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# Preparation, chemical reactions, and some physical properties of neptunium pentafluoride

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## Abstract

The preparation of $NpF_5$ by reacting a solution containing $NpF_6^-$ with the Lewis acid $BF_3$ in anhydrous HF is reported. The purity of $NpF_5$ was established by its Mössbauer spectrum, which showed only the presence of $Np^{5+}$. Thermal decomposition and some chemical reactions of $NpF_5$ are described. Debye–Scherrer powder data from $NpF_5$ appear similar to those obtained from $\alpha$-$UF_5$, indexing as tetragonal with cell constants $a = 6.5358(18)$ Å and $c = 4.4562(14)$ Å. Photochemical irradiation of $NpF_6$ produced an amorphous material believed, but not confirmed, to be $NpF_5$.

## 1. Introduction

Uranium pentafluoride ($UF_5$) is a well-characterized compound and is easily prepared by many different methods [1, 2]. Two isomorphs, $\alpha$-$UF_5$ and $\beta$-$UF_5$, are known (see Table 1). In contrast, neptunium pentafluoride is difficult to prepare and little is known of its chemical and physical properties.

$NpF_5$ was first prepared [3] by reduction with iodine in $IF_5$. It had an X-ray powder diffraction pattern similar to that of $\alpha$-$UF_5$ but Mössbauer spectroscopy showed the sample to be contaminated with $NpF_4$. This preparation was repeated more recently and some properties were reported [4]. Others prepared $NpF_5$ by the controlled fluorination of $NpF_4$ with $KrF_2$ at 20 °C in liquid anhydrous hydrogen fluoride [5, 6]. It was characterized by chemical analysis and some properties were described.

In a third method, $NpF_5$ was prepared by the reduction of $NpF_6$ with $PF_3$ in hydrogen fluoride at low temperature [7]. It was confirmed to have an X-ray powder diffraction pattern similar to that of $\alpha$-$UF_5$.

We undertook this study to develop a facile method for preparation of pure $NpF_5$ and to confirm its purity by the observation of a Mössbauer spectrum that showed only $Np^{5+}$. Mössbauer spectroscopy is more conclusive than X-ray powder diffraction, because of the possibility that a neptunium-containing amorphous material may be present and because neptunium phases isostructural with $\beta$-$UF_5$ and $\beta$-$UOF_4$, which are indistinguishable by X-ray diffraction, might form. In this study, $NpF_5$ was precipitated from a solution of an $Np^{5+}$ salt (as the Lewis base $NpF_6^-$) dissolved in liquid anhydrous hydrogen fluoride by addition of a Lewis acid, $BF_3$. Physical and chemical properties are reported.

## 2. Experimental methods

### *2.1. Equipment and materials*

#### *2.1.1. Equipment*

Gases were handled in all nickel or Monel metal high vacuum systems fitted with Monel metal Bourdon gauges that could be read to 1% accuracy at full scale. The reactions were carried out in 3/4 in outer diameter (OD) Kel-F tubes (35 $cm^3$) fitted with Kel-F valves that were attached to the vacuum system through Monel metal flare fittings.

Precipitations from liquid anhydrous hydrogen fluoride (AHF) were carried out in these reactors attached through 1/4 in OD flexible Kel-F tubes in a Y-connection that allowed the liquid HF to be decanted and then distilled back for washings. The reactors were preconditioned with fluorine and FNO and pumped to a good vacuum (*ca.* 0.01 Torr) before use. The reactors were small enough that they could be weighed before and after reactions on an analytical balance with a large sample chamber.

Desired amounts of gaseous reagents were measured tensimetrically in the metal manifold and then either expanded or condensed into the reactors. After reaction, the quantities of gaseous products and residual volatile reactants were measured tensimetrically. Then the reactors were pumped to a good vacuum, transferred to

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a dry box, and opened in the dry box to remove the solid products.

The photochemical irradiations were carried out using radiation from a 450 W high pressure mercury lamp, filtered through uranium glass.

#### 2.1.2. Materials

Liquid AHF (99% purity, minimum) was obtained from the Matheson Gas Products Company. It was further purified by treating 600 g batches in a Monel metal container with 2 atm of fluorine for several days. The excess fluorine was removed by pumping at −78 °C. When purified in this manner, the liquid HF gave no reaction with $NpF_6$ (which is extremely sensitive to traces of moisture or reducing impurities).

