Structural Study of the Ammonium Octafluoroneptunate, $[\text{NH}_4]_4\text{NpF}_8$

Frederic Poineau^{a*}, Chinthaka M. Silva^b, Charles B. Yeaman^c, Gary S. Cerefice^d, Alfred P. Sattelberger^{a,e}, Kenneth R. Czerwinski^a

a Department of Chemistry, University of Nevada-Las Vegas, Las Vegas, NV 89154, USA.

b Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

c. Lawrence Livermore National Laboratory, Livermore CA 94551, USA.

d Department of Health Physics, University of Nevada-Las Vegas, Las Vegas, NV 89154, USA.

e Argonne National Laboratory, Lemont, IL 60439, USA.

* **Corresponding author.** Department of Chemistry, University of Nevada-Las Vegas, Las Vegas, 4505 Maryland parkway, NV 89154-4009, USA. poineauf@unlv.nevada.edu

Abstract. The $[\text{NH}_4]_4\text{NpF}_8$ salt was prepared from the solid-state reaction of NpO_2 with NH_4HF_2 and characterized by powder x-ray diffraction and x-ray absorption fine structure spectroscopy. The diffraction results confirm the compound to be isostructural to $[\text{NH}_4]_4\text{UF}_8$ with the following lattice parameter ($a = 13.054(4) \text{ \AA}$, $b = 6.681(2) \text{ \AA}$, $c = 13.676(5) \text{ \AA}$, $\beta = 121.14^\circ$). For the first time, a Neptunium fluoride complex has been characterized by XAFS spectroscopy. The energy position of the white line and inflection of the XANES spectra of $[\text{NH}_4]_4\text{NpF}_8$ are consistent with the presence of Np(IV) . Adjustment of the EXAFS spectra indicates that the coordination number (7.4 ± 1.5) and the average Np-F distance ($2.26(1) \text{ \AA}$) are consistent with the presence of the NpF_8 dodecahedron. The average Np-F distance is $\sim 0.02 \text{ \AA}$ shorter than the U-F distance in $[\text{NH}_4]_4\text{UF}_8$ and is a result of the actinide contraction.

Keywords. Neptunium; Fluoride; EXAFS

1. Introduction

Tetravalent actinide (An) fluoride salts represent a rather large class of compounds and more than one hundred compounds have been reported [1]. The study of their crystallographic structures represents a significant advance in An coordination chemistry [2]. One class of compound of interest is those with the stoichiometry of $[\text{NH}_4]_4\text{AnF}_8$. The interest resides in the potential use of these salts for the preparation of An nitride fuels for advanced reactor systems. In previous studies, it was shown that the treatment of $[\text{NH}_4]_4\text{AnF}_8$ under ammonia gas at elevated temperature produced AnN_2 (An = U, Np) and ThNF [3, 4, 5].

Historically, $[\text{NH}_4]_4\text{AnF}_8$ (An = U, Np, Pu, Am) were prepared from the reaction of the AnF_4 with saturated NH_4F solution [6]. The Pa salt was obtained from the treatment of PaF_4 with NH_4F in an autoclave [7]. Another preparation method is the solid-state reaction of the AnO_2 (An = Th, U, Np) with NH_4HF_2 [8]. Powder X-ray diffraction (PXRD) measurements indicated the $[\text{NH}_4]_4\text{AnF}_8$ salts (An = Pa, Np, Pu, Am) were isostructural to the U salt, but lattice parameters were reported only for the Pa salt [9, 7]. Single-crystals of $[\text{NH}_4]_4\text{AnF}_8$ (An = Th and U) were obtained from the treatment of AnF_4 in saturated aqueous NH_4F solution. Single-crystal XRD (SCXRD) measurements reveal the U salt to consist of isolated UF_8 dodecahedra [9], while the Th salt contains infinite chains of ThF_9 polyhedra [10]. Due to the radiotoxicity of Np, Pu and Am, the preparation of single-crystals of $[\text{NH}_4]_4\text{AnF}_8$ from concentrated An solutions is challenging. In the cases where single-crystals cannot be obtained, X-ray absorption fine structure spectroscopy (XAFS) has proven an efficient technique for the structural characterization of micro-amounts of materials [11,12]. Recently, UF_4 and Pa(V) fluoride complexes were successfully studied by XAFS spectroscopy [13,14]. To the best of our knowledge, XAFS studies of Np fluorides are currently unknown. Due to the potential use of $[\text{NH}_4]_4\text{NpF}_8$ in the preparation of nitride fuels, its structural study is of importance. In the present article, the $[\text{NH}_4]_4\text{NpF}_8$ salt was prepared and studied by PXRD and XAFS spectroscopy.

