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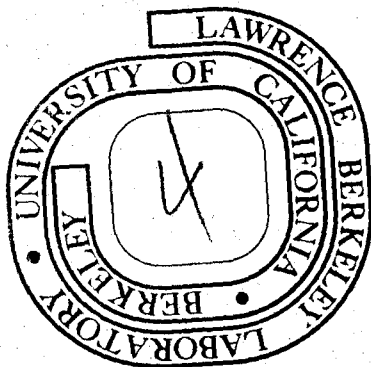
R. D. Peacock and Norman Edelstein

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Some Reactions of Neptunium Hexafluoride

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ABSTRACT

Hydrolysis of neptunium hexafluoride in nearly anhydrous hydrogen fluoride solution yields a new oxide fluoride, NpOF_4 , which is isostructural with the trigonal form of UOF_4 . NpOF_4 is not oxidised to Np(VII) by KrF_2 in anhydrous HF solution. The exchange reaction between NpF_6 and BCl_3 leads initially to the formation of NpF_4 . NpF_6 combines with CsF at 25° to yield CsNpF_6 ; in the presence of ClF_3 as solvent and at lower temperatures there is evidence for the possible formation of an unstable Np(VI) complex.

INTRODUCTION The chemistry of neptunium in its higher oxidation states is restricted.¹ Np(VI) is known in NpF_6 , in neptunyl salts and a number of complexes, whilst Np(VII) is known only in complex oxides and similar compounds.²⁻⁶ In the present work the reactions of neptunium hexafluoride with water in anhydrous hydrogen fluoride, boron trichloride, and caesium fluoride have been investigated in an attempt to widen the range of known compounds.

EXPERIMENTAL Hydrolysis of NpF_6 - About 0.35 g of NpF_6 in an FEP reaction tube was dissolved in $\sim 1 \text{ cm}^{-3}$ of anhydrous hydrogen fluoride (pretreated with fluorine gas). To the solution was added in successive small portions by condensation a solution of 0.02 g water in 4 ml anhydrous HF (i.e., nearly enough to cause hydrolysis according to the equation $\text{NpF}_6 + \text{H}_2\text{O} \rightarrow \text{NpOF}_4 + 2\text{HF}$). A brownish purple residue formed immediately. When the reaction was complete the volatile materials, which included a little NpF_6 , were pumped off and a portion of the remaining solid was retained for examination. Debye X-ray powder photographs indicated the residue was isostructural with the trigonal phase of UOF_4 .⁷⁻¹⁰ The measured d spacings are shown in Table I.

Reaction of Np oxide fluoride with KrF_2 - A portion of the residue obtained in the preceding experiment was suspended in anhydrous HF (3 cm^3) in an FEP tube, and treated with 0.2 g KrF_2 , obtained by the cyclotron method.¹¹ The temperature was maintained overnight at about -60° , and the volatile materials were removed. By visual examination it was evident that NpF_6 was now present, indicating that a proportion of the oxide fluoride had been fluorinated. The remaining solid, which X-ray examination showed to be

identical with the starting material, was yellow brown in colour.

A portion of the yellow brown solid, suspended in anhydrous HF, was treated with a further 0.2 g KrF_2 in the presence of CsF, but no evidence of further change occurred.

Reaction of CsF and NpF_6 - About 0.01 g dry CsF in a small monel reactor (volume about 1 cm^3) equipped with a Whitey valve was treated under vacuum with excess of NpF_6 ($\sim 0.1 \text{ g}$) at 25° for one month. A slight pressure of gas developed during the period and the white residue was shown to be CsNpF_6^{12} by Debye X-ray powder photography.

