Preparation and Crystallographic Properties of the Trichlorides, Tribromides, and Tri-iodides of Uranium, Neptunium, and Plutonium

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The preparation of uranium and neptunium trihalides has been investigated. Reduction of the appropriate tetrahalide by zinc at *ca.* 600 °C provides a safe, reliable route to UCl_3, UBr_3, UI_3, $NpCl_3$, and $NpBr_3$. This reaction is superior to reduction by aluminium metal. Direct union of the elements at 500 °C yields NpI_3 with no evidence for the formation of NpI_4. The new trivalent oxyhalides NpOCl, NpOBr, and NpOI have been identified crystallographically as by-products of certain reactions. Unit-cell dimensions are reported for these trihalides and oxyhalides, and for $PuBr_3$ and PuI_3.

THE uranium, neptunium, and plutonium trihalides have not been extensively investigated and few trivalent oxyhalides are known for these elements.[1,2] In particular, convenient and reliable preparative methods are not available for neptunium trichloride, tribromide, and tri-iodide. The last appears only to have been prepared in very small amounts by the reaction between neptunium dioxide and aluminium tri-iodide,[3] whilst the tribromide is formed during an analogous reaction involving the dioxide, aluminium tribromide, and aluminium metal,[3] and on the thermal decomposition of the tetrabromide above 475 °C *in vacuo*.[3,4] Hydrogen reduction of neptunium tetrachloride at 450 °C, and the reaction between neptunium dioxide and a carbon tetrachloride–hydrogen mixture at 350—400 °C both result in the formation of the trichloride.[3] However, in view of the

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[1] D. Brown, 'Halides of the Lanthanides and Actinides,' Wiley, London, 1968.

[2] D. Brown, ch. 3.6—3.8 in Gmelin 71 'Transuranium Elements,' to be published.

[3] S. Fried and N. Davidson, *J. Amer. Chem. Soc.*, 1948, **70**, 3539.

[4] D. Brown, S. Fletcher, and D. G. Holah, *J. Chem. Soc. (A)*, 1968, 1889.

inherent explosive hazards associated with hydrogen reductions at these temperatures such reactions are not recommended when large amounts of radioactive isotopes are involved. Reduction of neptunium tetrachloride by gaseous ammonia at 350—400 °C also yields neptunium trichloride.[5] An investigation of improved methods for the preparation of neptunium trihalides appeared worthwhile and this was extended to cover certain uranium trihalides.

We now report new preparative methods for uranium tribromide and tri-iodide, and neptunium trichloride, tribromide, and tri-iodide, together with further information on the reduction of uranium tetrachloride by zinc, which was briefly studied by Young.[6] Accurate unit-cell dimensions are reported for these trihalides and for plutonium tribromide and tri-iodide. The existence of β-$NpBr_3$ [7] has been confirmed and the trivalent neptunium oxyhalides, NpOBr and NpOI, have been identified for the first time by X-ray powder diffraction studies on the small residues formed during the high temperature sublimation of the corresponding trihalides. The formation of impure NpOCl has been observed during certain attempts to prepare the trichloride.

TABLE 1

Lattice parameters for the trihalides and oxyhalides

Compound	Colour	Symmetry * and structure-type	Lattice parameters (Å) † a_a	b_0	c_0	Molecular vol. (Å)
UCl_3	Dark green	H; UCl_3	7·440 ± 0·001		4·321 ± 0·001	103·5
$NpCl_3$	Green-brown		7·413 ± 0·001		4·282 ± 0·001	101·8
UBr_3	Brown		7·936 ± 0·001		4·438 ± 0·001	121·0
α-$NpBr_3$	Green-brown		7·916 ± 0·001		4·390 ± 0·001	119·2
β-$NpBr_3$	Green-brown	O; $PuBr_3$	12·618 ± 0·01	4·109 ± 0·004	9·153 ± 0·015	118·6
$PuBr_3$	Bright green		12·617 ± 0·01	4·097 ± 0·008	9·147 ± 0·010	118·2
UI_3	Black		13·996 ± 0·005	4·328 ± 0·002	9·984 ± 0·004	151·3
NpI_3	Burgundy		13·987 ± 0·010	4·326 ± 0·003	9·980 ± 0·006	150·9
PuI_3	Bright green		13·962 ± 0·020	4·326 ± 0·006	9·974 ± 0·010	150·6
NpOCl		T; PbFCl	4·028 ± 0·002		6·836 ± 0·004	111·0
NpOBr	Brown		4·040 ± 0·004		7·421 ± 0·006	121·1
NpOI	Burgundy		4·051 ± 0·001		9·193 ± 0·001	150·9