High purity nitric oxide (NO) was obtained from the Matheson Gas Products Company. Nitrosyl fluoride (FNO) was obtained by reacting NO with fluorine at 25 °C. IR spectra showed the FNO to be free of impurities. This reactive gas was stored with excess fluorine to prevent formation of traces of NO by slow reaction with the storage vessels. The fluorine was removed just prior to use.

$NpF_6$ was prepared by reaction of $NpF_6$ or $NpO_2$ with fluorine at high temperature. High purity CO and $BF_3$ were used directly from the cylinders. Analytical grade LiF was used.

### 2.2. Preparation of compounds

#### 2.2.1. Preparation of $NONpF_6$

About 1 mmol of $NpF_6$ and 2 mmol of FNO were condensed in a Kel-F reaction tube. (At low temperatures these condensed gases form an intense dark brown color but on warming they can be separated and recovered unchanged. This effect had been observed by others.) The mixture was irradiated for 2 h to give a light pink solid. The X-ray powder pattern is very similar to that of $NOUF_6$. The solid dissolved completely in liquid AHF to give a pale pink solution.

#### 2.2.2. Preparation of $NpF_5$ from $NONpF_6 + LiF + BF_3$

About 0.7 mmol of $NONpF_6$ was dissolved in AHF and then mixed with a solution of 2 mmol of LiF dissolved in AHF to give a total volume of 10 cm$^3$. The pink solution of $NONpF_6$ turns to a yellow color on addition of LiF. $BF_3$ gas was added and a yellow–brown solid precipitated. When the precipitation was complete, the supernatant was poured off and AHF was distilled back for washing. The product was washed two or three times with AHF by this means and then was dried by pumping under high vacuum. About 0.7 mmol of $NpF_5$ was recovered. The X-ray powder pattern was similar to that of $\alpha$-$UF_5$. Samples of $NpF_5$ prepared in this manner dissolved instantly and completely in liquid AHF containing LiF or NaF. The physical and chemical properties of $NpF_5$ reported in this paper were determined on $NpF_5$ prepared by this method.

Solutions of $NpF_5$ in AHF with NOF, NaF, or LiF should not be allowed to stand for any period of time. Slow attack on the Kel-F occurs, producing lower insoluble neptunium fluorides. If this decomposition occurs the solution should be poured into another container and $BF_3$ added to precipitate pure $NpF_5$.

If one attempts to obtain $NpF_5$ from AHF solution of $NONpF_6$ directly by addition of $BF_3$ without the addition of LiF, a pale green solid is precipitated. This gives the $NpF_5$ X-ray pattern but, on treatment with LiF in AHF, 20% remains undissolved.

#### 2.2.3. Reaction of $NpF_6 + CO + light$ to give $NpF_5$

In one experiment, about 0.25 mmol of $NpF_6$ and 1.0 mmol CO were irradiated for 1 h. The $NpF_6$ was consumed completely and $COF_2$ was identified as the gaseous product. About 0.23 mmol (as $NpF_5$) of a finely divided amorphous white powder was formed.

In another similar experiment the white product was contacted with 2.5 mmol of LiF dissolved in about 5 cm$^3$ of AHF. Most of the product dissolved slowly to give a yellow solution. After 1 h the solution was poured off, leaving the undissolved product, which was washed, dried, and weighed. About 0.05 mmol (as $NpF_5$, about 20% of the original) remained undissolved, and was probably $NpF_4$.

#### 2.2.4. Reaction of $NpF_6 + PF_3$ in anhydrous HF

In three separate experiments we attempted to form $NpF_5$ by reduction with $PF_3$. Others [7] have reported this reaction to give $NpF_5$. In each of our three experiments about 1 mmol of $NpF_6$ in 11 cm$^3$ of AHF was poured onto 0.5 mmol of $PF_3$ at −78 °C. A reaction took place immediately to give about 0.5 mmol of a light green product. The product was amorphous to X-rays but in one case faint $NpF_4$ powder diffraction lines were observed. A small amount of the solid dissolved in a Teflon mull gave an $NpF_4$ spectrum in a Cary 14 spectrophotometer. The solid product showed no evidence of dissolving when treated with a solution of NaF in liquid AHF.

