . The iodines were placed in the $4e$ positions with $y = \frac{1}{4}$ and respective x and z co-ordinates of 0.0 , 0.3333 ; 0.20 , 0.1333 ; 0.40 , 0.4333 ; 0.60 , 0.2333 ; 0.80 , 0.0333 and the niobium also in the $4e$ position with $x = 0.20$, $y = \frac{1}{2}$ and $z = 0.30$. These atomic positions give a hexagonal close packed iodine structure with niobium atoms in octahedral holes.

The twinned crystal showed pseudo orthorhombic character which could be interpreted on a cell with $a_0 = 6.58 \pm 0.01$, $b_0 = 13.88 \pm 0.02$ and $c_0 = 39.98 \pm 0.02$, in close agreement with the previously reported cell⁽¹⁶⁹⁾, for which the values were $a_0 = 6.54$, $b_0 = 14.01$ and $c_0 = 40.36 \text{ \AA}$, and, incidentally, very similar to the cell dimensions obtained for TaI_5 . NbI_5 was also stated to be pseudo hexagonal, that cell having the dimensions $a_0 = 4.00 \pm 0.02$ and $c_0 = 6.58 \pm 0.01$.

In view of the close similarities now observed between NbI_5 , TaI_5 and PaI_5 it is probable they have very similar structures containing dimeric M_2I_{10} units and may in fact all be isostructural.

Uranium tetrabromide

A structural change occurs in the actinide tetrabromides.

βThBr_4 (63) and PaBr_4 (62) are isostructural possessing tetragonal symmetry whereas UBr_4 (64) and NpBr_4 (65, 66) possess monoclinic symmetry and are isostructural. βThBr_4 and PaBr_4 have a crystal structure very similar to that of UCl_4 with eight bromines around each metal atom (53). Only the unit cell dimensions have been reported for UBr_4 . These were obtained from a single crystal study.

The study of the actinide (IV) oxydihalides required the preparation of UBr_4 and so some material was used to prepare a single crystal by vacuum sublimation. The crystal (0.07 x 0.05 x 0.03mm) was orientated on a precession camera with b_0 parallel to the spindle and photographs about a_0 and c_0 confirmed the reported unit cell. Weissenberg photographs indicated that the axes chosen were not the correct ones and that the symmetry was really orthorhombic with one axis very long, $\sim 50 \text{ \AA}$. The crystal appeared to be twinned very much in the same manner as that reported by I. L. Karle et al. (150) for D.L-6-Thioctic acid. This study has been suspended pending the preparation of new batches of crystals.

Chapter 5

CONCLUSIONS

No new actinide (IV) oxyfluorides have been prepared during this work and, in view of the failure of high temperature reactions between UO_2 and UF_4 ⁽¹⁵¹⁾ and PuO_2 and PuF_4 ⁽¹⁵²⁾ to produce tetravalent oxyfluorides, low temperature reactions will have to be developed. With the exception of the oxyfluorides, the reaction between antimony sesquioxide and the appropriate halide provides a general route to the actinide (IV) and (V) oxyhalides. A number of actinide (IV) oxydihalides have been successfully prepared by this reaction; some, such as NpOCl_2 and NpOBr_2 , for the first time on more than the few milligram scale. In order to prepare NpOBr_2 it was necessary to have a satisfactory, high yield reaction for the preparation of NpBr_4 and this was obtained by reacting neptunium metal and bromine at 400° . Following this work the Sb_2O_3 reaction has been successfully used by others⁽¹⁵³⁾ on the 10g scale for the preparation of UOCl_2 . Two new protactinium (V) oxyiodides have also been prepared using the Sb_2O_3 /halide reaction and it should be possible to prepare the other known protactinium (V) oxyhalides using this type of reaction. PaOBr_3 has, in fact, been successfully obtained by this route. It is also likely that the antimony sesquioxide-metal halide reaction will be useful for the preparation of oxyhalides of other elements. All the actinide (IV) oxydichlorides (Th to Np inclusive) are isostructural and the structure of one,

PaOCl_2 , was reported⁽¹²⁴⁾ whilst these studies were in progress. The structures of the actinide (IV) oxydibromides (Th to Np inclusive) and oxydiiodides (Th and Pa) are unknown, although each group forms an isostructural series. Infrared studies, however, indicate that these compounds are likely to possess polymeric bridged structures. PaOI_3 and PaO_2I also appear, on the basis of their infrared spectra, to possess oxygen bridged structures. Single crystals of these actinide oxybromides and oxyiodides will not be easy to prepare as no suitable solvent has yet been found and, with the exception of PaO_2I which has not been investigated, all the compounds are thermally unstable and cannot be sublimed.

The two new neptunium (V) oxyfluorides, NpOF_3 and ' NpO_2F ' have been prepared but only in a microcrystalline form. If single crystals are to be obtained for structural studies different preparative methods will have to be used. No new protactinium (V) oxyfluorides have yet been definitely established and further work on this system is obviously necessary. For example, it is planned to investigate the reaction between bromine trifluoride and the known protactinium (V) oxyhalides (apart from Pa_2OF_8). In addition, Pa_2OF_8 has been reported to thermally decompose⁽⁴⁷⁾ to PaF_5 and an unidentified residue and it is intended to further investigate this reaction using a metal apparatus currently under construction. The reaction products obtained from the interaction of hydrogen fluoride or hydrofluoric acid with protactinium (V) oxides have been fairly well characterised but the exact composition of the

Pa_2F_9 (formed at 500°C) has not been established. Thus the X-ray powder diffraction pattern shows it to be isostructural with U_2F_9 but analytical results indicate that the composition is Pa_4F_{17} (154). It would appear that improved dry box conditions are necessary for reactions involving the preparation of PaF_5 , for example, from PaCl_5 .

As may be seen the aims outlined in Chapter 2 have not all been achieved. The only neptunium (V) fully fluorinated complex obtained pure is Na_3PaF_8 but the use of a sapphire boat in place of the nickel one seems to be the solution to the successful preparation of other compounds of this type. The structures of Cs_2PaF_7 and Na_3PaF_8 have been examined and, while the former compound appears to have the nine co-ordinated K_2PaF_7 structure, Na_3PaF_8 is an example of the previously unknown cubic co-ordination (138). The apparent inconsistencies in the crystallographic results for K_3PaF_8 , Rb_3PaF_8 and Cs_3PaF_8 (Chapter 4), when positional parameters for the various atoms are taken into account, show that further structural work is necessary in this field. It will be interesting to see whether the expected cubic arrangement of the fluorine atoms occurs with K_3PaF_8 , Rb_3PaF_8 and Cs_3PaF_8 and also whether the structures of the corresponding niobium and tantalum compounds confirm that the cubic arrangement is energetically unfavourable in the absence of f orbital participation. Others have recently reported the structure of RbPaF_6 (89): each protactinium is surrounded by eight fluorine atoms, half of which are bridging. The Pa-F bond lengths are $2.08 \overset{\circ}{\text{A}}$ and $2.35 \overset{\circ}{\text{A}}$ for unshared and shared fluorines respectively.

It might be possible to overcome the problems encountered with twinned crystals of UBr_4 , PaI_5 and TaI_5 by growing crystals from a solvent system rather than by vacuum sublimation. The structural problems with the pentaiodides associated with the similarity in intensity of metal-metal, metal-iodine and iodine-iodine vectors would also be reduced if the structure of PaBr_3I_2 were investigated.

Finally, to bring the short review in Chapter 2 up-to-date, it seems worthwhile to mention some preparative achievements reported by others during the past three years. AmO_2F_2 ⁽¹⁵⁵⁾ has been prepared by evaporation of an americium (VI) solution in hydrofluoric acid and treatment of the residue with anhydrous hydrogen fluoride. There have been two reports^(156, 157) of new uranium (VI) oxyfluorides, one has a composition range $\text{UO}_{1.54}\text{F}_{2.92}$ to $\text{UO}_{1.78}\text{F}_{2.44}$, the other is $\text{U}_3\text{O}_5\text{F}_8$. β UF_5 has been prepared⁽¹⁵⁸⁾ by fluorine oxidation of suspensions of UF_4 in liquid anhydrous hydrogen fluoride but no oxidation of NpF_4 was observed under similar conditions. In the presence of caesium fluoride, however, oxidation did occur and CsNpF_6 was obtained; in the absence of fluorine, a suspension of CsNpF_6 in liquid anhydrous hydrogen fluoride disproportionated. It may, however, be possible to prepare NpF_5 by reduction of NpF_6 with HBr , analogous to the reported⁽¹⁵⁹⁾ reaction of UF_6 for the preparation of UF_5 .

The electronic absorption spectrum of gaseous PuCl_4 , obtained⁽¹⁶⁰⁾ by the reaction between PuCl_3 and Cl_2 at 925° , has been recorded. The preparation of the first protactinium (III) compound, PaI_3 ⁽¹⁶¹⁾, has

been reported. It is claimed that PaI_5 is thermally decomposed at 350° under a pumping vacuum. The reaction was only performed on a one milligram sample and the compound identified by its X-ray powder diffraction pattern, which showed it to be isostructural with CeI_3 .

A thorium (III) compound, $\text{ThOF}^{(162)}$, has also been observed to form when thorium metal, ThO_2 and ThF_4 are heated at 1200° for four days. The product is said to be neither air sensitive nor hygroscopic and forms a continuous solid solution with ThO_2 . A number of higher actinide (III) halides have been prepared, for example, the curium halides⁽¹⁶³⁾ and the berkelium and californium halides and oxyhalides⁽¹⁶⁴⁻¹⁶⁷⁾. Crystallographic properties have been reported for $\text{CmCl}_3^{(171)}$, $\text{CfCl}_3^{(172)}$, $\text{BkOCl}^{(173)}$ and $\text{CfOCl}^{(174)}$. The first berkelium (IV) halide, BkF_4 , has just been reported⁽¹⁷⁵⁾; it is isostructural with UF_4 .