* H, Hexagonal; O, orthorhombic. † Error limits (to give 95% confidence) are 2σ where σ is the average e.s.d. from different films and, where appropriate, from α_1 and α_2 sets of reflections.

Preparation of the Trihalides.—Neptunium tetrachloride and tetrabromide are reduced to their respective trihalides when heated with aluminium at *ca.* 600 °C in sealed, evacuated silica vessels. However, attempts to purify the products by vacuum sublimation have not been entirely successful since at the temperature required (900—1000 °C) the excess of aluminium reacts with the silica and, as a consequence of this reaction, a major part of the neptunium trihalide is converted to a mixture of the trivalent oxyhalide and neptunium dioxide, the yield of pure trihalide ranging from 15 to 60%. A third phase is also present on X-ray powder patterns of the residues but we have been unable to identify it.

Following these observations the reduction of uranium tetrachloride by zinc was investigated since preliminary studies[6] had previously shown that this provided one route to the trichloride. This reaction appeared promising because it is also possible to sublime zinc in evacuated silica vessels without reaction occurring between the zinc and the container. We find that when uranium tetrachloride is heated with a 50% excess of zinc at *ca.* 600 °C with the sealed, evacuated silica vessel completely enclosed in the furnace, reduction to the trichloride is quantitative. The excess reductant and the zinc dichloride produced during the reaction can be removed by vacuum sublimation at 650—700 °C.

Neptunium tetrachloride and tetrabromide are both reduced under similar conditions and virtually quantitative yields of the respective trihalides are obtained on subsequent sublimation of the product *in vacuo* at 900—1000 °C. A small amount of residue (<2%) from the sublimation of the tribromide has been identified by X-ray diffraction analysis as the previously unknown trivalent oxybromide, NpOBr. As observed previously,[8] uranium trichloride is partially converted to the dioxide when heated in evacuated silica vessels at 850 °C, the temperature required for sublimation. However, analysis of products from several reactions indicated that the trichloride obtained by zinc reduction of the tetrachloride was 98% pure before sublimation. Both uranium tetrabromide and tetraiodide are also conveniently reduced to the corresponding trihalide when heated with zinc at *ca.* 600 °C.

Direct combination of uranium and iodine is known to result in the formation of uranium tetraiodide [1,9] when an excess of iodine is used, whereas under similar conditions the reaction between plutonium and iodine yields plutonium tri-iodide.[10] It has been suggested [11] that neptunium tetraiodide may exist but we find that neptunium and iodine react at 500—550 °C, under conditions employed for the preparation of uranium tetraiodide,[9] to yield only neptunium tri-iodide. Subsequent vacuum sublimation of the burgundy coloured product

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[5] I. Sheft and S. Fried, *J. Amer. Chem. Soc.*, 1953, **75**, 1236.

[6] H. S. Young, Paper 79 in U.S. Report TID-5290, 1958.

[7] W. H. Zachariasen, *Acta Cryst.*, 1948, **1**, 265.

[8] O. Johnson, T. Butler, and A. S. Newton, Paper 1 in U.S. Report TID-5290, 1958.

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

[10] D. Brown and F. J. G. Rogers, unpublished results.

[11] F. Lux, F. A. Smidt, D. Dempf, D. Graw, and W. Hagenberg, *Radiochim. Acta*, 1970, **14**, 57.