### 2.3. Thermal decomposition and chemical reactions of $NpF_5$

#### 2.3.1. Thermal decomposition of $NpF_5$

0.0552 g was placed in a weighed nickel cup in a nickel reactor that was connected to the vacuum line through a Kel-F U-tube. While pumping under high vacuum the sample was heated at the rate of about 5 °C min$^{-1}$. $NpF_6$ began to evolve rapidly at 318 °C and was collected in the U-tube. A small amount of original solid was "blown" into the U-tube. The mass of $NpF_6$ collected was estimated, from its pressure and the volume in which it was confined, to be 23±2 mg. 21.4 mg of green powder remained in the cup and was identified as $NpF_4$ by its X-ray powder pattern.

### *2.3.2. Reaction of $NpF_5$ with $BCl_3$*

0.0415 of $NpF_5$ was transferred into a glass tube in the dry box. On the vacuum line, $BCl_3$ gas was added to a pressure of 600 Torr. There was no reaction at 25 °C. There was no visible reaction on warming at 50 °C. The X-ray powder pattern of the solid showed only $NpF_5$; therefore there was no reaction.

In a similar experiment 0.130 g of $UF_5$ was treated with $BCl_3$. There was no reaction at 25 °C but at 40 °C the sample turned a brown color. The X-ray pattern of the product was not identified but was not that of either $UF_5$ isomorph.

### *2.3.3. Preparation of $LiNpF_6$*

This product was obtained by pouring a solution of LiF in AHF onto excess $NpF_5$. The resulting solution was poured off and evaporated to dryness to give $LiNpF_6$, which gave an X-ray powder pattern that indicated that it is isostructural with $LiUF_6$.

### *2.3.4. Hydrolysis of $NpF_5$*

9.9 mg of $NpF_5$ was hydrolyzed in 1 M $HClO_4$ in a centrifuge cone. The turbid solution was centrifuged and the supernatant transferred to a spectrophotometer cell and diluted to 4 ml. The absorption spectrum was determined from 1400 nm to 350 nm with 1 M $HClO_4$(aq) in the reference beam. Optical densities were measured for the peaks at 720 nm ($Np^{4+}$), 980 nm ($NpO_2^+$) and 1200 nm ($NpO_2^{2+}$). These showed the concentration of neptunium ions to be $6.2\times10^{-4}$ mol $l^{-1}$ of $NpO_2^+$ and $3.3\times10^{-3}$ mol $l^{-1}$ of $NpO_2^{2+}$. Complexing with $F^-$ prevented the determination of $Np^{4+}$ in the original hydrolysis supernatant.

A small amount of $NaNO_2$ was added to reduce the $NpO_2^{2+}$ to $NpO_2^+$. The 1200 nm ($NpO_2^{2+}$) band disappeared and the 980 nm band ($NpO_2^+$) was measured. The mass of $NpF_5$ hydrolyzed, determined from the optical absorption of this band, was calculated to be 9.65 mg, in good agreement with the original mass of 9.9 mg.

The solid in the centrifuge cone was metathesized with NaOH and the solid dissolved in $HClO_4$ in an attempt to determine the amount of $Np^{4+}$ present. Only about 10% of neptunium was found in this residue.

### *2.4. Physical property determinations*

X-Ray powder samples were heat sealed with wax in 0.3 mm diameter quartz capillaries in a nitrogen-filled dry box. Diffraction patterns were obtained with nickel-filtered copper radiation in 57.3 mm diameter Debye–Scherrer cameras. A Mössbauer spectrometry sample was encapsulated by enclosing 36 mg of $NpF_5$ in a Kel-F holder in the dry box and was sealed in the dry box in a cemented Lucite secondary container. A $^{237}Np$ Mössbauer spectrum was obtained in the transmission mode, using the E1 transition between spin states $5/2^-$ and $5/2^+$. The sample and the $^{241}Am$ metal source were kept at 4.2 K for the measurement. The $\gamma$ ray selection from this source is straightforward, since the 59.4 keV line is the only one present. The absence of other lines permits the direct use of the output current from the scintillation detector, which results in high counting rates.

## 3. Results and discussion

### *3.1. Preparation studies*

The inherent instability of $NpF_5$ with respect to $NpF_4$ and $NpF_6$ makes $NpF_5$ difficult to isolate in a pure state with preparative procedures using fluorinating or reducing agents. This instability contrasts with the stability of $UF_5$, which is always formed as the stable product whenever mixtures of $UF_4$ and $UF_6$ are reacted by any chemical procedures.