Appendix A

Observed and calculated structure factors for Na_3PaF_8

h k l	$ F_{\text{obs}} $	$ F_{\text{calc}} $	h k l	$ F_{\text{obs}} $	$ F_{\text{calc}} $
0 0 4	53.37	54.68	8	59.37	65.20
6	50.42	51.99	10	50.53	49.51
8	80.98	91.46	12	49.44	46.43
10	57.41	58.77	14	21.83	37.70
12	60.14	54.76	16	42.24	39.60
14	46.28	42.95	0 5 1	57.30	52.29
16	45.62	45.42	3	41.15	44.67
18	32.20	37.95	5	43.11	46.49
20	37.22	36.29	7	44.53	49.94
0 1 3	63.63	66.64	9	38.42	44.10
5	60.46	64.71	11	33.18	37.83
7	62.10	63.04	13	23.36	36.96
9	54.24	54.99	15	28.70	36.35
11	49.44	48.61	0 6 0	46.38	48.54
13	47.59	45.48	2	40.93	43.54
15	40.38	42.38	4	51.30	57.17
17	41.69	38.68	6	42.35	45.61
19	29.80	35.39	8	36.67	43.95
0 2 0	67.23	50.39	10	31.76	36.07
2	79.67	61.47	12	30.78	40.76
4	125.40	125.20	0 7 1	31.65	38.92
6	74.11	69.76	3	34.38	41.46
8	61.56	60.13	5	30.67	39.18
10	45.18	46.02	7	29.03	34.89
12	68.43	57.52	0 8 0	39.51	42.00
14	58.50	44.97	2	26.52	36.37
16	47.67	43.03	4	33.07	37.63
18	41.15	36.14	1 1 2	112.20	106.06
0 3 1	61.12	58.28	4	73.45	67.62
3	63.08	67.78	6	86.55	85.89
5	55.44	58.57	8	59.59	56.55
7	40.16	47.59	10	70.94	64.02
9	42.02	48.92	12	55.77	47.94
11	53.04	49.16	14	59.70	49.85
13	42.35	43.54	16	40.27	40.33
15	38.31	38.61	18	33.40	39.59
0 4 0	102.59	95.13	1 2 1	72.80	65.62
2	51.08	59.10	3	73.34	68.45
4	52.28	56.00	5	69.96	61.49
6	42.24	45.68	7	59.81	53.68

1 2 9	54.24	51.64	2 2 2	88.19	68.26
11	55.33	49.27	4	74.98	58.15
13	54.02	44.56	6	58.83	48.50
15	45.18	40.34	8	75.31	75.77
17	33.83	37.36	10	62.86	53.83
1 3 0	74.65	62.32	12	61.45	50.22
2	78.58	85.07	14	51.08	40.07
4	59.48	57.89	16	48.46	42.30
6	64.61	70.95	2 3 1	71.05	61.27
8	52.39	52.18	3	60.46	50.99
10	64.50	58.44	5	57.19	53.05
12	43.22	44.44	7	54.57	56.44
14	42.89	45.42	9	55.01	49.11
16	32.52	38.10	11	50.10	41.93
18	32.89	37.53	13	41.26	40.59
1 4 1	55.99	55.90	15	40.60	39.36
3	52.39	52.20	17	51.30	35.99
5	45.95	51.31	2 4 0	65.70	54.91
7	45.95	50.76	2	59.48	50.27
9	45.51	46.68	4	82.95	76.85
11	43.22	42.20	6	50.75	54.67
13	39.95	39.80	8	50.75	50.94
15	44.75	37.71	10	39.95	40.11
17	34.05	34.86	12	51.30	47.61
1 5 0	64.28	49.76	14	45.62	40.14
2	72.25	61.86	16	33.51	37.99
4	54.46	48.78	2 5 1	51.73	46.00
6	70.40	57.03	3	62.97	50.93
8	50.20	44.02	5	57.41	46.79
10	46.82	46.84	7	49.11	39.79
12	37.76	39.38	9	45.07	40.37
14	39.07	40.40	11	44.97	41.76
1 6 1	49.99	43.98	13	34.05	37.90
3	49.00	44.36	2 6 0	64.94	56.93
5	42.56	42.81	2	53.48	44.66
7	47.59	40.10	4	60.25	45.72
9	42.24	38.63	6	49.66	38.32
11	35.14	37.59	8	59.37	46.85
1 7 0	40.27	40.23	10	46.49	40.23
2	45.29	46.05	12	34.82	37.99
4	39.29	39.00	2 7 1	48.13	39.57
6	42.24	42.37	3	35.58	36.44
8	34.49	36.76	5	48.46	36.70
1 8 1	34.49	35.42	7	42.46	38.35
3	30.67	34.68	9	44.31	35.66
5	35.91	34.06	11	35.91	31.47

2 8 0	38.42	37.39	5	33.51	40.13
2	33.51	34.24	7	44.75	42.54
4	48.13	39.04	9	37.76	39.24
6	34.82	34.75	4 6 0	42.13	42.43
3 3 0	62.65	54.02	2	39.62	38.28
2	70.72	70.28	4	45.73	46.21
4	53.37	53.82	6	41.26	39.79
6	63.52	65.26	8	39.62	38.59
8	40.71	46.89	4 7 1	34.71	34.64
10	51.30	50.05	3	30.45	36.17
12	27.70	42.06	5	31.21	34.88
14	37.98	43.84	4 8 0	37.76	36.01
3 4 1	46.17	48.39	2	26.74	32.43
3	50.42	52.27			
5	46.17	48.56			
7	36.45	42.05			
9	40.27	41.80			
11	38.96	42.64			
13	36.13	38.95			
3 5 0	50.42	46.76			
2	56.21	56.25			
4	44.64	44.13			
6	54.02	48.86			
8	42.13	42.03			
10	45.62	46.11			
12	29.90	36.89			
3 6 1	39.07	42.01			
3	39.73	39.37			
5	42.56	39.08			
7	39.07	40.23			
9	37.65	37.80			
3 7 0	38.64	37.39			
2	40.60	41.88			
4	40.16	37.14			
6	41.47	40.96			
8	30.56	34.34			
3 8 1	30.34	33.04			
3	43.44	33.55			
4 4 0	66.79	65.25			
2	47.26	48.50			
4	49.55	48.99			
6	37.54	40.27			
8	51.84	51.56			
10	40.05	43.31			
12	43.44	40.50			
4 5 1	48.89	43.97			
3	39.84	39.79			

Intensity results for TaI₅*

h	k	l	I _{obs}	h	k	l	I _{obs}	h	k	l	I _{obs}
2	5	0	2483	16			912	16			1789
	7		650	18			2053	18			1416
	9		4341	20			720	20			8556
	11		1388	22			1714	24			1775
	13		3565	24			632	26			3076
	15		1780	10	3	0	1076	28			681
	17		3509		5		2306	30			1356
	19		1203		9		410	1	6	1	427
	23		1554		13		2526		7		54
	25		1399		15		1846		8		777
	27		1955		17		2031		9		1130
4	0	0	3450		23		780		10		786
	4		1615	12	0	0	10436		11		86
	6		898		4		1533		12		254
	8		3078		8		633		13		665
	10		3579		10		9767		14		724
	12		1813		14		2025		15		247
	14		593		16		1164		17		335
	18		3486		18		1035		18		515
	20		2375		20		3149		19		441
	22		2839	14	1	0	3546		23		429
	32		1011		9		4294		24		379
	34		1087		11		1327	2	5	1	5304
6	1	0	2281		13		1195		7		172
	3		911		17		748		9		377
	5		17540		19		2011		11		267
	9		4319		21		720		13		142
	11		216	16	8	0	1224		15		3952
	13		1337		10		580		17		485
	15		15705		12		853		19		335
	19		3049		20		1388		21		255
	21		2683	18	5	0	4808		25		1468
	23		563		15		2253	3	4	1	713
	25		2783	20	4	0	2158		5		804
	33		1967		6		1609		6		225
8	4	0	5342		14		1484		7		62
	6		3256	0	6	0	489		8		584
	8		1605		8		1681		9		776
	12		953		10		19060		10		583
	14		4622		14		5160		12		270

*indexed for space group Pnma

3	13	1	367	8	0	1	5169	10		191	
	14		477		4		289	14	5	1	2798
	15		214		8		113		15		1586
	17		397		10		4769	15	0	1	195
	18		478		12		278	16	0	1	1040
	22		275		14		466	18	1	1	592
	23		219		18		386	20	0	1	493
4	0	1	4232		20		2592	0	8	2	1941
	6		435	9	0	1	709		10		3831
	10		4554		1		310		12		1481
	12		284		3		319		14		386
	16		429		4		508		16		380
	20		2435		5		448		18		1465
5	0	1	1050		6		115		20		3839
	1		690		8		333		22		2492
	3		436		9		435		32		1343
	4		1034		10		318		34		1184
	5		1128		13		368	2	9	2	1619
	6		410		14		331		13		1016
	8		548		18		406		15		2701
	9		833	10	1	0	351		17		156
	10		473		5		1515		19		903
	12		150		11		465		21		823
	13		732		15		1807		23		696
	14		894	11	0	1	746		25		435
	15		232		1		484	4	6	2	786
	18		452		3		133		8		725
6	1	1	634		4		362		10		4939
	5		310		5		416		14		2191
	9		513		6		142		18		648
	11		263		8		352		20		1807
7	0	1	979		9		520		24		930
	1		564		10		324		26		471
	3		328		13		303	6	1	2	1191
	4		891		14		317		3		668
	5		885	12	0	1	389		5		3820
	6		370		4		732		7		375
	8		412		6		578		9		907
	9		690		14		612		11		629
	10		462	13	0	1	485		13		1458
	12		172		1		486		15		2584
	13		641		4		333		17		1221
	14		583		5		395		23		1008
	15		257		8		301		25		1962
	18		429		9		371		27		1343

8	0	2	3990	2	5	3	4391	5	288
	4		381		9		249	9	595
	8		733		11		305	13	165
	10		2786		13		319	7 0 3	777
	14		222		15		3146	1	471
	16		806		25		1241	4	325
	18		898	3	4	3	1176	5	339
	20		846		5		1128	7	291
	26		933		6		674	8	616
10	1	2	1677		8		665	9	764
	3		171		9		1208	10	492
	5		5658		10		810	13	293
	9		2404		11		358	17	445
	11		166		12		173	18	549
	13		425		13		729	19	249
	15		2304		14		913	8 0 3	5464
12	0	2	1813		15		386	4	165
	4		921		17		381	10	3631
	6		676		18		545	14	464
	8		564		19		364	16	370
	10		1517		21		579	20	1728
	12		473		24		296	9 0 3	834
	14		219	4	0	3	3125	1	837
	18		1030		6		316	3	182
	20		1213		10		4195	4	767
14	5	2	1033		12		274	5	904
	13		406		16		489	6	346
	15		520		20		2314	8	428
16	0	2	3958	5	0	3	1069	9	784
	4		1649		1		604	10	525
	8		747		3		76	11	183
	12		2327		4		404	13	404
	16		1530		5		432	14	566
18	1	2	544		6		92	18	606
1	6	3	259		7		133	10 1 3	351
	8		282		8		713	5	2571
	9		421		9		863	11	596
	10		234		10		688	15	2078
	12		377		12		241	11 0 3	392
	13		889		13		363	3	171
	14		802		14		334	4	537
	15		370		16		191	5	548
	16		171		17		475	8	387
	17		430		18		651	9	466
	18		396		19		461	13	466
	24		872	6	1	3	400	14	406

11	18	3	386		8	1199		13	224		
12	0	3	374		10	755		14	390		
	4		645		12	598		17	184		
	6		402		18	758		18	592		
13	4	3	284		20	430		19	423		
	5		361		22	767		20	225		
14	5	3	3058	5	1	4	170	2	0	5	201
	15		1546		2		153		5		3943
15	0	3	584	6	1	4	709		15		2669
16	0	3	729		3		190	3	0	5	200
17	0	3	397		5		7901		4		132
0	2	4	39		7		134		5		257
	4		1616		9		1857		8		240
	6		122		13		498		9		265
	8		543		15		4549		10		109
	10		8678		19		647		13		189
	14		1774		21		564		17		254
	16		565		25		496		18		340
	18		356	8	4	4	1927	4	0	5	3706
	20		3368		6		1450		10		3550
	26		873		8		636		20		947
1	3	4	91		12		215	5	0	5	480
	4		178		14		929		1		402
	5		271		18		445		2		292
	6		215	10	3	4	417		3		522
2	1	4	1103		15		715		4		1174
	3		612	12	0	4	7749		5		1254
	5		445		4		757		6		449
	7		155		10		5433		9		466
	9		1568		14		1096		10		125
	11		328		20		1190		12		194
	13		1240	14	1	4	1753		13		520
	15		461		9		1627		14		668
	17		676	18	5	4	1781		15		178
	19		322	1	0	5	315	6	1	5	257
	23		745		1		317		9		255
	27		720		2		132	7	0	5	569
3	3	4	144		4		408		1		404
	4		145		5		402		3		508
	5		115		6		239		4		1089
	6		65		7		163		5		1002
	7		97		8		959		6		575
	8		81		9		1454		9		372
4	0	4	836		10		1009		10		295
	4		770		11		261		12		332
	6		381		12		205		13		704

7	14	5	746	14	5	6	492
	15		395	16	0	6	842
8	0	5	3979		10		731
	10		2705				
	20		813				
10	5	5	1768				
	15		788				
11	0	5	813				
	1		449				
	4		291				
	8		386				
	9		532				
	10		413				
12	4	5	514				
13	0	5	550				
	1		551				
	8		460				
	9		550				
	10		485				
14	5	5	1651				
0	10	6	1637				
	12		299				
	18		481				
	20		627				
2	9	6	634				
	13		337				
	15		1002				
	19		298				
4	10	6	2314				
	14		936				
6	1	6	431				
	3		254				
	5		1363				
	9		397				
	11		152				
	13		579				
	15		776				
	17		443				
8	0	6	1893				
	10		901				
10	1	6	625				
	5		2647				
	9		915				
	15		740				

Appendix B

Hexavalent curium

The results of solvent extraction and ion exchange studies with ozonised solutions of curium (III) have been interpreted⁽¹⁷⁶⁾ as evidence for oxidation of curium (III) to curium (VI).