2. Experimental methods

Caution! Neptunium-237 is an alpha emitter ($E_{\text{max}} = 5.3 \text{ MeV}$). All manipulations were performed in a radiochemistry laboratory designed for chemical synthesis using efficient HEPA-filtered fume hoods and glove boxes and following locally approved radioisotope handling and monitoring procedures.

Preparation of $[\text{NH}_4]_4\text{NpF}_8$. In a glove box, brown NpO_2 (113 mg) and NH_4HF_2 (96 mg) were placed in a Teflon bottle. The compounds were mixed with a plastic spatula for 10 min. The Teflon bottle was closed with a cap, removed from the glove-box and placed in an oven at 100°C for 7 days under air. After this time, a yellow-green microcrystalline $[\text{NH}_4]_4\text{NpF}_8$ powder was obtained in quantitative yield.

Physical measurements. XAFS measurements were performed at the Advanced Photon Source at the BESSRC-CAT 12 BM station at Argonne National Laboratory. The Np salt was diluted ($\sim 1\%$ Np by mass) in boron nitride, ground in a mortar, and placed in an aluminum sample holder equipped with Kapton windows. XAFS spectra were recorded at the Np- L_3 edge ($17\,610 \text{ eV}$) in fluorescence mode at room temperature using a 13-element germanium detector. A double crystal of Si $[1\,1\,1]$ was used as a monochromator. Energy calibration was performed using a Zr foil (K edge = $17\,998 \text{ eV}$). Five EXAFS spectra were recorded over the k range of $0\text{--}13 \text{ \AA}^{-1}$ and averaged. The background contribution was removed using Athena [15] software and data analysis performed using WINXAS [16]. For the fitting procedure, scatterings wave functions were calculated by FEFF8.2 [17]; the input files were generated by ATOMS [18]. The threshold energy E_0 was defined at $17\,620 \text{ eV}$. Adjustment of the EXAFS spectrum was performed under the constraints $S_0^2 = 0.9$.

X-ray powder diffraction measurements were performed using a Philips PANalytical X'Pert Pro instrument with a $\text{Cu-K}\alpha$ target and a Ni filter, using 40 mA current and 45 kV tension.

3. Results and Discussion

The first report of $[\text{NH}_4]_4\text{NpF}_8$ appeared in the literature in 1964; the compound was obtained from the reaction of the tetrafluoride in concentrated aqueous NH_4F solution and was isostructural to $[\text{NH}_4]_4\text{UF}_8$ [6]. A second report from 1979 indicated that $[\text{NH}_4]_4\text{NpF}_8$ was prepared from the reaction of NpO_2 with NH_4HF_2 at 100 °C [8]. Thermo-gravimetric analysis under Ar atmosphere indicated that the $[\text{NH}_4]_4\text{NpF}_8$ prepared from NpO_2 decomposed to $[\text{NH}_4]_2\text{NpF}_6$, $[\text{NH}_4]_7\text{Np}_6\text{F}_{31}$, $[\text{NH}_4]\text{NpF}_5$ and $[\text{NH}_4]\text{Np}_3\text{F}_{13}$. Powder XRD measurements indicated the $[\text{NH}_4]_2\text{NpF}_6$ and $[\text{NH}_4]\text{Np}_3\text{F}_{13}$ salts were isostructural to their U analogs, but no structural data on $[\text{NH}_4]_4\text{NpF}_8$ was reported.

In the present study, $[\text{NH}_4]_4\text{NpF}_8$ was prepared from the reaction of NpO_2 with NH_4HF_2 at 100 °C. After the reaction, the micro-crystalline powder was analyzed by PXRD which confirms the compound is isostructural to $[\text{NH}_4]_4\text{AnF}_8$ (An = Pa, U) and crystallizes in the monoclinic $C2/c$ space group. The lattice parameters for the Pa, U and Np salts are presented in Table 1.