### *3.1.1. Precipitation of $NpF_5$ from $NpF_6^-$ solutions*

$NONpF_6$ dissolves in liquid AHF to give a pink solution of $(NO^+)(NpF_6^-)$. On addition of the Lewis base LiF, a yellow solution of $(Li^+)(NpF_6^-)$ is formed:

$$(NO^+)(NpF_6^-)+LiF \longrightarrow (Li^+)(NpF_6^-)+FNO(g)$$

On addition of the Lewis acid $BF_3$, insoluble $NpF_5$ is precipitated:

$$(Li^+)(NpF_6^-)+BF_3 \longrightarrow (Li^+)(BF_4^-)+NpF_5(s)$$

It is interesting to observe this precipitation. As small amounts of $BF_3$ are added, a small amount of precipitate forms and then redissolves as the solution is mixed. A similar reaction has been used by others [8] to prepare $UF_5$.

### *3.1.2. Reaction of $NpF_6$+CO+light to give $NpF_5$*

The reaction of $NpF_6$ and CO under irradiation produces a finely divided amorphous white solid. The product, however, is impure. About 20% remains undissolved when treated with liquid AHF containing LiF. A similar reaction has been used by others to convert $UF_6$ quantitatively to $UF_5$.

These results suggest, however, that the product of this reaction might be used as the starting material for producing pure $NpF_5$, thus avoiding the use of the very reactive FNO.

### 3.1.3. Reaction of $PF_3$ with $NpF_6$ in anhydrous HF

Others [7] have claimed to produce $NpF_5$ by the reaction of $PF_3$ and $NpF_6$ in AHF. In that work excess $PF_3$ and $NpF_6$ and AHF were condensed at liquid nitrogen temperatures and allowed to warm slowly. Reaction occurred at low temperature and the product was identified by X-ray powder crystallography.

In three separate attempts we were not able to reproduce their results. Our conditions were somewhat different. We used excess $NpF_6$ and the reactants were cooled only to dry ice (−78 °C) temperature.

## 3.2. Chemical studies

### 3.2.1. Reaction of $NpF_5$ with 1 M $HClO_4(aq)$

We have found that $NpF_5$ is hydrolyzed in dilute acid to give $Np^{4+}$ and $NpO_2^{2+}$. The presence of $F^-$ ion suppresses the usual rapid recombination that otherwise gives the stable $NpO_2^+$ species. This path is similar to the dissociation observed on the hydrolysis of $UF_6$ but in the case of uranium $UO_2^+$ undergoes further decomposition since it is not stable in aqueous solution.

Our result disagrees with the observations of others [5] on hydrolysis of their product. On hydrolysis in dilute $HNO_3$ they observed a clear solution and imply that this is evidence that the initial product on hydrolysis is Np(V).

### 3.2.2. Reaction with $BCl_3$

We found that $NpF_5$ did not react with $BCl_3$ at 50 °C. Under similar conditions we observed $UF_5$ to react with $BCl_3$. Others [9] have shown this product to be $UCl_5$.

### 3.2.3. Reaction to give $LiNpF_6$

LiF in AHF was contacted with excess $NpF_5$ and the solution decanted and evaporated; $LiNpF_6$ was obtained.

## 3.3. Physical studies

### 3.3.1. X-Ray diffraction

The powder patterns we observed for $NpF_5$ are similar to those obtained by Baluka *et al.* [7] with additional lines, all of which were indexed as tetragonal, and the lattice parameters were refined, using least-squares program LCR-2 [10], to $a=6.5354(18)$ Å and $c=4.4562(14)$ Å. Experimental lattice parameters and intensities agree well with those calculated using the positional parameters obtained from $\alpha$-$UF_5$ [11], as input into the program LAZY PULVERIX [12]. The literature lattice parameters are cited in Table 1.

Powder patterns alone are not sufficient to establish the purity of $NpF_5$ because in all the reactions to produce $NpF_5$ (here and elsewhere) an impurity, $NpOF_4$, could be formed. $NpOF_4$ is known (Table 1) and is not isostructural with $NpF_5$. There are two isomorphs of $UOF_4$ (Table 1) and, if $NpOF_4$ has two isomorphs, the second form would probably be isostructural with $\beta$-$UOF_4$ and would give an X-ray powder pattern indistinguishable from that of $NpF_5$. To clarify the comparison, all relevant uranium and neptunium analogs are shown in Table 1.