Trace amounts of ^{242}Cm ($t_{\frac{1}{2}} 162.5\text{d}$) were used by Akatsu but, since the results of tracer scale studies can be misleading, milligram amounts of ^{242}Cm ($t_{\frac{1}{2}} 17.6\text{yr.}$) were used during the present study. The use of the longer-lived curium isotope should also present more favourable conditions for the formation of higher valency states, as was the case with CmF_4 ^(41, 42). A saturated extractant, diisooctylamine, was used instead of Amberlite LA1, because of the known reactivity of ozone with olefinic double bonds, and comparable extraction results were obtained. However, examination of the absorption spectrum of the aqueous phase throughout the ozonisation revealed only the maxima⁽¹⁷⁷⁾ at 375.4, 381.2 and 396.5 μ associated with curium (III).

Thin layer chromatography⁽¹⁷⁸⁾ was used to examine the stability of diisooctylamine during ozonolysis. It was found that the amine was completely destroyed by the ozone in the aqueous phase and most of the decomposition products were amine oxides. The similarity in the extraction of hexavalent actinides with the original amine to that of the ozonised curium (III) with some amine decomposition products was thus purely fortuitous.

Ozonised De Acidite FF ion exchange resin similarly showed

considerably increased adsorption of curium(III) compared to the un-ozonised resin. However, tracer iron (^{59}Fe) was also adsorbed on the ozonised resin.

The above results led to the conclusion that curium (III) was not oxidised by ozone in aqueous media and results from an independent investigation⁽¹⁷⁹⁾ confirmed these conclusions.

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Preparation, Crystallographic Properties, and Infrared Spectra of Quadri-valent Oxyhalides of Thorium, Protactinium, Uranium, and Neptunium

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Preparation, Crystallographic Properties, and Infrared Spectra of Quadrivalent Oxyhalides of Thorium, Protactinium, Uranium, and Neptunium

By K. W. Bagnall,† D. Brown, and J. F. Easey, Chemistry Division, Building 220, A.E.R.E., Harwell, Didcot, Berkshire

Actinide(IV) oxydihalides of the type MOX_2 ($M = \text{Th, Pa, U, and Np}$; $X = \text{Cl, Br, and I}$) have been prepared by reaction of the appropriate tetrahalide with antimony sesquioxide, Sb_2O_3 , at 400° in a vacuum. Unit cell parameters are reported for the isostructural series of oxydichlorides which possess orthorhombic symmetry, space-group *Pbam*. Infrared spectra have been recorded for all the compounds and the results are compared with previous assignments for $UOCl_2$. Metal-oxygen vibrations occur in the region $600\text{--}225\text{ cm}^{-1}$.

THORIUM(IV) and uranium(IV) oxydihalides, MOX_2 ($M = \text{Th and U}$; $X = \text{Cl and Br}$), and thorium oxydiiodide have previously been prepared, for example, by interaction of the appropriate dioxide and tetrahalide¹⁻⁴ or, less satisfactorily, by thermal decomposition⁵ of the hydrated tetrahalides. We recently reported⁶ the preparation of protactinium(IV) oxydichloride and oxydibromide by reaction of antimony sesquioxide with the tetrahalides



Since the infrared spectra of these protactinium(IV) oxyhalides were inconsistent with the assignments of Selbin and Schober⁷ for $UOCl_2$, we have studied the preparation of other quadrivalent actinide oxydihalides using both the antimony sesquioxide-metal tetrahalide and metal dioxide-metal tetrahalide methods and have recorded infrared spectra for a series of oxydichlorides, oxydibromides, and oxydiiodides. The preparation and properties of neptunium(IV) oxydichloride and oxydibromide were of particular interest since the former had previously been observed⁸ only in microgram amounts as a residue from the sublimation of neptunium tetrachloride and no preparative details were available⁹ for $NpOBr_2$. In addition, unit-cell parameters are reported for the isostructural series of oxydichlorides $MOCl_2$ ($M = \text{Th--Np inclusive}$).

All the known actinide tetrachlorides and tetrabromides MX_4 ($M = \text{Th--Np inclusive}$; $X = \text{Cl and Br}$), and thorium tetraiodide, react with antimony sesquioxide at about 150° in a vacuum. The antimony trihalides so produced sublime out of the reaction zone at this temperature but in order to obtain reasonably crystalline oxyhalides it is necessary to heat the product for several hours at 450° *in vacuo*. Neptunium(IV) oxydichloride was also obtained during attempts to prepare neptunium pentachloride or neptunium(V) oxychlorides by reaction of neptunium(V) hydroxide with thionyl chloride below 200° in an apparatus similar to that

described¹⁰ for the preparation of protactinium pentachloride. However, this reaction is less satisfactory for the preparation of $NpOCl_2$ because at higher temperatures further chlorination occurs and neptunium tetrachloride is the major product. The quadrivalent oxydichlorides and oxydibromides form two isostructural series of compounds; the partial X-ray powder diffraction pattern for $ThOCl_2$ is given in Table 1 which lists observed and calculated values of $\sin^2 \theta$ and visually estimated intensities. Following the recent determination¹¹ of the structure of $PaOCl_2$ our X-ray powder diffraction results have been interpreted on the basis of the reported orthorhombic unit cell, space-group *Pbam*, and the resulting cell parameters are listed in Table 2. The effect of the actinide contraction is illustrated by the decreasing cell parameters with increasing atomic number of the metal atoms. The partial X-ray powder diffraction pattern of $NpOBr_2$ (Table 3) can be compared with data⁶ for $PaOBr_2$. The oxydibromides possess low symmetry and the results have not been interpreted.

Although the reaction between a particular metal dioxide and the corresponding tetrahalide constitutes an excellent preparative method for the quadrivalent oxydihalides the antimony sesquioxide-metal tetrahalide method described here provides an attractive alternative. In particular it obviates the necessity of preparing 'reactive' dioxide samples and this is of particular importance in the case of protactinium because the only satisfactory preparation of PaO_2 presently available consists of hydrogen reduction of the pentoxide at 1600° . Not unnaturally, the dioxide so obtained is not sufficiently reactive to yield pure oxydihalides.⁶

Few investigations of the infrared spectra of quadrivalent actinide oxyhalides have been reported. Scaife *et al.*³ state that no band is observed in the spectrum of $ThOI_2$ above 600 cm^{-1} whilst Prigent¹² has reported two bands, $500s,b$ and $546sh.\text{ cm}^{-1}$ for $UOBr_2$. Selbin and Schober⁷ have reported a detailed study of the spectra of various hydrated uranium(IV) hydroxychlorides such as

⁷ J. Selbin and M. Schober, *J. Inorg. Nuclear Chem.*, 1966, **28**, 817.

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³ D. E. Scaife, A. G. Turnbull, and A. W. Wylie, *J. Chem. Soc.*, 1965, 1432.

⁴ M. V. Smirnov and L. E. Ivanovskii, *Zhur. neorg. Khim.*, 1956, **1**, 1843.

⁵ E. Chauvenet, *Ann. Chim. Phys.*, 1911, **23**, 425.

⁶ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 719.

$U(OH)Cl_3 \cdot xH_2O$ ($x = 1.5$ and 3.0) and of samples of composition $UO_{1.15}Cl_{2.1}$, the last obtained by thermal decomposition of the hydrates. The last compound,

Bands in similar positions to the last two were also recorded in the spectra of the various hydrated hydroxytrichlorides and assigned $\nu(U-O)_{OH}$. Although it is not clear from their discussion whether the 555 and 515 cm^{-1} bands for $UO_{1.15}Cl_{2.1}$ are also considered to be $(U-O)_{OH}$ vibrations Selbin and Schober state that a sample of $UOCl_2$ prepared by heating together uranium tetrachloride and dioxide at 700° gave a strong band at 730 cm^{-1} .

Our results show that the infrared spectra of anhydrous $UOCl_2$ and other actinide(IV) oxydihalides, including $ThOF_2$,¹³ exhibit no absorption band in the region of 730 cm^{-1} . In fact there is no band above 600 cm^{-1} in the spectra of $UOCl_2$ and $NpOCl_2$ prepared either by the antimony sesquioxide method or by interaction of the appropriate tetrachlorides and dioxides. The spectra of the oxydichlorides and oxydibromides of thorium to neptunium inclusive are very similar between 600 and 225 cm^{-1} , the only differences being the appearance of