TABLE 2

X-Ray powder diffraction data for α-$NpBr_3$ †

h,k,l	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{est} *
1,0,0 α_1	0·0129	0·0129	s
1,1,0 α_1	0·0384	0·0384	m
1,0,1 α_1	0·0439	0·0439	w+
2,0,0 α_1	0·0510	0·0511	m
1,1,1 α_1	0·0694	0·0693	m+
2,0,1 α_1	0·0820	0·0820	s
2,1,0 α_1	0·0892	0·0891	m
3,0,0 α_1	0·1144	0·1144	m+
2,1,1 α_1	0·1200	0·1200	m+
α_2	0·1206	0·1206	
0,0,2 α_1	0·1240	0·1240	w−
1,0,2 α_1	0·1364	0·1366	w−
2,2,0 α_1	0·1521	0·1521	m−
α_2	0·1533	0·1532	
3,1,0 α_1	0·1651	0·1650	m−
α_2	0·1658	0·1660	
2,0,2 α_1	0·1745	0·1745	w−
3,1,1 α_1	0·1957	0·1958	m−
α_2	0·1966	0·1969	
4,0,0 α_1	0·2031	0·2029	m−
α_2	0·2039	0·2040	
2,1,2 α_1	0·2124	0·2125	w+
α_2	0·2134	0·2136	
3,0,2 α_1	0·2378	0·2377	m−
α_2	0·2390	0·2390	
3,2,0 α_1	0·2409	0·2409	w+
α_2	0·2425	0·2422	
4,1,0 α_1	0·2662	0·2661	m
α_2	0·2676	0·2676	
3,2,1 α_1	0·2717	0·2717	m
α_2	0·2732	0·2732	
3,2,2 α_1	0·2755	0·2756	w−
α_2	0·2770	0·2771	
3,1,2 α_1	0·2884	0·2883	w
α_2	0·2900	0·2898	
5,0,0 α_1	0·3167	0·3166	w
α_2	0·3182	0·3184	
4,0,2 α_1	0·3261	0·3262	w
α_2	0·3284	0·3280	
2,0,3 α_1	0·3285	0·3286	w+
α_2	0·3304	0·3303	
5,0,1 α_1	0·3476	0·3473	w+
α_2	0·3494	0·3493	
3,2,2 α_1	0·3640	0·3640	w
α_2	0·3661	0·3660	
2,1,3 α_1	0·3661	0·3665	w+
α_2	0·3685	0·3684	
4,2,1 α_1	0·3855	0·3853	m−
α_2	0·3871	0·3874	
4,1,2 α_1	0·3892	0·3893	m
α_2	0·3913	0·3914	
5,1,1 α_1	0·4233	0·4232	m+
α_2	0·4256	0·4255	
5,0,2 α_1	0·4396	0·4398	w−
α_2	0·4425	0·4421	
3,1,3 α_1	0·4424	0·4422	w
α_2	0·4449	0·4446	
6,0,0 α_1	0·4556	0·4555	w−
3,3,2 α_1	0·4650	0·4650	w
α_2	0·4681	0·4676	
4,3,0 α_1	0·4680	0·4681	w+
α_2	0·4707	0·4706	
6,0,1 α_1	0·4863	0·4863	w−
α_2	0·4899	0·4889	
5,2,0 α_1	0·4933	0·4933	w+
α_2	0·4958	0·4960	
4,3,1 α_1	0·4988	0·4989	w+
α_2	0·5016	0·5015	
5,1,2 α_1	0·5154	0·5155	w−
3,2,3 α_1	0·5179	0·5179	w+
α_2	0·5204	0·5206	
5,2,1 α_1	0·5243	0·5241	w−
6,1,0 α_1	0·5434	0·5438	w−
α_2	0·5466	0·5467	
4,1,3 α_1	0·5434	0·5431	w−
α_2	0·5466	0·5460	
6,1,1 α_1	0·5744	0·5746	m−
α_2	0·5779	0·5776	
2,1,4 α_1	0·5817	0·5818	w−
4,3,2 α_1	0·5912	0·5911	w
α_2	0·5940	0·5942	
3,0,4 α_1	0·6072	0·6070	m−
α_2	0·6102	0·6102	
5,2,2 α_1	0·6164	0·6164	m
α_2	0·6195	0·6196	
4,2,3 α_1	0·6312	0·6314	w
α_2	0·6343	0·6345	
7,0,1 α_1	0·6503	0·6502	m−
α_2	0·6538	0·6537	
5,3,1 α_1	0·6503	0·6502	m−
α_2	0·6538	0·6537	
3,1,4 α_1	0·6573	0·6575	w+
α_2	0·6610	0·6609	
6,2,0 α_1	0·6573	0·6573	w+
α_2	0·6610	0·6608	
6,1,2 α_1	0·6669	0·6668	w−
5,1,3 α_1	0·6693	0·6692	m
α_2	0·6725	0·6727	
6,2,1 α_1	0·6881	0·6880	m+
α_2	0·6916	0·6917	
4,0,4 α_1	0·6956	0·6953	w−
7,1,0 α_1	0·7204	0·7203	m
α_2	0·7242	0·7241	
4,4,2 α_1	0·7300	0·7298	w+
α_2	0·7335	0·7336	
5,3,2 α_1	0·7423	0·7424	w+
α_2	0·7465	0·7463	
7,0,2 α_1	0·7423	0·7424	w+
α_2	0·7465	0·7463	
4,1,4 α_1	0·7583	0·7583	w+
α_2	0·7618	0·7622	
5,2,3 α_1	0·7701	0·7701	w−
α_2	0·7742	0·7741	
6,2,2 α_1	0·7800	0·7802	w
α_2	0·7844	0·7843	
5,4,1 α_1	0·8015	0·8015	m
α_2	0·8057	0·8057	
5,0,4 α_1	0·8085	0·8087	w+
α_2	0·8126	0·8129	
8,0,0 α_1	0·8085	0·8086	w+
α_2	0·8126	0·8128	
6,1,3 α_1	0·8206	0·8205	m
α_2	0·8248	0·8249	
3,3,4 α_1	0·8339	0·8339	w−
7,1,2 α_1	0·8434	0·8433	m+
α_2	0·8474	0·8477	
2,1,5 α_1	0·8584	0·8584	w+
α_2	0·8628	0·8628	
7,2,1 α_1	0·8768	0·8771	m−
α_2	0·8817	0·8817	
5,3,3 α_1	0·8961	0·8961	m−
α_2	0·9008	0·9007	
7,0,3 α_1	0·8961	0·8961	m−
α_2	0·9008	0·9007	
6,3,2 α_1	0·9189	0·9189	w
α_2	0·9236	0·9237	