Table 1. Lattice parameters and unit cell volume for $[\text{NH}_4]_4\text{AnF}_8$ (An = Pa, U, Np).

$[\text{NH}_4]_4\text{AnF}_8$	a (Å)	b (Å)	c (Å)	β (deg)	V (Å ³)
Pa [7]	13.18	6.71	13.22	117.1	1040.8
U [9]	13.126(5)	6.692(3)	13.717(5)	121.19	1030.7
Np	13.054(4)	6.681(2)	13.676(5)	121.14	1020.9

A decrease of the unit cell volume is observed in the series: Pa > U > Np. This decrease is due to the actinide contraction and has already been observed in several An (IV) fluorides, e.g., AnF_4 , Rb_2AnF_6 and LiAnF_5 [19, 20, 21].

Because the ionic radius of $\text{Np}(4+)$ is ~ 0.02 Å smaller than that of $\text{U}(4+)$ [22], it is expected that in the $[\text{NH}_4]_4\text{AnF}_8$ salts the Np-F distances will be ~ 0.02 Å shorter than the corresponding U-F distances. In order to determine the average Np-F distance in $[\text{NH}_4]_4\text{NpF}_8$, XAFS spectroscopy measurements were performed.

The XANES spectra of $[\text{NH}_4]_4\text{NpF}_8$ exhibits an intense white line which is due to the excitation of a $2p_{3/2}$ core electron into 6d unoccupied states. The position of the maximum of the white line (17620.3 eV) and the first inflection point (17615.2 eV) are similar to those of other Np(IV) complexes (Table 2) and confirm the presence of Np(IV) in the salt.

Table 2. Position (eV) of the maximum of the white line and first inflection point in NpO_2 [23], $\text{Np(IV)}_{\text{aq}}$ [24] and $[\text{NH}_4]_4\text{NpF}_8$.

	White line	First inflection point
NpO_2	17 621.8(5)	17 616.5(5)
$\text{Np(IV)}_{\text{aq}}$ in 1 M HClO_4	17 620.9	17 616.1
$[\text{NH}_4]_4\text{NpF}_8$	17 620.3(5)	17 615.2(5)

Figure 1. Normalized Np- L_3 XANES spectra of $[\text{NH}_4]_4\text{NpF}_8$.

The extracted EXAFS spectrum of $[\text{NH}_4]_4\text{NpF}_8$ was k^3 -weighted and the Fourier Transform (FT) performed in the k -range $[0.75 - 10] \text{ \AA}^{-1}$. The EXAFS spectrum was fit using the scatterings calculated in $[\text{NH}_4]_4\text{NpF}_8$. The $[\text{NH}_4]_4\text{NpF}_8$ salt was constructed

using the known crystallographic structure of $[\text{NH}_4]_4\text{UF}_8$ by replacing the U by Np atoms [9]. The structure of $[\text{NH}_4]_4\text{UF}_8$ consists of discrete UF_8 distorted dodecahedra linked via the ammonium ions through N-H...F hydrogen bonding. A representation of the UF_8 polyhedron in $[\text{NH}_4]_4\text{UF}_8$ is shown in Figure 2. In the fitting procedure, all the parameters: coordination number (C.N), R, σ^2 , and ΔE_0 were allowed to vary. The fitted k^3 -EXAFS spectra and FT are presented in Figure 3. The structural parameters are presented in Table 3.

Figure 2. Ball and stick representation of the UF_8 dodecahedra in $[\text{NH}_4]_4\text{UF}_8$. Color of atom: U in grey and F in yellow-green.

Figure 3. Fitted k^3 - EXAFS spectra (bottom) and Fourier Transform (top) of k^3 -EXAFS spectra of $[\text{NH}_4]_4\text{NpF}_8$. Adjustment between $k = [0.75 - 10] \text{ \AA}^{-1}$. Residual = 1.65 %. Experimental data in black and fit in red.

Table 3. Structural parameters obtained from the adjustment of the k^3 - EXAFS spectra of $[\text{NH}_4]_4\text{NpF}_8$.