TABLE 1
Partial X-ray powder diffraction results for thorium oxydichloride

$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	h, k, l	I (est.)	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	h, k, l	I (est.)
0.0072	0.0073	0,2,0	w+	0.1107	0.1111	3,7,0	w-
0.0097	0.0097	1,2,0	s		0.1109	2,6,1	
0.0100	0.0099	2,0,0	s	0.1139	0.1138	5,3,1	vw-
0.0172	0.0172	2,2,0	w	0.1168	0.1161	0,8,0	vw-
0.0188	0.0188	1,3,0	w+	0.1187	0.1185	1,8,0	w
0.0262	0.0262	2,3,0	w	0.1204	0.1206	4,5,1	w-
0.0288	0.0290	0,4,0	w+	0.1232	0.1232	3,6,1	w
0.0357	0.0357	0,0,1	w+		0.1230	7,1,0	
0.0387	0.0386	3,3,0	w+	0.1265	0.1265	6,1,1	vw-
0.0390	0.0389	2,4,0	w-		0.1265	5,4,1	
0.0397	0.0396	4,0,0	vw-	0.1320	0.1320	6,2,1	vw-
0.0431	0.0430	0,2,1	w	0.1345	0.1344	6,5,0	vw-
0.0455	0.0455	1,2,1	w		0.1344	2,7,1	
0.0468	0.0458	2,0,1	w	0.1405	0.1405	4,6,1	w+
0.0474	0.0469	4,2,0	s	0.1427	0.1428	5,5,1	m
	0.0474	2,1,1			0.1428	0,0,2	
0.0527	0.0528	2,2,1	vw-		0.1536	6,4,1	
0.0545	0.0545	1,3,1	w	0.1538	0.1542	6,6,0	w-
0.0553	0.0553	2,5,0	w+		0.1542	1,8,1	
0.0596	0.0598	3,1,1	w	0.1565	0.1568	2,9,0	w-
0.0645	0.0648	0,4,1	m	0.1583	0.1583	8,0,0	w-
	0.0676	3,5,0			0.1587	7,1,1	
0.0673	0.0672	1,4,1	m	0.1616	0.1615	1,3,2	w-
	0.0678	1,6,0			0.1616	2,8,1	
0.0691	0.0685	4,4,0	w	0.1643	0.1641	7,2,1	w-
	0.0690	5,2,0			0.1641	4,7,1	
0.0746	0.0746	2,4,1	m	0.1690	0.1690	2,3,2	w-
0.0770	0.0771	4,1,1	m	0.1690	0.1691	3,9,0	w-
0.0780	0.0781	5,3,0	w	0.1732	0.1732	7,3,1	w
0.0828	0.0825	4,2,1	w+		0.1813	3,3,2	
0.0838	0.0836	1,5,1	w-	0.1813	0.1813	0,10,0	w+
0.0848	0.0849	4,5,0	w+		0.1816	2,4,2	
0.0876	0.0871	3,4,1	w-	0.1901	0.1895	4,2,2	w+
	0.0876	3,6,0			0.1900	6,6,1	
0.0890	0.0890	6,0,0	w-	0.1921	0.1925	2,9,1	w-
0.0908	0.0908	6,1,0	w-	0.1960	0.1957	8,1,1	w-
	0.0908	5,4,0		0.1987	0.1986	4,3,2	w
0.0970	0.0968	6,2,0	w+		0.2102	8,3,1	
0.0989	0.0994	5,1,1	w+	0.2106	0.2103	3,5,2	w-
	0.0988	2,7,0			0.2105	1,6,2	
0.1011	0.1010	0,6,1	w+	0.2111	0.2113	4,4,2	w-
0.1034	0.1033	3,5,1	w+	0.2193	0.2194	1,10,1	
	0.1035	1,6,1		0.2224	0.2221	4,9,1	w-
	0.1043	4,4,1			0.2229	8,4,1	
0.1046	0.1048	4,6,0	w+	0.2304	0.2302	3,6,2	vw-
	0.1048	5,2,1		0.2329	0.2335	6,1,2	w-

s, Strong; m, medium; w, weak.

TABLE 2
Crystallographic properties* of the actinide oxydichlorides

	Lattice parameters (Å)		
	a_0	b_0	c_0
$ThOCl_2$	15.494	18.095	4.078
$PaOCl_2$	15.332	17.903	4.012
$UOCl_2$	15.255	17.828	3.992
$NpOCl_2$	15.209	17.670	3.948
Standard deviations	± 0.008	± 0.008	± 0.002

* All possess orthorhombic symmetry, space-group $Pbam$

which contained traces of residual OH^- and H_2O , gave medium-intensity bands at 736 and 719 cm^{-1} (assigned to $O-U-O$ modes) and strong bands at 555 and 515 cm^{-1} which were assigned to $U-O$ stretching vibrations.

TABLE 3

Partial X-ray powder diffraction results for neptunium oxydibromide

$\sin^2 \theta$ (obs.)	I (est.)	$\sin^2 \theta$ (obs.)	I (est.)
0.0094	s+	0.0358	m
0.0178	w	0.0910	m
0.0247	w	0.0930	m
0.0273	w	0.0971	w
0.0366	s	0.0985	w+
0.0443	w+	0.1010	w
0.0462	w	0.1025	w+
0.0482	m+	0.1049	w-
0.0521	w	0.1116	w+
0.0546	w+	0.1172	w
0.0600	w-	0.1274	w-
0.0614	w-	0.1307	w-
0.0642	w	0.1361	w
0.0665	m+	0.1421	w-
0.0737	m+	0.1482	s-
0.0762	m+	0.1572	w
0.0802	m+	0.1675	w
0.0813	m+		

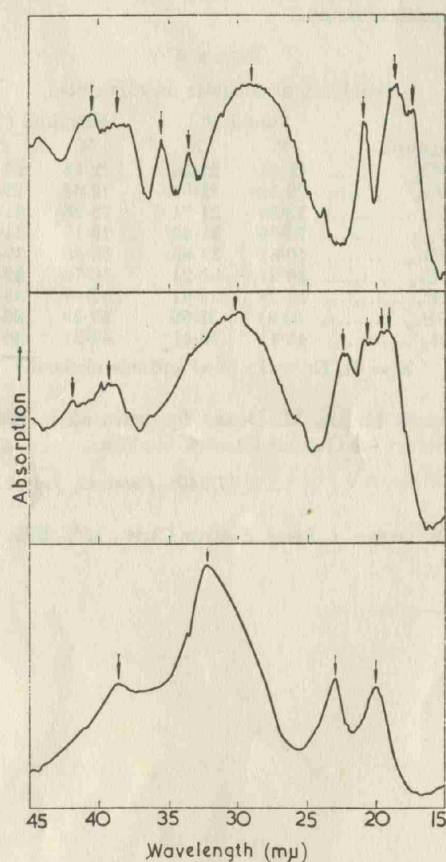
two weak bands in the spectra of certain of the oxydichlorides and a shift of band positions to longer wavelengths with increasing atomic number of both actinide element and halogen (Table 4). We have tentatively assigned the two weak bands around 290 and 280 cm^{-1} to metal-chlorine stretching vibrations; the strong, broad band which is common to all the oxydichloride spectra is centred around 300 cm^{-1} for $UOCl_2$ and this may account for the absence of the two weak bands from the spectrum of this compound. Certain of the spectra are illustrated in the Figure. In view of the close similarity in the positions of the remaining bands in the spectra of the oxydichlorides and oxydibromides we have assigned all of these to metal-oxygen vibrations. The large difference in the position of $M-Cl$ and $M-Br$ vibrational frequencies (*ca.* 260 and 180 cm^{-1} , respectively) of the quadrivalent actinide hexahalogeno-complexes¹⁴ suggests that it is unlikely that any of the bands we have observed, apart from, possibly, the two

¹³ D. Brown and J. F. Easey, to be published.

¹⁴ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 243.

weak ones discussed above, can be associated with metal-halogen vibrations. In addition, metal-iodide vibrations are not likely to be observed above 225 cm^{-1} and therefore all four bands in the spectra of ThOI_2 and PaOI_2 are also assigned to metal-oxygen vibrational modes.

The spectra show that actinide compounds of the type MOX_2 do not contain discrete MO^{2+} groups. Protactinium-oxygen stretching vibrations are also observed below 600 cm^{-1} for the quinquevalent oxychlorides,¹⁰ oxybromides,^{15,16} and oxyiodides,¹⁶ and recent structure



Infrared spectra of, from top to bottom, ThOCl_2 , ThOBr_2 , and PaOI_2

determinations have shown that both PaOBr_2 ¹⁷ and PaOCl_2 ¹¹ possess extensively oxygen-bridged structures with certain oxygen atoms co-ordinated to three or four protactinium atoms. Structural data are not available for actinide(IV) oxydibromides but the above infrared results suggest that they also possess oxygen-bridged, polymeric structures.

It is difficult to reconcile the observations of Selbin and Schober,⁷ namely that anhydrous UOCl_2 prepared from

¹⁵ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 262.
¹⁶ D. Brown, J. F. Easey, and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 1698.

¹⁷ D. Brown, T. J. Petcher, and A. J. Smith, *Nature*, in press.

¹⁸ H. W. Dunn, U.S. Report ORNL-2092, 1956.

¹⁹ S. A. Shchukarev, I. V. Vasil'kova, N. S. Martynova, and Yu. G. Mal'tsev, *Zhur. neorg. Khim.*, 1958, **3**, 2647.

the tetrachloride and dioxide possesses a strong band at 730 cm^{-1} , with our results for quadrivalent actinide oxydihalides. Unfortunately they do not report crystallographic data for their compound nor do they state whether the bands around 500 cm^{-1} occurred in the

TABLE 4

Metal-oxygen and metal-halogen stretching vibrations in the infrared spectra of quadrivalent actinide oxydihalides

Compound	Colour	$\nu_{\text{M-O}}$ (cm^{-1})	$\nu_{\text{M-X}}$ (cm^{-1})
ThOCl_2	White	571sh, 540s, 481s, 344s,b, 259m, 246m	298w, 282w
PaOCl_2	Yellow-green	555sh, 523s, 471s, 256sh, 243m	290w, 278w
UOCl_2	Green	555sh, 521s, 455m, 259m, 242m	300s, b
NpOCl_2	Light brown	555s, 529s, 460m, 255m, 240m	335s, b, 306w
ThOBr_2	White	543s, 529s, 495s, 333s,b, 256m, 243vw	463s, 243vw
PaOBr_2	Orange	546sh, 518s, 495s, 446s, 319s,b, 259m, 240vw	240vw
UOBr_2	Pale green	538sh, 505s, 429s, 253w	294s, b
NpOBr_2	Orange	540sh, 500s, 315s,b, 258w	424s, b
ThOI_2	White	500m, 444m, 325s,b	
PaOI_2	Burgundy	459m, 434m, 303s,b	

spectrum of this compound. Our preparations of UOCl_2 all gave identical X-ray powder patterns and these were the same as that recorded by Dunn.¹⁸ Possibly their uranium dioxide contained U_3O_8 so that some uranium(V) oxytrichloride, UOCl_3 , was obtained. This is usually obtained by heating together uranyl chloride and uranium tetrachloride¹⁹ and we have in fact observed a strong band around 730 cm^{-1} in the spectrum of an impure sample of UOCl_3 so prepared. Further, all the compounds discussed here were perfectly anhydrous, no band being observed around 3400 cm^{-1} (OH stretching vibration) or 1600 cm^{-1} (H_2O wagging mode) so the strong bands in the 500 cm^{-1} region of the spectra are certainly not associated with $(\text{U-O})_{\text{OH}}$ modes.

EXPERIMENTAL

Work with protactinium and neptunium was carried out in glove-boxes on account of the radioactive hazards associated with weighable amounts of protactinium-231 and neptunium-237, the isotopes used. Following preparation all compounds were handled in an argon atmosphere box (oxygen content < 50 p.p.m.; water content < 60 p.p.m.) in which samples were prepared for X-ray powder diffraction, infrared studies, and analysis.

Materials.—Tetrachlorides^{6,20,21} (thorium to neptunium inclusive), tetrabromides^{6,22} (thorium to uranium inclusive), and thorium tetraiodide²³ were prepared by published methods. Neptunium tetrabromide was prepared²⁴ by

²⁰ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc. (A)*, 1966, 737.

²¹ K. W. Bagnall and J. B. Laidler, *J. Chem. Soc. (A)*, 1966, 516.

²² K. W. Bagnall, D. Brown, and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 1763.

²³ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J. Chem. Soc.*, 1965, 350.