* Visually estimated, s, strong; m, medium, w, weak.
† Lattice parameters obtained by individual refinement of α_1 and α_2 reflections ($\lambda_{\alpha_1} = 1{\cdot}54081$, $\lambda_{\alpha_2} = 1{\cdot}54433$ Å) for this film are: α_1: $a_0 = 7{\cdot}915$, $c_0 = 4{\cdot}389$ Å; α_2: $a_0 = 7{\cdot}914$, $c_0 = 4{\cdot}389$ Å. Parameters obtained for other samples agree within the error limits quoted in Table 1.

at 900 °C resulted in the formation of a small residue of neptunium(III) oxyiodide, NpOI. Undoubtedly the reaction between neptunium metal and mercuric iodide, employed previously for the preparation of plutonium and lanthanide element tri-iodides,[12] will also yield NpI_3.

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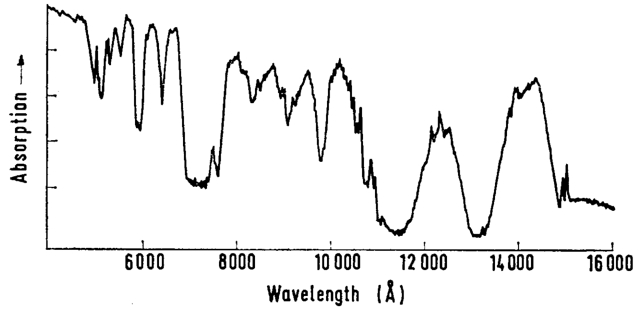
[12] L. B. Asprey, T. K. Keenan, and F. H. Kruse, *Inorg. Chem.*, 1964, **3**, 1137.

