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Some Reactions of Neptunium Hexafluoride

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Hydrolysis of neptunium hexafluoride in nearly anhydrous hydrogen fluoride solution yields a new oxide fluoride, $\text{NpOF}_4$, which is isostructural with the trigonal form of $\text{UOF}_4$. $\text{NpOF}_4$ is not oxidised to $\text{Np(VII)}$ by $\text{KrF}_2$ in anhydrous HF solution. The exchange reaction between $\text{NpF}_6$ and $\text{BCl}_3$ leads initially to the formation of $\text{NpF}_4$. $\text{NpF}_6$ combines with $\text{CsF}$ at $25^\circ$ to yield $\text{CsNpF}_6$; in the presence of $\text{ClF}_3$ as solvent and at lower temperatures there is evidence for the possible formation of an unstable $\text{Np(VI)}$ 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.\(^2\) 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 \(\sim 1\) 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 NpF\(_6\) + H\(_2\)O \(\rightarrow\) NpOF\(_4\) + 2HF). 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\(_{\text{oxide}}\) 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 \(-60^\circ\), 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 KrF₂ in the presence of CsF, but no evidence of further change occurred.

**Reaction of CsF and NpF₆** - About 0.01 g dry CsF in a small monel reactor (volume about 1 cm³) equipped with a Whitey valve was treated under vacuum with excess of NpF₆ (≈ 0.1 g) at 25° for one month. A slight pressure of gas developed during the period and the white residue was shown to be CsNpF₁₂ by Debye X-ray powder photography.

**Reaction of CsCl with NpF₆ in ClF₃ solution** - Chlorine trifluoride (1 cm³) 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 Cl₂) were pumped off. The ClF₃ was then taken off into a side vessel, and the operation repeated three times in order to complete the conversion of CsCl to CsClF₄. Finally a further 2 cm³ of ClF₃ was condensed on the solid, this was sufficient to dissolve the CsClF₄ completely. The FEP tube was cooled to -180° and NpF₆ (≈ 0.2 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 Cs₂SiF₆ as the principal phase. Checking with a probe indicated the presence of only a small proportion of Np in the residue.

Reaction of NpF₆ with BCl₃ - The NpF₆/ClF₃ mixture remaining after the preceding experiment was condensed at -180°C in a polytetrafluoroethylene (FEP) tube. BCl₃, purified by "topping" and "tailing", was added very carefully in small amounts (in order to convert the ClF₃ to Cl₂ at the same time as reaction with the NpF₆ 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 BCl₃ 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 NpF₆ 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 NpF₄. 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 (~ 2 cm³). 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 NpF₄.

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. NpF₆ was synthesised
in a flow system from NpO$_2$ and fluorine at 250 - 450°C. Caesium fluoride
was ignited in a platinum dish before use and loaded in an efficient dry
box. Caesium chloride was dried at 110°C. 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
UOF$_2$, 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 β-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 hydro-
lysis of NpF$_6$. This reactive material has been identified by X-ray diffract-
on as the trigonal form of NpOF$_4$. A least squares fitting$^{27}$ of the trigonal
unit cell parameters to the observed data gives the lattice constants
a$_0$ = 13.17 ± 0.02; c$_0$ = 5.70 ± 0.02. The smaller unit cell for NpOF$_4$ as compared
to UOF$_4$ $^7$ (a$_0$ = 13.22; c$_0$ = 5.72 $\AA$) follows the expected trend due to the
decreased ionic radius of the higher Z...
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.

$$\text{NpOF}_4 + \text{KrF}_2 \rightarrow \text{NpF}_6 + \text{Kr} + \frac{1}{2}\text{O}_2$$

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$_2$F$_3$ could have resulted from the direct fluorination of NpO$_2$ (cf. ReO$_2$F$_3$), and the only remaining chance here would be to attempt the oxidation of the rather unreactive NpO$_2$F$_2$. There appears on the surface to be a marginally better chance of getting NpO$_3$F, since, with manganese and technetium, compounds of similar stoichiometry may be isolated without great difficulty.$^{28,29}$ Unlike MnO$_3$F and TcO$_3$F, however, it is not likely that an NpO$_3$F 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, whilst the action of boron trichloride on rhenium hexafluoride certainly gives ReCl₅. The present work indicates that a competing reaction, which gives some tetrafluoride in the uranium system, becomes exclusive in the neptunium system.

\[ 3\text{NpF}_6 + 2\text{BCl}_3 \rightarrow 3\text{NpF}_4 + 3\text{Cl}_2 + 2\text{BF}_3 \]

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, are formed. It is interesting that \( \text{NpF}_5 \), which has been fully characterised by X-ray photography, is not isolated, though it could be responsible for the transient green colouration (cf.).

The uranium salts \( \text{Na}_2\text{UF}_9 \), \( \text{K}_2\text{UF}_8 \), and \( \text{CsUF}_7 \) have been known for some time, 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 \( \text{Np(V)} \) salts. The strong colorations seen at lower temperatures have been reported by other workers. It is tempting to ascribe these to \( \text{Np(VI)} \) complexes, but clearly further work is required in this area.

ACKNOWLEDGEMENTS

We thank Drs. L. Asprey and R.T. Paine for sending us an experimental powder pattern and the line list for \( \text{UOF}_4 \); and Prof. N. Bartlett for pointing out the similarities between the powder patterns of \( \text{UOF}_4 \) and \( \text{NpOF}_4 \).
Table I.

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UOF₄⁺⁺: Calculated from the reported structure.

NpOF₄⁺⁺: Not certainly observed in NpOF₄ due to strong background.
REFERENCES