²⁴ D. Brown and J. F. Easey, unpublished observations.

direct union of the elements at 600°. Protactinium(IV) oxydihalides were already available.⁶ Commercial antimony trioxide and bromine were used and neptunium metal was kindly provided by Mr. J. A. C. Marples (Ceramics Division, A.E.R.E., Harwell). Individual preparations were carried out with 20–200 mg. of actinide element.

Oxydihalides.—These were prepared by reaction of the appropriate tetrahalide with antimony trioxide in sealed, evacuated vessels as described,⁶ for the protactinium compounds. In certain instances (UOCl₂, NpOCl₂, and NpOBr₂) they were also prepared by reaction of the actinide tetrahalide with the stoichiometric amount of the actinide dioxide at 500° in a vacuum. Analyses are in Table 5.

Analysis.—Thorium, uranium, and protactinium were weighed as ThO₂, U₃O₈, and Pa₂O₅, respectively, after ignition of the hydrous oxides obtained by hydrolysis of the oxydihalides with aqueous ammonia. Neptunium-237 was determined by α -assay (specific activity of ²³⁷Np = 1.562×10^6 α -disintegrations min.⁻¹ mg.⁻¹) and halides were determined either by titration against standard silver nitrate solution or weighed as the silver salt.

Physical Measurements.—X-Ray powder diffraction photographs were obtained with both a Debye-Scherrer 19 cm. camera and a Guinier focusing camera with filtered Cu-K α radiation ($\lambda_{\alpha 1} = 1.54051$ Å). Scales were contact-printed on the Guinier films before development to counteract film shrinkage during processing. Thoria was used as an internal standard for Guinier work to allow an accurate camera constant to be determined for each sample. The specimens were mounted between strips of Sellotape which were sealed with Bostikote to contain the α -activity. Protactinium(IV) oxydichloride slowly decomposed under such conditions but the remaining oxydichlorides were relatively stable. Cell constants for the orthorhombic oxy-

dihalides were obtained by refining Guinier film results using a computer programme based on the Cohen-Hess method to obtain the best least-squares fit between observed and calculated $\sin^2 \theta$. Between 70 and 90 independent reflections were refined for each compound and the agreement between observed and calculated values of $\sin^2 \theta$ for ThOCl₂ is shown in Table 1 which lists part of the recorded powder pattern. Infrared spectra were recorded with an Infracan spectrometer (4000–600 cm.⁻¹) and a Grubb-Parsons DM-4 spectrometer (660–225 cm.⁻¹). Samples were mounted either as Nujol mulls or in wax discs as described²⁵ elsewhere; the absence of OH and H₂O vibrations from the Infracan region confirmed that the compounds remained anhydrous during spectral studies.

TABLE 5
Analyses of actinide oxydihalides

Compound	Found (%)		Required (%)	
	M	X	M	X
ThOCl ₂	72.61	22.25	72.75	22.23
PaOCl ₂	72.15	22.07	72.66	22.30
UOCl ₂	73.38	21.71	73.25	21.82
NpOCl ₂	72.96	21.62	73.17	21.88
ThOBr ₂	56.81	38.89	56.86	39.22
PaOBr ₂	56.81	39.21	56.76	39.31
UOBr ₂	57.18	38.67	57.49	38.65
NpOBr ₂	56.81	38.69	57.38	38.74
ThOI ₂	46.41	50.41	46.21	50.60

X = Cl, Br, or I; M = actinide element.

We thank Mr. A. M. Deane for infrared facilities, and Mr. R. Street for Guinier Camera facilities.

[7/849 Received, July 11th, 1967]

²⁵ A. M. Deane, *J. Inorg. Nuclear Chem.*, 1965, **27**, 751.

X-Ray Single-crystal and Powder Diffraction Results for Cæsium Heptafluoroprotactinate(v)

By D. Brown, J. F. Easey, and D. G. Holah, Chemistry Division, A.E.R.E., Harwell, Didcot, Berkshire

The structure of the compound was determined from single-crystal X-ray diffraction data. The compound is a monoclinic crystal with space group $C2/m$. The unit cell dimensions are $a = 1.125 \text{ nm}$, $b = 0.715 \text{ nm}$, and $c = 0.715 \text{ nm}$. The structure is based on the protactinate ion, PaO_7^{5-} , which is coordinated by seven fluorine atoms. The cesium ions are located in the interstitial sites of the lattice. The structure is similar to that of the other heptafluoroprotactinates, but the coordination of the protactinate ion is different. The structure is shown in Figure 1.

h	k	l	d (Å)	I (rel)	h	k	l	d (Å)	I (rel)
0	0	0		100	0	0	0		100
1	0	0	1.125	10	1	0	0	1.125	10
2	0	0	0.5625	40	2	0	0	0.5625	40
3	0	0	0.375	10	3	0	0	0.375	10
4	0	0	0.28125	10	4	0	0	0.28125	10
5	0	0	0.225	10	5	0	0	0.225	10
6	0	0	0.1875	10	6	0	0	0.1875	10
7	0	0	0.1607	10	7	0	0	0.1607	10
8	0	0	0.1406	10	8	0	0	0.1406	10
9	0	0	0.125	10	9	0	0	0.125	10
10	0	0	0.1125	10	10	0	0	0.1125	10
11	0	0	0.1023	10	11	0	0	0.1023	10
12	0	0	0.0938	10	12	0	0	0.0938	10
13	0	0	0.0864	10	13	0	0	0.0864	10
14	0	0	0.0801	10	14	0	0	0.0801	10
15	0	0	0.0747	10	15	0	0	0.0747	10
16	0	0	0.0701	10	16	0	0	0.0701	10
17	0	0	0.0662	10	17	0	0	0.0662	10
18	0	0	0.0629	10	18	0	0	0.0629	10
19	0	0	0.0601	10	19	0	0	0.0601	10
20	0	0	0.0577	10	20	0	0	0.0577	10
21	0	0	0.0556	10	21	0	0	0.0556	10
22	0	0	0.0537	10	22	0	0	0.0537	10
23	0	0	0.0520	10	23	0	0	0.0520	10
24	0	0	0.0505	10	24	0	0	0.0505	10
25	0	0	0.0491	10	25	0	0	0.0491	10
26	0	0	0.0479	10	26	0	0	0.0479	10
27	0	0	0.0468	10	27	0	0	0.0468	10
28	0	0	0.0458	10	28	0	0	0.0458	10
29	0	0	0.0449	10	29	0	0	0.0449	10
30	0	0	0.0441	10	30	0	0	0.0441	10
31	0	0	0.0434	10	31	0	0	0.0434	10
32	0	0	0.0427	10	32	0	0	0.0427	10
33	0	0	0.0421	10	33	0	0	0.0421	10
34	0	0	0.0415	10	34	0	0	0.0415	10
35	0	0	0.0410	10	35	0	0	0.0410	10
36	0	0	0.0405	10	36	0	0	0.0405	10
37	0	0	0.0401	10	37	0	0	0.0401	10
38	0	0	0.0397	10	38	0	0	0.0397	10
39	0	0	0.0393	10	39	0	0	0.0393	10
40	0	0	0.0390	10	40	0	0	0.0390	10
41	0	0	0.0387	10	41	0	0	0.0387	10
42	0	0	0.0384	10	42	0	0	0.0384	10
43	0	0	0.0382	10	43	0	0	0.0382	10
44	0	0	0.0380	10	44	0	0	0.0380	10
45	0	0	0.0378	10	45	0	0	0.0378	10
46	0	0	0.0376	10	46	0	0	0.0376	10
47	0	0	0.0375	10	47	0	0	0.0375	10
48	0	0	0.0374	10	48	0	0	0.0374	10
49	0	0	0.0373	10	49	0	0	0.0373	10
50	0	0	0.0372	10	50	0	0	0.0372	10
51	0	0	0.0371	10	51	0	0	0.0371	10
52	0	0	0.0371	10	52	0	0	0.0371	10
53	0	0	0.0370	10	53	0	0	0.0370	10
54	0	0	0.0370	10	54	0	0	0.0370	10
55	0	0	0.0370	10	55	0	0	0.0370	10
56	0	0	0.0370	10	56	0	0	0.0370	10
57	0	0	0.0370	10	57	0	0	0.0370	10
58	0	0	0.0370	10	58	0	0	0.0370	10
59	0	0	0.0370	10	59	0	0	0.0370	10
60	0	0	0.0370	10	60	0	0	0.0370	10

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The structure of the compound was determined from single-crystal X-ray diffraction data. The compound is a monoclinic crystal with space group $C2/m$. The unit cell dimensions are $a = 1.125 \text{ nm}$, $b = 0.715 \text{ nm}$, and $c = 0.715 \text{ nm}$. The structure is based on the protactinate ion, PaO_7^{5-} , which is coordinated by seven fluorine atoms. The cesium ions are located in the interstitial sites of the lattice. The structure is similar to that of the other heptafluoroprotactinates, but the coordination of the protactinate ion is different. The structure is shown in Figure 1.

X-Ray Single-crystal and Powder Diffraction Results for Cæsium Heptafluorotactinate(v)

By D. Brown, J. F. Easey, and D. G. Holah, Chemistry Division, A.E.R.E., Harwell, Didcot, Berkshire

Single-crystal studies have shown that Cs_2PaF_7 possesses monoclinic symmetry with $a_0 = 14.937$, $b_0 = 7.270$, $c_0 = 8.266 \text{ \AA}$, and $\beta = 125.32^\circ$, space-group $C2/c-C_{2h}^6$.

THE crystal structure of potassium heptafluorotactinate(v), K_2PaF_7 , has been reported¹ and on the basis of X-ray powder diffraction results it was found^{2,3} that $(\text{NH}_4)_2\text{PaF}_7$ and Rb_2PaF_7 could be classified as isostructural with K_2PaF_7 . However, on the basis of the differences between the X-ray powder patterns of these three complexes and that of the cæsium analogue, Cs_2PaF_7 , it was reported independently^{2,3} that Cs_2PaF_7 appeared to possess a different structure. We report now single-crystal X-ray diffraction studies which show

tion was chosen as the oscillation axis for the collection of Weissenberg data and as the spindle axis for obtaining precession photographs. The conditions governing the reflections on the combined zero-, first-, second-, and third-layer photographs (hkl : $h+k=2n$; $h0l$, $h=2n$, $l=2n$; $0k0$, $k=2n$) showed the lattice to be C-centred monoclinic and the space-group to be $C2/c-C_{2h}^6$ as for K_2PaF_7 . The unit-cell dimensions, $a_0 = 14.937 \pm 0.005$, $b_0 = 7.270 \pm 0.002$, $c_0 = 8.266 \pm 0.003 \text{ \AA}$, and $\beta = 125.32^\circ \pm 0.02^\circ$ show that a_0 and c_0 are appreciably