The room-temperature transmission spectrum of solid neptunium trichloride in the region 5000—17,000 Å is



The Spectrum of solid $NpCl_3$ at room temperature (4000—17,000 Å). Band positions (s, sharp; sh, shoulder; m, medium; w, weak; b, broad): 4984s, 5031s,sh, 5195s 5250s, 5390m,b, 5652b, 5890w,s, 6062s,sh, 6187b, 6578m,b, 6687m,b, 7484w,s, 8000b, 8187b,sh, 8437b,sh, 8750b, 8968b,sh, 9187b,sh, 9500b, 10,156b, 10,469s,sh, 10,562s,sh, 10,625s,sh, 10,843m, 10,937s,sh, 12,140s, 12,296s, 12,500m,b, 13,781sh, 13,937b, 14,343b, 14,906w,s, 14,992w,s Å

shown in the Figure. As the resolution at room temperature is not very good it is not possible to make assignments analogous to those of Krupke and Gruber[13] for Np^{3+} in $LaBr_3$. Band positions are listed with the spectrum.

On exposure to the atmosphere the above neptunium trihalides initially hydrate and then undergo oxidation to neptunium(IV) species. They dissolve readily in aqueous nitric or hydrochloric acids to yield solution containing neptunium(IV) unless precautions are taken to exclude oxygen. The addition of aqueous ammonia results in the formation of neptunium(IV) hydroxide.

Crystallographic Properties.—Although recent values of the unit-cell dimensions are available for the transplutonium element trihalides it is many years since values were obtained for most of the uranium, neptunium, and plutonium trihalides. The availability of computer programmes for processing *X*-ray powder diffraction data has increased the precision with which unit cell dimensions can be determined and since, in general, the products obtained during the present studies gave high quality *X*-ray powder photographs, their unit cell dimensions have been re-determined. On most films α_1/α_2 splitting of the reflections was observed at θ values of *ca.* 15°; lattice parameters calculated for the trichlorides and tribromides using both α_1- and α_2-series of reflections agreed within the error limits listed with the lattice parameters in Table 1. Observed and calculated values of $\sin^2\theta$ for neptunium tribromide, which are typical of those measured for the hexagonal trichlorides and tribromides, are shown in Table 2. The orthorhombic tribromides did not give such excellent powder patterns (reflections were measured to θ values of *ca.* 45°)

TABLE 3

X-Ray powder diffraction data (α_1 reflections) for UI_3

h	*k*	*l*	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{est} *
0	2	0	0·0125	0·0124	m+
0	4	1	0·0550	0·0550	w
1	3	0	0·0595	0·0595	w+
1	3	1	0·0656	0·0655	m+
0	2	3	0·0665	0·0663	m+
0	4	2	0·0732	0·0729	m
1	1	3	0·0892	0·0890	m−
0	0	4	0·0960	0·0959	w
0	2	4	0·1081	0·1081	w
1	5	0			
0	6	0	0·1101	0·1098	w
1	5	1	0·1134	0·1141	m
0	6	1	0·1160	0·1158	w
2	0	0	0·1273	0·1275	w
0	6	2	0·1337	0·1337	s
0	4	4	0·1446	0·1445	w−
1	7	0	0·1810	0·1810	w
1	7	1	0·1869	0·1870	w
2	2	3	0·1933	0·1933	m−
0	8	0	0·1950	0·1948	m−
0	8	1	0·2006	0·2007	m
1	7	2	0·2051	0·2048	m
1	3	5	0·2086	0·2086	m−
0	0	6	0·2150	0·2152	w
2	2	4	0·2349	0·2350	w
1	5	5	0·2570	0·2571	m−
2	6	2	0·2602	0·2605	m−
1	9	1	0·2838	0·2840	w+
1	9	2	0·3019	0·3018	w−
1	10	0	0·3042	0·3039	w+
3	3	1	0·3193	0·3193	w−
0	10	2	0·3275	0·3277	w
1	9	3	0·3319	0·3316	m−
2	6	4			
3	1	3	0·3429	0·3427	m−
1	3	7	0·3514	0·3515	m−
3	3	3	0·3675	0·3670	w
2	6	5	0·3854	0·3855	w
3	5	2		0·3856	
1	7	6	0·3950	0·3953	w
1	11	0	0·3992	0·3992	w+
0	8	6	0·4091	0·4091	w
2	8	4	0·4161	0·4168	w
1	1	8		0·4165	
2	10	0	0·4307	0·4306	w+
0	12	0	0·4368	0·4372	w
3	3	5	0·4616	0·4621	w+
2	8	5	0·4701	0·4703	w
0	12	3	0·4905	0·4907	w+
3	5	5	0·5111	0·5106	w−
1	1	9	0·5178	0·5177	w
0	4	9	0·5324	0·5316	w
4	2	2	0·5434	0·5437	w−
1	13	1	0·5499	0·5504	w
2	4	8	0·5571	0·5569	w
2	12	1	0·5696	0·5697	w
3	9	3	0·5848	0·5849	w
2	8	7	0·6132	0·6130	w+
1	11	6		0·6133	
2	12	3	0·6175	0·6173	m−
4	6	2	0·6409	0·6405	w
0	14	3	0·6481	0·6481	w
1	9	8	0·6588	0·6587	w
1	13	5	0·6933	0·6931	w+