Reaction of CsCl with NpF_6 in ClF_3 solution - Chlorine trifluoride (1 cm^3) was condensed at -180° on CsCl (0.0445 g) under vacuum in a polytetrafluoroethylene tube ($3/8''$ o.d.) equipped with a Whitey valve. The temperature was allowed to rise slowly to 0° to complete the reaction, and the lower boiling products (chiefly Cl_2) were pumped off. The ClF_3 was then taken off into a side vessel, and the operation repeated three times in order to complete the conversion of CsCl to CsClF_4 . Finally a further 2 cm^3 of ClF_3 was condensed on the solid, this was sufficient to dissolve the CsClF_4 completely. The FEP tube was cooled to -180° and NpF_6 ($\sim 0.2 \text{ g}$) was then admitted. On allowing to warm, a reddish solution formed which left a purple-black solid residue on removing the solvent. On successively adding and removing the solvent over the course of a number of hours the dark colourations gradually faded, and finally a greenish-white residue (0.0644 g) remained. A dry portion of the purple-black residue behaved similarly, and consequently it was not possible to obtain an X-ray powder photograph with

the available equipment. Repetition of the complete experiment gave similar results. An X-ray photograph of the residue disclosed the presence of Cs_2SiF_6 as the principal phase. Checking with a probe indicated the presence of only a small proportion of Np in the residue.

Reaction of NpF_6 with BCl_3 - The $\text{NpF}_6/\text{ClF}_3$ mixture remaining after the preceding experiment was condensed at -180° in a polytetrafluoroethylene (FEP) tube. BCl_3 , purified by "topping" and "tailing", was added very carefully in small amounts (in order to convert the ClF_3 to Cl_2 at the same time as reaction with the NpF_6 took place), and the temperature was adjusted to maintain a liquid phase by judicious movement of the liquid nitrogen dewar. Initially, each time a new portion of BCl_3 came into contact with the reaction mixture a dark green colouration appeared in the liquid phase; this faded within a few seconds and a light green solid precipitated. While excess of NpF_6 was still present, all volatile materials were removed by condensation to a side trap, and a portion of the greenish white residue was retained for examination. Debye X-ray powder photographs indicated this to be a NpF_4 . The remainder of the residue, together with the volatile materials, were returned to the original FEP tube and treated with a large excess of boron trichloride ($\sim 2 \text{ cm}^3$). A dark brown supernatant appeared over the solid; after standing for 16 hours the volatile materials were pumped off, leaving a golden brown solid. An X-ray examination of this phase showed the absence of NpF_4 .

Materials and apparatus - Experiments were carried out in a monel vacuum system equipped with high pressure valves, using FEP tubing (3/8" or 1/4" o.d.) closed at one end or Kel-F traps as appropriate. NpF_6 was synthesised

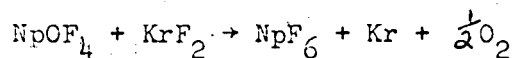
in a flow system from NpO_2 and fluorine at $250 - 450^\circ\text{C}$. Caesium fluoride was ignited in a platinum dish before use and loaded in an efficient dry box. Caesium chloride was dried at 110° . Chlorine trifluoride and anhydrous hydrogen fluoride were redistilled before use, and the tail and head fractions were discarded.

X-ray powder patterns were obtained using a modified 57.3 mm Debye-Scherrer camera. A Jarrell-Ash microfocus X-ray generator was used to obtain Cu radiation which was filtered with a Ni foil.

DISCUSSION The hydrolysis of UF_6 has only recently been re-examined after early reports had suggested that UF_6 did not react with water in the vapour phase to give the oxide tetrafluoride.^{25,26} However, two sets of workers have now independently shown that in anhydrous hydrogen fluoride solution the carefully controlled hydrolysis of UF_6 does give UOF_4 , formally analogous to the well-known oxide tetrafluorides of Mo and W.^{8,9,10} Unlike UO_2F_2 , this is an extremely reactive material; the structure is quite different from the 6-coordinated MoOF_4 and WOF_4 , and in fact two different phases are known, one of which is isostructural with $\beta\text{-UF}_5$ and both of which contain uranium in high co-ordination.

In the present work it has been shown that a reactive material almost insoluble in anhydrous hydrogen fluoride is the first product of the hydrolysis of NpF_6 . This reactive material has been identified by X-ray diffraction as the trigonal form of NpOF_4 . A least squares fitting²⁷ of the trigonal unit cell parameters to the observed data gives the lattice constants $a_0 = 13.17 \pm 0.02$; $c_0 = 5.70 \pm 0.02$. The smaller unit cell for NpOF_4 as compared to UOF_4 ⁷ ($a_0 = 13.22$; $c_0 = 5.72 \text{ \AA}$) follows the expected trend due to the decreased ionic radius of the higher Z.....

element. When the NpOF_4 was allowed to stand in capillaries in incompletely dry conditions, it led to decolorization and the appearance of a further unidentified crystalline phase. The attempted oxidation of NpOF_4 with krypton difluoride did not lead to the hoped for NpOF_5 (which one might expect to be volatile), but only to the partial re-formation of NpF_6 , perhaps according to the equation.