Partial X-ray powder diffraction results for Cs_2PaF_7

$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	h, k, l	$I_{\text{est.}}$	$\sin^2 \theta$ (obs.)	$\sin^2 \theta$ (calc.)	h, k, l	$I_{\text{est.}}$
0.0154	0.0154	1,1,0	M	0.1896	0.1893	6,2,0	M-
0.0162	0.0162	2,0,0	M-	0.1911	0.1911	1,1,4	W+
0.0200	0.0202	1,1,1	W-	0.1935	0.1937	5,3,3	W
0.0452	0.0453	0,2,0	S-	0.1977	0.1977	6,2,4	M-
0.0474	0.0475	3,1,0	S	0.1979	0.1979	8,0,4	W+
0.0495	0.0496	3,1,2	S	0.2091	0.2093	0,0,4	W+
	0.0497	4,0,2		0.2297	0.2292	5,1,5	W-
0.0511	0.0511	1,1,2	M-	0.2296	0.2296	4,4,2	W-
0.0525	0.0526	0,0,2	M+	0.2328	0.2327	7,3,2	M-
0.0582	0.0584	0,2,1	W	0.2377	0.2374	9,1,2	M-
0.0612	0.0613	2,2,0	W-	0.2404	0.2399	3,3,2	M-
0.0828	0.0829	5,1,1	W-	0.2403	0.2403	3,1,3	W
0.0853	0.0857	3,1,1	W-	0.2437	0.2437	9,1,4	M-
0.0948	0.0947	4,2,2	W	0.2435	0.2441	4,4,0	W
0.0963	0.0963	6,0,2	M	0.2462	0.2462	3,3,4	M-
0.0976	0.0976	0,2,2	M+	0.2544	0.2542	0,2,4	M
0.1015	0.1020	2,0,2	W-	0.2722	0.2724	7,3,4	W
0.1080	0.1081	1,1,3	W	0.2761	0.2761	6,4,2	W+
0.1092	0.1094	4,2,0	W	0.2812	0.2810	1,3,4	W+
0.1104	0.1103	1,3,1	W	0.2812	0.2817	2,4,2	W
0.1257	0.1255	3,3,1	W+	0.2919	0.2912	6,4,3	W
0.1375	0.1376	3,3,0	M	0.2919	0.2921	2,0,4	W
0.1397	0.1396	3,3,2	M+	0.2973	0.2974	7,3,0	W+
0.1414	0.1411	1,3,2	M	0.2973	0.2976	0,4,3	W
	0.1413	6,2,2		0.3169	0.3173	3,5,0	W
0.1427	0.1428	7,1,2	W+	0.3169	0.3173	9,3,3	W
0.1445	0.1444	6,0,0	M-	0.3207	0.3208	1,5,2	M-
0.1469	0.1470	2,2,2	W	0.3236	0.3240	6,4,0	W-
0.1502	0.1500	3,1,2	M	0.3236	0.3240	6,4,0	W-
0.1529	0.1522	6,2,1	M	0.3274	0.3272	9,3,2	M-
	0.1528	6,2,1		0.3274	0.3270	4,2,3	W
	0.1528	6,0,4		0.3341	0.3335	9,3,4	W
	0.1558	4,2,1		0.3341	0.3338	4,0,6	W
0.1563	0.1563	3,1,4	M+	0.3354	0.3354	9,1,0	W
	0.1565	6,2,3		0.3372	0.3372	11,1,3	W
0.1803	0.1799	3,3,3	W+	0.3372	0.3370	2,2,4	W
	0.1802	0,4,0		0.3372	0.3372	5,3,2	W
0.1828	0.1826	7,1,4	W+	0.3416	0.3417	6,2,2	W+
0.1847	0.1846	4,2,4	W+				

that Cs_2PaF_7 also possesses monoclinic symmetry and that the unit cell is similar to that of the other fluorotactinates(v).

Single crystals of Cs_2PaF_7 , grown slowly from hydrofluoric acid solution, are needle-shaped with the [001] direction parallel to the longest crystal edges. This direc-

greater than the corresponding values for K_2PaF_7 ($a_0 = 13.84$, $b_0 = 6.76$, $c_0 = 8.24 \text{ \AA}$, and $\beta = 125.5^\circ$) whereas c_0 and β are almost identical. This is significant when one recalls that the PaF_9 units in the latter¹ are linked in infinite chains parallel to [001] by fluorine bridges. The similarity between the c_0 values suggests

¹ D. Brown and A. J. Smith, *Chem. Comm.*, 1965, 554.

² D. Brown and J. F. Easey, *J. Chem. Soc. (A)*, 1966, 254.

³ L. B. Asprey, F. H. Kruse, A. Rosenweig, and R. A. Penneman, *Inorg. Chem.*, 1966, 5, 659.

that this arrangement is probably retained in Cs_2PaF_7 . The agreement between observed and calculated $\sin^2\theta$ values for the reflections observed on X-ray powder patterns of Cs_2PaF_7 is shown in the Table together with visually estimated intensities.

EXPERIMENTAL

Cæsium heptafluoroprotactinate(v) was prepared as described previously² and recrystallised from dilute hydrofluoric acid. The crystals were washed first with ice-cold 5M-hydrofluoric acid and then with acetone, and vacuum-dried at room temperature. A well-formed, elongated

crystal ($0.35 \times 0.09 \times 0.03$ mm.) was mounted in a thin-walled capillary and Weissenberg and precession data collected with Unicam Weissenberg and Buerger precession cameras with filtered Cu-K_α and Mo-K_α radiations. X-Ray powder diffraction photographs were obtained with a Guinier focusing camera as described previously.¹ Accurate unit-cell parameters were obtained by refining the powder results by use of the computer programme based on the Cohen-Hess method to obtain the best least-squares fit between observed and calculated $\sin^2\theta$ values. This programme incorporates the Nelson-Riley function.

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The Existence of Curium(VI)

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(Received March 17, 1966)

Some recently reported solvent extraction and ion-exchange results obtained with ozonised solutions of curium(III) have been interpreted [1] as possible evidence for the oxidation of curium(III) to curium(VI). Since this seemed to be unlikely, because of the expected stability of the half-filled 5f shell and the known difficulty of oxidising solid curium(III) compounds even to the +4 state, we have repeated the work, but with milligram amounts of ^{244}Cm (17.6 yr), in the media described by AKATSU [1].

We have found that solvent extraction with diisooctylamine, which is somewhat more stable to oxidation than Amberlite LA1, gave results in good agreement with those reported by AKATSU, but that the absorption spectrum of the aqueous phase remained that of curium(III) throughout the ozonisation, the maxima [2] being at 375.4, 381.2 and 396.5 $m\mu$. Samples of the extractant were then examined by thin layer chromatography and it was found that diisooctylamine had been completely destroyed by the

ozone in the aqueous phase, so that the observed extraction results, which resemble those for the actinide(VI) by the original amine, must have been due to the extraction of curium(III) by one, or a number, of the decomposition products of the amine, so that the resemblance to actinide(VI) behaviour is quite fortuitous.

Similarly, distribution experiments showed that ozonised De-Acidite FF ion exchange resin had a considerably increased K_d for both curium(III) and for tracer iron (^{59}Fe) as compared with the K_d for the unozonised resin.

It is therefore quite clear that curium(III) is not oxidised by ozone in aqueous media, a result which serves to emphasize that a great deal of care is needed in the interpretation of trace scale experimental results.

1. J. AKATSU, *Radiochim. Acta* 4, 58 (1965).

2. R. A. PENNEMAN and T. K. KEENAN, U.S. Report NAS-NS 3006, p. 26 (1960).

Protactinium(v) Iodides

By D. Brown, J. F. Easey, and P. J. Jones, Chemistry Division, Building 220, A.E.R.E., Harwell, Didcot, Berkshire

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Protactinium(v) Iodides

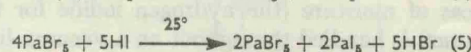
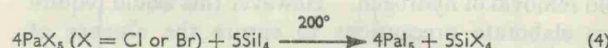
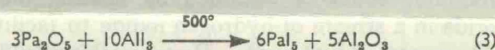
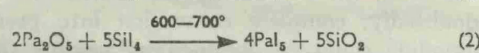
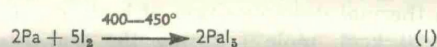
By D. Brown, J. F. Easey, and P. J. Jones, Chemistry Division, Building 220, A.E.R.E., Harwell, Didcot, Berkshire

Protactinium pentaiodide, PaI_5 , is best prepared by direct union of the elements at 400–450° in a vacuum, but, if protactinium is not available, the pentaiodide is obtained in good yield by the reaction of silicon tetraiodide with protactinium pentachloride, pentabromide (both at 150–200°), or pentoxide (600°). Protactinium oxyiodides, PaOI_3 and PaO_2I , are obtained by reaction of the pentaiodide with antimony trioxide at 150° *in vacuo* or, less satisfactorily, by the action of oxygen on the pentaiodide. The oxytri-iodide disproportionates above 450° in a vacuum to yield the volatile pentaiodide and a residue of the dioxymonoiodide. The mixed bromo-iodide PaBr_3I_2 is obtained when the component pentahalides react together at 350°. Some chemical properties, X-ray powder diffraction results, and infrared spectra are reported for these compounds and for the hexaiodoprotactinate(v), $\text{Ph}_3\text{MeAsPaI}_6$, which is formed by reaction of the component halides in non-aqueous solvents. Further infrared studies are also reported for the protactinium(v) oxybromides.

A SINGLE protactinium(v) oxyfluoride,¹ Pa_2OF_8 , and several oxychlorides^{2,3} and oxybromides^{3,4} are now known, but protactinium(v) oxyiodides have not previously been characterised. In addition, the pentaiodide has been prepared⁵ in only milligram amounts by the reaction of aluminium tri-iodide and protactinium pentoxide, which we have found to give poor yields when more than 50 mg. of oxide are involved. As part of an investigation of the quinquevalent and quadrivalent halides^{2-4,6,7}, oxyhalides,^{2-4,7} and halogeno-complexes^{6,8-11} of protactinium we studied various methods for the preparation of protactinium pentaiodide and examined the preparation of protactinium(v) oxyiodides. We report here the conditions suitable for the preparation of 0.5-gram amounts of protactinium pentaiodide by two different methods, namely the reaction between protactinium pentoxide and silicon tetraiodide at 600–700° in a vacuum and the metathesis of protactinium pentachloride or pentabromide at 150–200° with silicon tetraiodide. Alternative procedures are also discussed. The non-volatile oxyiodides, PaOI_3 and PaO_2I , which occur together as by-products of the interaction of the pentoxide and silicon tetraiodide, are conveniently prepared from protactinium pentaiodide by reactions involving either antimony trioxide or, less satisfactorily, oxygen. Thermal decomposition of protactinium(v) oxytri-iodide in a vacuum provides an alternative route to the dioxymonoiodide. During these investigations we also characterised the first mixed halide of protactinium(v), namely protactinium tri-bromodi-iodide, PaBr_3I_2 , and prepared triphenylmethyl-arsonium hexaiodoprotactinate(v), $\text{Ph}_3\text{MeAsPaI}_6$, by reactions in non-aqueous solvents.