* Visually estimated, s, strong; m, medium; w, weak.

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[13] W. F. Krupke and J. B. Gruber, *J. Chem. Phys.*, 1967, **46**, 542.

and this is reflected in the somewhat larger error limits quoted in Table 1.

It is well established that a change in structure-type occurs within the actinide tribromides between neptunium and plutonium,[1,2] the earlier members possessing the nine-co-ordinate UCl_3-type of structure whilst the later members are isostructural with $PuBr_3$ in which the actinide element exhibits eight-co-ordination. Zachariasen [7] originally reported neptunium tribromide to be dimorphic but recent work [4] failed to confirm the existence of the β-phase ($PuBr_3$-type) for which no preparative conditions were available. However, during the present investigation it has been observed as the major phase present on sublimation (900—1000 °C) of the product of one reaction in which neptunium tetrabromide was reduced by aluminium. Resublimation under apparently identical conditions yielded pure α-$NpBr_3$ (UCl_3-type of structure). In contrast to the large change in molecular volume associated with the change in structure-type of the actinide tri-iodides,[14] from the $PuBr_3$-type to the BiI_3-type between plutonium and americium, there is little difference in the molecular volumes of α- and β-$NpBr_3$ (Table 1).

Although uranium tri-iodide gave reasonable quality *X*-ray powder photographs too few α_2 lines were sufficiently intense to justify refinement (Table 3). Films obtained for neptunium and plutonium tri-iodide were not quite as good and this is reflected by the larger error limits placed on the unit-cell dimensions (Table 1). The previously unknown neptunium(III) oxyhalides all possess the PbFCl-type of structure recorded for analogous trivalent transneptunium element oxyhalides.[1,2] Observed and calculated values of $\sin^2\theta$ for NpOI are listed, together with visually estimated intensities, in Table 4.