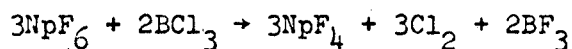


The residue was almost unchanged starting material.

It is now evident that an Np(VII) fluoride or oxide fluoride will not be easily prepared. To isolate NpF_7 or NpOF_5 will require stronger oxidising conditions than those used, and it is difficult to see how these can be accomplished with materials presently to hand. NpO_2F_3 could have resulted from the direct fluorination of NpO_2 (cf. ReO_2F_3), and the only remaining chance here would be to attempt the oxidation of the rather unreactive NpO_2F_2 . There appears on the surface to be a marginally better chance of getting NpO_3F , since, with manganese and technetium, compounds of similar stoichiometry may be isolated without great difficulty.^{28,29} Unlike MnO_3F and TcO_3F , however, it is not likely that an NpO_3F would prove to be volatile, so that the reaction conditions which might result in its isolation would need careful selection.

The highest certain chloride of neptunium is the tetrachloride in NpCl_4 , though there is slight evidence for a pentachloride in the vapour phase. Exchange reactions have proved successful in preparing tungsten

and uranium hexachlorides from their hexafluorides by treatment with boron trichloride,^{19,20} whilst the action of boron trichloride on rhenium hexafluoride certainly gives ReCl_5 .²¹ The present work indicates that a competing reaction, which gives some tetrafluoride in the uranium system,²⁰ becomes exclusive in the neptunium system.



The further reaction of neptunium tetrafluoride with excess of boron trichloride leads to a change of phase, and it seems probable that chloride fluorides, analogous to the known uranium compounds,²² are formed. It is interesting that NpF_5 , which has been fully characterised by X-ray photography,^{23,24} is not isolated, though it could be responsible for the transient green colouration (cf. ²⁰).

The uranium salts Na_2UF_9 , K_2UF_8 , and CsUF_7 have been known for some time,^{13,14,15} but the corresponding neptunium salts have not been isolated. The present work confirms earlier conclusions that the reaction of neptunium hexafluoride with alkali metal fluorides at 25° leads only to Np(V) salts.¹⁶ The strong colorations seen at lower temperatures have been reported by other workers.^{17,18} It is tempting to ascribe these to Np(VI) complexes, but clearly further work is required in this area.

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Table I.
Partial X-Ray Powder Diffraction Data for UO_2 and NpO_2 .

hkl	hkl	hkl	hkl	UO_2^a		NpO_2	
				d(A)	Int.	d(A)	Int.
110				6.610	31*		
101				5.117	41	4.864	S
021				4.046	100	3.927	MS
030	300			3.816	75	3.732	MS
211				3.451	61	3.371	M
220				3.305	32	3.227	M
131	012			2.776	14		
401	202			2.560	34	2.492	MW
140	410			2.498	8	2.466	MW
321	122			2.387	43	2.342	M
330				2.203	5		
051	312			2.126	43	2.092	MW
241	042			2.024	21	1.996	MW
511	232			1.935	36	1.909	M
060	600	003		1.908	8		
520	250	113		1.833	27	1.803	M
431	502			1.788	29	1.764	MW
422				1.726	3		
303	033			1.706	15	1.680	W
161	152			1.670	7	1.652	VW
440	223			1.653	9	1.630	VVW
351	701	342		1.573	20	1.550	MS
621				1.530	3		
170	710	143	413	1.516	13	1.500	VVW
621				1.490	1	1.475	VVW
360	630	333		1.442	4		
541	072	532	104	1.420	21	1.402	M
081	262	024		1.388	8	1.371	VW
271	214			1.359	12	1.342	W
063	603			1.349	2		
550	523	253		1.322	23	1.306	M

^aCalculated from the reported structure.⁷

* Not certainly observed in NpO_2 due to strong background.

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