Protactinium Pentaiodide and Tribromodi-iodide.—Some of the reactions (1)–(4) which we have studied for the preparation of protactinium pentaiodide are shown. Protactinium metal reacts quantitatively with excess of iodine above 400° to yield a sublimate of the

crystalline, black pentaiodide. This is undoubtedly the easiest method for the preparation of protactinium pentaiodide but since protactinium metal is difficult to prepare various ways of converting the pentoxide or the easily prepared pentachloride and pentabromide into the pentaiodide have been investigated. We have been unable to obtain satisfactory yields from the previously reported⁵ method [reaction (3)] involving reaction between aluminium tri-iodide and protactinium pentoxide in a vacuum, only about 30% conversion being observed



with 50 milligram batches of the pentoxide. However, silicon tetraiodide reacts more readily [reaction (2)] and yields in excess of 70% are obtained by heating the reactants together in a sealed, evacuated silica vessel completely enclosed in a furnace at 600–700°. X-Ray powder diffraction analysis showed that the dark brown residue from this reaction contained both protactinium(v) oxytri-iodide and dioxymonoiodide. The resulting protactinium pentaiodide and excess of silicon tetraiodide are easily separated by sublimation in a clean evacuated tube, the pentaiodide subliming at about 450/10⁻⁴ mm. Hg. The only other example of the use of silicon tetraiodide for the conversion of a metal oxide into an iodide is the preparation¹² of plutonium tri-iodide from the dioxide. However it has recently been employed¹³ for the preparation of niobium and tantalum pentaiodides from their respective pentachlorides. The analogous reactions involving protactinium pentachloride and

¹ L. Stein, *Inorg. Chem.*, 1964, **3**, 995.

² D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 874.

³ D. Brown, "Physico-Chimie du Protactinium," Publ. No. 154, Centre National de la Recherche Scientifique, Paris, 1966.

⁴ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 262.

⁵ A. G. Maddock, unpublished observations.

⁶ D. Brown and P. J. Jones, *Chem. Comm.*, 1966, 280.

⁷ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 719.

⁸ K. W. Bagnall and D. Brown, *J. Chem. Soc.*, 1964, 3021.

⁹ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 247.

¹⁰ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1967, 243.

¹¹ D. Brown and J. F. Easey, *Nature*, 1965, **205**, 589; *J. Chem. Soc. (A)*, 1966, 254.

¹² K. W. Bagnall and D. Robertson, unpublished observations.

¹³ L. A. Nisel'son and I. V. Petrisevitch, *Zhur. neorg. Khim.*, 1960, **5**, 249.

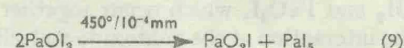
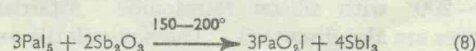
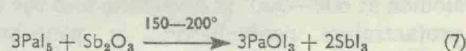
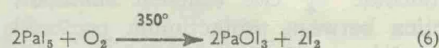
pentabromide proceed rapidly at 200° in a vacuum [reaction (4)], whereupon the volatile silicon halides sublime out of the reaction zone. Reaction (4) shows silicon tetrachloride and tetrabromide as the products of these metatheses but in the presence of excess of silicon tetraiodide the products are more probably mixed halides of the type $\text{SiI}_n\text{X}_{4-n}$ ($\text{X} = \text{Cl}$ or Br). Following resublimation of the product yields in excess of 95% of protactinium pentaoidide are invariably obtained from this type of reaction and in view of the simple methods now available for the preparation of PaCl_5 ² and PaBr_5 ⁴ it provides an attractive route to the pentaoidide. Either of the above reactions involving silicon tetraiodide could easily be employed on the gram scale.

Protactinium pentachloride and pentabromide both react with anhydrous hydrogen iodide. Thus, when the pentachloride and a five-fold excess of hydrogen iodide for the reaction $\text{PaCl}_5 + 5\text{HI} \rightarrow \text{PaI}_5 + 5\text{HCl}$ are heated together at 300° in a sealed vessel and the products then separated by sublimation in a clean, evacuated tube 50% conversion into the pentaoidide is observed, the remaining pentachloride being reduced to protactinium tetrachloride. This reduction is probably a consequence of the presence of hydrogen produced by the thermal decomposition of hydrogen iodide ($\Delta H_f = +6.20$ kcal. mole⁻¹) during the sealed-tube reaction. Undoubtedly, complete conversion into protactinium pentaoidide could be obtained by heating the pentachloride in a stream of hydrogen iodide to facilitate the rapid removal of hydrogen. However this would require more elaborate precautions to ensure the absence of traces of moisture (the hydrogen iodide for the above reaction is handled throughout on a vacuum-line) and it offers no advantage over the pentachloride-silicon tetraiodide reaction. In a single experiment at room temperature protactinium pentachloride and hydrogen iodide appeared to react in a sealed tube to yield a black product. However *X*-ray diffraction analysis showed the solid to be unchanged pentachloride and on sublimation in a vacuum approximately 80% of unchanged pentachloride was obtained, the remainder having been reduced to the tetrachloride. The reaction between the pentabromide and hydrogen iodide at room temperature proved even more interesting. The initial black product was shown by *X*-ray diffraction analysis to be a mixture of protactinium pentabromide and pentaoidide [reaction (5)]. When heated in a clean, evacuated tube the components of this mixture reacted and formed a black liquid at 350–400°, which vaporised at this temperature and deposited black crystals in a cooler portion of the tube. A small amount of black residue (*ca.* 6 mg.) obtained in this reaction was not identified but the sublimate was shown to be protactinium tribromodiiodide, PaBr_3I_2 . Subsequently this compound was prepared when equimolar amounts of the component pentahalides were heated together. Three fractions of the sublimed material all gave identical powder patterns, a small amount of amorphous residue again remaining uncharacterised, so the interaction of these

pentahalides appears to proceed in such a manner as to give the maximum yield of protactinium tribromodiiodide.

Obviously it is likely that other mixed halides of protactinium(v) will exist and it is intended to study the preparation and properties of such compounds and, if possible, to identify the by-product of the above reaction by using larger quantities of the reactants.

Protactinium(v) Oxyiodides.—Protactinium oxytriiodide is obtained by heating the pentaoidide with just less than sufficient oxygen for reaction (6). It is a chocolate-brown, non-volatile solid from which excess of pentaoidide can be separated by sublimation of the latter at 400–425° *in vacuo*. Above 450° PaOI_3 disproportionates [reaction (9)] in the same way as protactinium(v) oxytribromide,⁴ yielding a sublimate of the pentaoidide and a residue of protactinium dioxymonoioidide, PaO_2I . Both oxyiodides are more conveniently prepared when the appropriate amounts of protactinium pentaoidide and antimony trioxide, as indicated by reactions (7) and (8), are heated together in sealed tubes. The reactions proceed rapidly above 150°, whereupon the volatile antimony tri-iodide sublimes out of the reaction zone. However, in order to obtain reasonably crystalline samples of the protactinium(v) oxyiodides it is necessary to continue heating the products at about 400° for several hours. These reactions are analogous to those recently used⁷ for the characterisation of certain quadrivalent protactinium oxyhalides.



Some Chemical and Physical Properties of Protactinium(v) Iodides.—Protactinium pentaoidide is reported⁵ to possess orthorhombic symmetry with $a_0 = 7.22$, $b_0 = 21.20$, $c_0 = 6.85$ Å. Powder patterns from our many preparations showed only a few strong lines, so we have been unable to confirm these values. Powder patterns from the tribromodi-iodide show some similarities to those of the pentaoidide with the strong lines occurring at slightly larger values of $\sin^2\theta$ and the two compounds may therefore be isostructural. We propose to prepare crystals of each compound suitable for full structure analyses and the results of this work will be reported later. Values of $\sin^2\theta$ for the reflections observed on the *X*-ray powder patterns of PaBr_3I_2 are listed in Table I, together with visually estimated intensities.

Both protactinium pentaoidide and tribromodi-iodide are obtained as black crystals on sublimation and when finely ground are dark brown. They are moisture-sensitive and hydrolyse immediately on the addition of water or dilute aqueous ammonia, forming the characteristic

white protactinium(v) hydroxide. The pentaiodide is soluble in anhydrous methyl cyanide and alcohol but insoluble in chloroform, carbon tetrachloride, isopentane, and cyclohexane. It reacts with triphenylmethylarsonium iodide in anhydrous methyl cyanide or chloroform to form $\text{Ph}_3\text{MeAsPaI}_6$, analogous to the known hexachloro-⁸ and hexabromo-complexes.⁹ The

oxyiodides are obtained as dark brown solids but PaO_2I prepared by thermal decomposition of PaOI_3 [reaction (9)] is obtained as a mustard coloured, fluffy solid. Both samples of PaO_2I give the same powder pattern and the results have been interpreted on the basis of a hexagonal unit cell with $a_0 = 12.64 \pm 0.01$ and $c_0 = 4.07 \pm 0.01$ Å. In the absence of single-crystal data this unit cell must be considered as tentative. Protactinium(v) oxytriiodide gives poor X-ray powder diffraction patterns even

TABLE 1

Partial X-ray powder diffraction patterns for protactinium tribromodi-iodide and protactinium(v) dioxymonoiodide

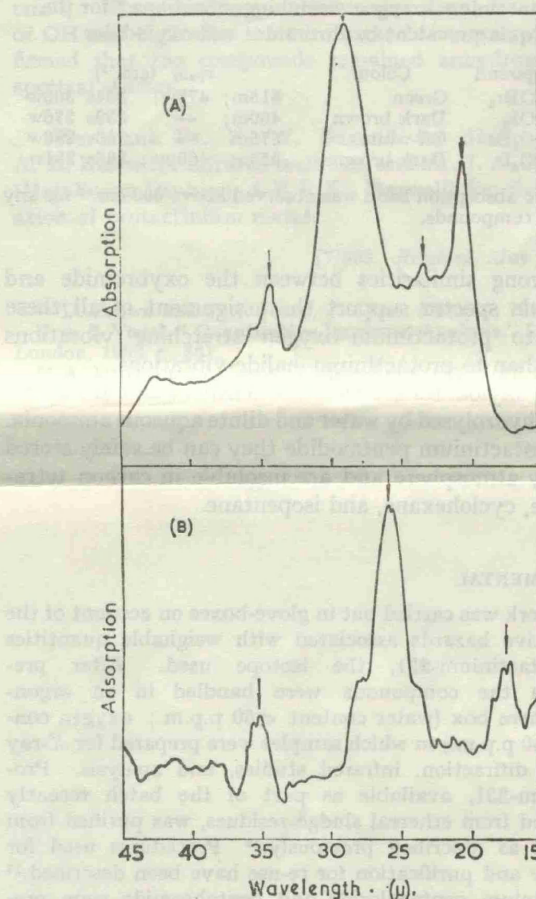
PaBr ₃ I ₂		PaO ₂ I			
sin ² θ (obs.)	I (est.)	sin ² θ (obs.)	sin ² θ (calc.)	h, k, l	I (est.)
0.0138	m	0.0349	0.0351	0,0,1	s
0.0161	w	0.0400	0.0400	1,0,1	w-
0.0186	w	0.0438	0.0439	3,0,0	w-
0.0225	w	0.0546	0.0547	2,0,1	s
0.0249	w-	0.0779	0.0781	4,0,0	m
0.0409	vw-	0.0804	0.0796	3,0,1	m
0.0533	w	0.0935	0.0930	3,2,0	w+
			0.0941	2,2,1	
0.0570	w-				
0.0607	s	0.0998	0.0992	3,1,1	m-
0.0625	w	0.1136	0.1138	4,0,1	w-
0.0678	w,d	0.1292	0.1288	3,2,1	w-
0.0718	w-	0.1327	0.1323	3,3,0	w-
0.0758	w-	0.1365	0.1374	4,2,0	w+
0.0816	w-	0.1410	0.1418	0,0,2	w
0.1011	m	0.1766	0.1767	6,0,0	w+
			0.1767	2,1,2	
0.1039	w-				
0.1231	w-	0.1915	0.1915	5,2,0	m
0.1260	w+	0.2135	0.2129	6,0,1	w,d
0.1408	w+	0.2210	0.2205	4,0,2	w,d
0.1456	w	0.2362	0.2360	3,2,2	w,d
			0.2360	4,4,0	
0.1685	w-				
0.1800	w-	0.2764	0.2768	7,0,1	w,d

s, Strong; m, medium; w, weak; d, diffuse.

products initially obtained on removal of the solvent under vacuum are oily, and prolonged vacuum drying at about 50° is required to produce the unsolvated complexes. Like the pentaiodide, triphenylmethylarsonium hexaiodoprotactinate(v) is a dark brown, moisture-sensitive solid which reacts rapidly with water and aqueous ammonia. It is soluble in methyl cyanide, methylene dichloride, and chloroform, but insoluble in carbon tetrachloride. As expected, protactinium-iodide stretching vibrations are not observed above 220 cm.⁻¹ in the infrared spectra of either the pentaiodide or the hexaiodo-complex.