TABLE 4

X-Ray powder diffraction data for NpOI †

h,k,l	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I_{est} *
1,0,2 α_1	0·0647	0·0647	s
1,1,0 α_1	0·0729	0·0728	m−
1,0,3 α_1	0·1000	0·0999	w+
0,0,4 α_1	0·1132	0·1129	m
2,0,0 α_1	0·1453	0·1453	m
α_2	0·1461	0·1463	
1,0,4 α_1	0·1490	0·1491	m−
α_2	0·1499	0·1501	
2,0,2 α_1	0·1729	0·1733	w
1,1,4 α_1	0·1854	0·1853	m+
α_2	0·1865	0·1866	
2,1,2 α_1	0·2097	0·2096	s−
α_2	0·2108	0·2109	
2,1,3 α_1	0·2442	0·2446	w
α_2	0·2461	0·2463	
1,1,5 α_1	0·2487	0·2485	w+
α_2	0·2505	0·2502	
0,0,6 α_1	0·2533	0·2534	w−
2,0,4 α_1	0·2576	0·2576	w+
α_2	0·2592	0·2593	
2,2,0 α_1	0·2899	0·2899	m
α_2	0·2917	0·2917	
2,1,4 α_1	0·2938	0·2938	w−
2,0,5 α_1	0·3206	0·3209	w−
3,0,0 α_1	0·3255	0·3260	w−
3,0,2 α_1	0·3540	0·3542	w+
α_2	0·3566	0·3563	
3,1,0 α_1	0·3624	0·3625	m−
α_2	0·3645	0·3644	
1,0,7 α_1	0·3809	0·3809	m−
α_2	0·3833	0·3832	
3,0,3 α_1	0·3898	0·3893	vw−
2,0,6 α_1	0·3978	0·3981	w−
2,2,4 α_1	0·4020	0·4023	w
α_2	0·4045	0·4046	
1,1,7 α_1	0·4171	0·4170	vw−
2,1,6 α_1	0·4341	0·4342	m−
2,2,5 α_1	0·4654	0·4654	vw−
3,1,4 α_1	0·4747	0·4746	m
α_2	0·4772	0·4773	
1,0,8 α_1	0·4859	0·4861	w
α_2	0·4887	0·4889	
3,2,2 α_1	0·4987	0·4988	m+
α_2	0·5019	0·5015	
2,1,7 α_1	0·5256	0·5254	w=
α_2	0·5286	0·5284	
3,2,3 α_1	0·5333	0·5337	w−
3,1,5 α_1	0·5379	0·5377	w−
α_2	0·5409	0·5407	
4,0,0 α_1	0·5793	0·5791	w+
α_2	0·5823	0·5822	
2,0,8 α_1	0·5944	0·5945	w−
1,0,9 α_1	0·6054	0·6053	w
α_2	0·6082	0·6087	
2,1,8 α_1	0·6307	0·6306	w+
α_2	0·6340	0·6341	
4,1,2 α_1	0·6432	0·6432	m
α_2	0·6466	0·6467	
4,0,4 α_1	0·6913	0·6913	w−
2,0,9 α_1	0·7141	0·7137	w
α_2	0·7176	0·7176	
3,2,6 α_1	0·7234	0·7232	m+
α_2	0·7273	0·7270	
4,2,0 α_1	0·7234	0·7236	m+
α_2	0·7273	0·7273	
1,0,10 α_1	0·7385	0·7385	m+
2,2,8 α_1	0·7385	0·7389	
2,1,9 α_1	0·7498	0·7498	m−
α_2	0·7539	0·7538	
3,2,7 α_1	0·8144	0·8143	w+
α_2	0·8184	0·8185	
4,2,4 α_1	0·8358	0·8358	w
α_2	0·8397	0·8400	
2,2,9 α_1	0·8580	0·8581	w
α_2	0·8622	0·8626	
4,1,6 α_1	0·8676	0·8676	w+
α_2	0·8720	0·8720	
3,0,9 α_1	0·8940	0·8942	w
1,1,11 α_1	0·9220	0·9219	w
α_2	0·9269	0·9267	
4,3,2 α_1	0·9322	0·9322	w
α_2	0·9367	0·9367	
5,0,2 α_1	0·9322	0·9322	w
α_2	0·9367	0·9367	

* Visually estimated, s, strong; m, medium; w, weak. † Lattice parameters obtained by individual refinement of the α_1 and α_2 reflections ($\lambda_{\alpha_1} = 1·54051$ Å, $\lambda_{\alpha_2} = 1·54433$ Å) for this film are: $\alpha_1 : a_0 = 4·051$, $c_0 = 9·192$ Å; α_2: $a_0 = 4·051$, $c_0 = 9·193$ Å. Parameters obtained for other samples agree within the error limits quoted in Table 1.

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EXPERIMENTAL

Uranium tetrachloride,[15] tetrabromide,[16] tetraiodide,[9] neptunium tetrachloride,[17] and tetrabromide [18] were prepared according to the methods given in the references cited. The plutonium trihalides were prepared by direct union of the elements; [10] plutonium and neptunium metal were provided by Dr. J. A. Lee (Process Technology Division, A.E.R.E. Harwell). AnalaR zinc metal was sublimed *in vacuo* prior to use. Silica tubes were employed for all reactions and they were heated to 600 °C, whilst being pumped, before use. All compounds were handled in nitrogen atmosphere boxes (water content <30 p.p.m., oxygen content <10 p.p.m.).