### 3.3.2. Thermal decomposition

Once formed, $NpF_5$ is surprisingly stable. We observed decomposition to take place at 318 °C to give $NpF_6$ and $NpF_4$. In contrast $UF_5$ can be observed to decompose at as low as 150 °C, giving off $UF_6$ and proceeding in a stepwise fashion to produce $U_2F_9$, $U_4F_{17}$ and $UF_4$.

### 3.3.3. Mössbauer studies

The $^{237}Np$ Mössbauer spectrum of the sample is shown in Fig. 1. The spectrum is consistent with one type of neptunium, pentavalent, in an axial crystal field, and with no discernable hyperfine field. There is no evidence of either $Np^{4+}$ or $Np^{6+}$ impurity phases. This result is strong evidence for essentially single-phase $NpF_5$ because $^{237}Np$ Mössbauer spectroscopy can be

TABLE 1. A comparison of crystal data for $UF_5$, $UOF_4$, $NpF_5$, and $NpOF_4$

| Compound | Symmetry | Space group | a (Å) | c (Å) | Reference |
|---|---|---|---|---|---|
| $\alpha$-$UF_5$ | Tetragonal | *I*4/*m* | 6.518(4) | 4.470(1) | 11 |
| $NpF_5$ | Tetragonal | | 6.5358(18) | 4.4562(14) | This work[a] |
| | | | 6.53(3) | 4.45(3) | 7 |
| | | | 6.535(2) | 4.458(2) | 4 |
| $\beta$-$UF_5$ | Tetragonal | $I\bar{4}2d$ | 11.456(2) | 5.195(1) | 13 |
| $\alpha$-$UOF_4$ | Trigonal | *R*3*m* | 13.22(1) | 5.72(1) | 14 |
| $\beta$-$UOF_4$ | Tetragonal | $I\bar{4}2d$ | 11.4743(11) | 5.2043(5) | 15 |
| $NpOF_4$ | Trigonal | | 13.17(2) | 5.70(2) | 16 |

[a] Error limits for $NpF_5$ (this work) are 95% confidence limits.

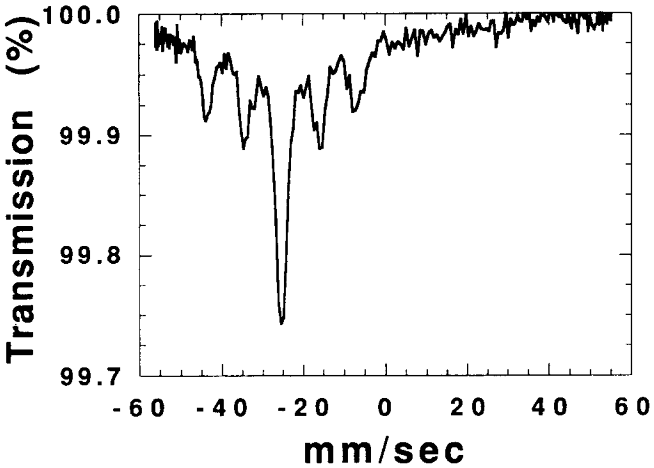

Fig. 1. $^{237}Np$ Mössbauer spectrum of $NpF_5$ relative to $^{241}Am$ metal source.

expected to detect small amounts of impurity charge states, on the order of 2%.

The spectrum is fitted to yield an isomer shift (IS) of 25.2±0.2 mm $s^{-1}$ relative to the americium metal source. The IS is consistent with, but an extreme value of, the IS expected for formally pentavalent neptunium. This behavior is consistent with other binary fluorides $NpF_x$ [17], which are assumed to be the most ionic of the metal binaries. It has been demonstrated previously that covalency effects increase with increasing formal oxidation number for actinide binary fluorides [18], but this increase is not linear because of increasing covalency. These results support this argument. The electric field gradient, $\pm 62 \pm 2$ mm $s^{-1}$, is best fitted with the asymmetry parameter $\eta = 0$, indicating that the neptunium sits on a site with 3-fold or higher rotational symmetry. This is consistent with the similarity of the X-ray powder pattern of $NpF_5$ to that of $\alpha$-$UF_5$, which has uranium on a 4-fold tetragonal symmetry axis [11, 19]. The sign of the electric field gradient is not distinguishable in the absence of any hyperfine interactions. The linewidth of 3.8±0.4 mm $s^{-1}$ is slightly broader than the source linewidth of 2.5 mm $s^{-1}$, but there is no evidence of a Goldanski–Karyagin effect.

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