The reduction of protactinium pentaiodide with either hydrogen or aluminium has been described.⁷ In similar conditions it is likely that PaBr₃I₂ will be reduced to quadrivalent mixed halides such as PaBr₃I or PaBr₂I₂, analogous to those already characterised¹⁴ for uranium (iv).

When prepared by reaction of antimony trioxide with protactinium pentaiodide, both the quinquevalent



Infrared spectra of (A) PaOBr₃ and (B) PaO₂Br

after prolonged heating at 400°; the results have not been interpreted. Observed and calculated values of sin²θ for the dioxymonoiodide are shown in Table 1 together with visually estimated intensities.

The positions of the protactinium-oxygen stretching vibrations (Table 2) indicate the absence of discrete PaO³⁺ and PaO₂²⁺ groups from the oxyiodides. The values are similar to those found for protactinium(v) oxychlorides² and oxybromides (Table 2) and it is likely that the oxyiodides possess polymeric, oxygen-bridged structures similar to the one recently reported¹⁵ for protactinium(v) oxytribromide. We have now ob-

¹⁴ J. C. Warf and N. Baenziger, U.S. Report TID-5290, 120, 1958.

¹⁵ D. Brown, J. T. Petcher, and A. J. Smith, *Acta Cryst.*, to be published.

tained infrared spectra of the oxybromides which are superior to those previously measured.⁴ The more reliable band positions are given in Table 2 and the spectra are shown in Figure 1. The spectra for PaO_2Br and PaO_2I are almost identical, the only difference being that the very weak band observed at 469 cm^{-1} for the latter was not detected in the spectrum of PaO_2Br .

TABLE 2

Protactinium-oxygen stretching vibrations * for the quinquevalent oxybromides and oxyiodides

Compound	Colour	$\nu_{\text{Pa-O}}$ (cm^{-1})		
PaOBr_3	Green	515m; 476w;	364s	303w
PaOI_3	Dark brown	480m; —	339s	276w
PaO_2Br	Off-white	575m —	386s	286w
PaO_2I	Dark brown	555m 469vw;	386s	281w

* No absorption band was observed above 600 cm^{-1} for any of the compounds.

The strong similarities between the oxybromide and oxyiodide spectra support the assignment of all these bands to protactinium-oxygen stretching vibrations rather than to protactinium-halide vibrations.

Both oxyiodides are moisture-sensitive and are immediately hydrolysed by water and dilute aqueous ammonia. Like protactinium pentaoidide they can be safely stored in a dry atmosphere and are insoluble in carbon tetrachloride, cyclohexane, and isopentane.

EXPERIMENTAL

All work was carried out in glove-boxes on account of the radioactive hazards associated with weighable quantities of protactinium-231, the isotope used. After preparation the compounds were handled in an argon-atmosphere box (water content <50 p.p.m.; oxygen content <40 p.p.m.) in which samples were prepared for X-ray powder diffraction, infrared studies, and analysis. Protactinium-231, available as part of the batch recently recovered from ethereal sludge residues, was purified from niobium as described previously.¹⁶ Procedures used for recovery and purification for re-use have been described.¹⁷ Protactinium pentachloride and pentabromide were prepared as described earlier^{2,4} and commercial iodine, silicon tetraiodide, and hydrogen iodide were used. Glass reaction vessels were evacuated and heated at 500° before use to ensure the absence of adsorbed moisture. Solvents were purified by distillation and dried over molecular sieves. Individual preparations involved 20–200 mg. of protactinium-231.

Protactinium Pentaoidide.—Protactinium metal (20 mg.) or a mixed protactinium-thorium metal phase (100 mg.) was heated at 400 – 450° in a sealed, evacuated (10^{-4} mm. Hg) silica tube with excess of iodine. The black, crystalline product was purified by sublimation at about 450° *in vacuo*. Alternatively, excess of silicon tetraiodide was heated in a sealed, evacuated tube with protactinium pentoxide (250 mg. at 600 – 700°), protactinium pentachloride, or protactinium pentabromide (both 250 mg. at 200°). After

12–24 hours' heating in the former case, during which the reaction vessel was completely enclosed in the furnace, the protactinium pentaoidide was slowly sublimed away from the reaction zone and purified by vacuum sublimation in a clean vessel (yield $>70\%$). The reaction between silicon tetraiodide and protactinium pentachloride or pentabromide was carried out with the evacuated tube vertical with only the reaction zone in the furnace. Two hours were sufficient to achieve complete metathesis and the mixed silicon tetrahalides were sublimed, below 350° , to the end of the vessel remote from the product, which was purified by sublimation as above (yield $>95\%$). For the fourth and least satisfactory preparation of protactinium pentaoidide a five-fold excess of hydrogen iodide was condensed on the pentachloride at liquid-nitrogen temperature, then the mixture was allowed to react at room temperature for two days. The pentachloride was then heated to about 300° during 5 hr. The products, protactinium pentaoidide (*ca.* 50%) and protactinium tetrachloride were separated by vacuum sublimation in a clean silica vessel [Found (typically): Pa, 26.7; I, 73.8. Calc. for PaI_5 : Pa, 26.67; I, 73.33%].

Protactinium Tribromodi-iodide.—Equimolar amounts of protactinium pentabromide (63 mg.) and pentaoidide (77 mg.) were heated together at 300° in a vacuum for a few hours, then the temperature was slowly raised to 400° and the product sublimed along the reaction tube (Found: Pa, 32.2; Br, 33.3; I, 34.9. PaBr_3I_2 requires Pa, 31.86; Br, 33.11; I, 35.03%).

Protactinium(v) Oxytri-iodide.—Protactinium pentaoidide was heated with a slight deficiency of oxygen for reaction (6) in a sealed, previously evacuated 'Pyrex' tube. The reaction vessel was totally enclosed in a furnace at 300 – 350° for several hours, then the excess of pentaoidide was sublimed to one end of the reaction vessel leaving a dark-brown residue of the non-volatile oxytri-iodide. Alternatively, stoichiometric quantities of the reagents for reaction (7) were intimately ground together and heated in a vacuum at 150 – 200° . The volatile antimony tri-iodide rapidly sublimed to one end of the reaction tube and the residual oxytri-iodide was then heated at about 400° for several hours. Both products gave virtually identical analyses (Found: Pa, 36.8; I, 60.5. PaOI_3 requires Pa, 36.78; I, 60.67%).

Protactinium(v) Dioxymonoiodide.—This was also prepared by two different methods. Thermal decomposition of PaOI_3 at 450° (10^{-4} mm. Hg) resulted in the sublimation of protactinium pentaoidide and the formation of the non-volatile dioxymonoiodide. Alternatively the compound was obtained by heating together antimony trioxide and protactinium pentaoidide [reaction (8)] as described above, followed by heating the product at 500° in a vacuum (Found: Pa, 61.2; I, 34.1. PaO_2I requires Pa, 61.76; I, 33.96%).

Triphenylmethylarsonium Hexaiodoprotactinate(v).—Equimolar quantities of protactinium pentaoidide (65.6 mg.) and triphenylmethylarsonium iodide (33.9 mg.) were mixed in anhydrous chloroform at room temperature. Protactinium pentaoidide is insoluble in chloroform but under the above conditions some dissolution took place to give an intensely brown solution which was heated at 50 – 60° for a few minutes in a stoppered vessel. The chloroform was finally removed under vacuum at about 50° to leave a dark brown solid (Found: Pa, 17.7; I, 57.6. $\text{Ph}_3\text{MeAsPaI}_6$ requires

¹⁶ D. Brown and P. J. Jones, *J. Inorg. Nuclear Chem.*, 1964, **22**, 2296.

¹⁷ D. Brown, S. N. Dixon, and P. J. Jones, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2529.

Pa, 17.58; I, 58.0%). Similar reactions in anhydrous methyl cyanide were less satisfactory because the oily product initially obtained was more difficult to dry completely. Excess of methyl cyanide co-ordinated to the hexaiodoprotactinate(v) was probably responsible for this behaviour. We have been unable to find a suitable solvent for recrystallisation of this compound to establish unambiguously that it has the composition $\text{Ph}_3\text{MeAsPaI}_6$. However X-ray powder diffraction patterns, although of poor quality, did show the absence of both protactinium pentaiodide and Ph_3MeAsI and it is therefore tentatively assumed that we have obtained the hexaiodoprotactinate(v) and not, for example, a mixture of $(\text{Ph}_3\text{MeAs})_x\text{PaI}_{5+x}$ ($x > 1$) and excess of pentaiodide or even a mixture of Ph_3MeAsI and PaI_5 .

Analysis.—Protactinium(v) was weighed as the pentoxide following ignition of the hydrous oxide, obtained by hydrolysis of the iodides with aqueous ammonia, at 750° in air. The iodides were cooled in liquid nitrogen before hydrolysis as described previously¹⁸ for the protactinium(v) nitrates, to prevent loss of halogen during analysis. Iodide and bromide in the supernatant liquid were determined by potentiometric titration against 0.1N-silver nitrate or weighed as the silver halide. The iodide content of PaBr_3I_2 was obtained by titration against 0.1N-potassium iodate¹⁹ and the bromide content from the difference between that and total halide content.

Physical Measurements.—X-Ray diffraction photographs were obtained with a Debye-Scherrer 19 cm. camera with filtered Cu-K α radiation ($\lambda_{\alpha 1} = 1.54051 \text{ \AA}$). Cell constants for the hexagonal dioxymonoiodide were refined with the Cohen-Hess computer programme to obtain the best least-squares fit between observed and calculated $\sin^2\theta$. The programme incorporates the Nelson-Riley function but the accuracy of the resulting lattice parameters is of course governed by the limited diffraction data obtained owing to the poor crystallinity of the preparations. Infrared spectra were recorded with an Infracan spectrometer (4000—600 cm^{-1}) and a Grubb-Parsons DM-4 spectrometer (660—225 cm^{-1}). Samples were mounted in wax discs;²⁰ the absence of OH and H $_2$ O vibrations from the Infracan region confirmed that the compounds remained anhydrous during spectral studies.

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¹⁸ D. Brown and P. J. Jones, *J. Chem. Soc. (A)*, 1966, 733.

¹⁹ A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, London, 1953, p. 361.

²⁰ A. M. Deane, *J. Inorg. Nuclear Chem.*, 1965, 27, 751.