Uranium Trihalides, Neptunium Trichloride and Tribromide.—The appropriate tetrahalide (0·3—1·0 g) and a 50% excess of zinc metal over that required for reduction to the trihalide were sealed together in an evacuated (10^{-4}—10^{-5} mmHg) silica vessel. This was placed completely inside a tube furnace and heated at 550—600 °C for 12—24 h following which it was placed with one end out of the furnance and the excess reductant and zinc dihalide were sublimed to this end of the tube. The trihalide was subsequently sublimed in a clean, evacuated silica tube. Typical temperatures required for a reasonable rate of sublimation were, $NpCl_3$ and $NpBr_3$ 950—1000 °C, UI_3, 700—750 °C. Uranium trichloride reacts partially with silica at the temperature required even for slow sublimation (850—900 °C), the product being uranium dioxide. This problem was not encountered with uranium tri-iodide or neptunium trichloride; a small amount of residue remained after one sublimation of neptunium tribromide. This was identified by *X*-ray diffraction analysis as NpOBr.

Neptunium Tri-iodide.—Neptunium metal (0·1—0·2 g) and a 100% excess of iodine for tri-iodide formation were sealed together in an evacuated tube (10^{-3} mmHg) which was placed completely in a tube furnance and heated at 500 °C for several hours. The excess iodine was subsequently sublimed to one end of the tube (100 °C) and the product shown to be the tri-iodide, and not the tetraiodide, by *X*-ray diffraction analysis. Purification by vacuum sublimation (900 °C) left a small residue of neptunium oxyiodide.

Analysis.—Uranium was determined gravimetrically as U_3O_8 following ignition of the hydroxide formed on the addition of aqueous ammonia. Neptunium-237 was determined by α-assay of aliquot parts of an aqueous nitric acid solution of known volume (specific activity [19] $= 1{\cdot}562 \times 10^6$ α-d min^{-1} mg^{-1}). Halides were weighed as their respective silver salts. Analytical results are listed in Table 5.

Crystallographic Methods.—Samples were mounted in thin-walled silica capillaries in a nitrogen atmosphere box.

TABLE 5

Analytical results

	Found		Required	
Compound	% M	% X	% M	% X
UCl_3	69·1	30·85	69·1	30·9
UBr_3	49·7	50·2	49·8	50·2
UI_3	38·2	61·25	38·45	61·55
$NpCl_3$	68·85	30·65	69·05	30·95
$NpBr_3$	49·6	50·15	49·7	50·3
NpI_3	38·4	61·5	38·35	61·65

* For sublimed material. Analysis of UCl_3 prior to sublimation indicated a purity of 98%.

Films were recorded using a 19 cm Debye–Scherrer camera with nickel-filtered copper radiation and exposure times of 8—16 h (35 kV, 15 mA). Positions of both α_1 and α_2 reflections were measured where possible, each film being measured by two people. Since the structure-type was either known or could be anticipated for each compound it was possible to calculate an appropriate powder pattern using the programme Genstruck [20] and then index the observed reflections by comparison with the calculated pattern. The indexed reflections were refined by a least-squares method using the programme Cohen [20] with the appropriate wavelength (Cu-α_1, 1·54051 Å or Cu-α_2 1·54433 Å). The agreement limit was set to 0·0004 for values of $\sin^2\theta$ and two cycles of refinement were sufficient to ensure the correct indexing of the film. Results for different samples and for α_1 and α_2 sets of reflections agreed within the error limits (2σ) quoted in Table 1. The reliability of the camera constants employed was checked by determination of the unit-cell parameters for samples of silicon and thoria. The value obtained for silicon, 5·4303 Å, agrees with the literature value [21] (5·4303 Å) and that obtained for the sample of thoria, 5·5968 Å, agrees with the value determined for the same sample on other cameras [22] (5·5970 Å).

Spectral Studies.—Samples for solid state spectral studies (*ca.* 10 mg) were mounted as mulls in Voltalef-91 between silica plates. The sample holder was fixed in a small Perspex box fitted with silica windows in order to protect the air-sensitive sample and to contain the radioactivity. Spectra were recorded using a Cary 14 spectrometer.

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