Scattering	Structural parameter			
	C.N	R ($\text{\AA}$)	σ^2 ($\text{\AA}^2$)	ΔE_0
Np-F	7.3 ± 1.5	2.26(1)	0.0095	1.57

The results of adjustment indicate that the environment around the Np atom is constituted by 7.3 ± 1.5 fluorine atoms at 2.26(1) $\text{\AA}$. The average Np-F distance in $[\text{NH}_4]_4\text{NpF}_8$ was compared to the one found by SCXRD in other Np(IV) fluoride complexes. Currently six Np(IV) fluoride salts have been characterized by SCXRD (Table 4): $\text{Np}_3\text{F}_{12} \cdot \text{H}_2\text{O}$ [25], NaNp_2F_9 [26], $\text{NaNp}_3\text{F}_{13}$ [27], $\text{NaFeNp}_3\text{F}_{15}$ [28], $\text{CuNp}_2\text{F}_{10} \cdot 8\text{H}_2\text{O}$ and $\text{CoNp}_2\text{F}_{10} \cdot 8\text{H}_2\text{O}$ [29]. In those complexes, the Np atom is either 8 or 9 coordinate; the geometry of the NpF_9 polyhedron is a tri-capped trigonal prism, while the NpF_8 polyhedron is a dodecahedron. The average Np-F distances in the NpF_8 dodecahedra are 0.06 - 0.08 $\text{\AA}$ shorter than those in the NpF_9 tri-capped trigonal prisms (Table 4); this difference is a result of the packing geometry of the fluorine atoms within the polyhedron. The average Np-F distance found by EXAFS in $[\text{NH}_4]_4\text{NpF}_8$ is similar to the ones found in the NpF_8 dodecahedron in $\text{Np}_3\text{F}_{12} \cdot \text{H}_2\text{O}$. In $\text{Np}_3\text{F}_{12} \cdot \text{H}_2\text{O}$, the Np atoms are 8 and 9 coordinate.

As expected, the average Np-F distance in $[\text{NH}_4]_4\text{NpF}_8$ is ~ 0.02 $\text{\AA}$ shorter than the one in $[\text{NH}_4]_4\text{UF}_8$ (i.e., 2.28[3] $\text{\AA}$). Further analysis of the literature indicates that among the Np complexes reported in Table 4, only two complexes have a U homologue that has been characterized by SCXRD, *viz.*, $\text{U}_3\text{F}_{12} \cdot \text{H}_2\text{O}$ [30] and NaU_2F_9 [31]. In those compounds, the average Np-F distance is also ~ 0.02 $\text{\AA}$ shorter than the one in the analogous U complexes (Table 5) and is a further evidence of the actinide contraction.

Table 4. Average Np-F distances (Å) and coordination numbers (C.N.) of the Np atom found by SCXRD in Np(IV) fluorides. The values in brackets are the variances on the Np-F distances.

compound	Np-F	C.N
Np ₃ F ₁₂ •H ₂ O	2.25[3]	8
	2.31[8]	9
NaNp ₂ F ₉	2.31[3]	9
NaNp ₃ F ₁₃	2.33[8]	9
NaFeNp ₃ F ₁₅	2.31[6]	9
CoNp ₂ F ₁₀ •8H ₂ O	2.32[5]	9
CuNp ₂ F ₁₀ •8H ₂ O	2.32[6]	9

Table 5. Average Np-F distances (Å) found by EXAFS in [NH₄]₄NpF₈ and by SCXRD in [NH₄]₄UF₈, An₃F₁₂•H₂O and NaAn₂F₉ (An = U, Np). The value in brackets is the variance on the Np-F distances.

An	[NH ₄] ₄ AnF ₈	An ₃ F ₁₂ •H ₂ O	NaAn ₂ F ₉
U	2.28[3]	2.28[2] for CN=8 2.33[7] for CN= 9	2.33[3]
Np	2.26(1)	2.25[3] for CN= 8 2.31[8] for CN= 9	2.31[3]

4. Conclusion

In summary, the [NH₄]₄NpF₈ salt was prepared from the solid-state reaction of NpO₂ with NH₄HF₂ and characterized by PXRD and XAFS spectroscopy. The PXRD results confirm the compound is isostructural to [NH₄]₄UF₈ and lattice parameters are reported. For the first time, an Np fluoride complex has been characterized by XAFS spectroscopy. The energy position of the white line and inflection of the XANES spectra of [NH₄]₄NpF₈

are consistent with the presence of Np(IV). Adjustment of the EXAFS spectra indicates that the coordination number and the average Np-F distance are consistent with the presence of a NpF₈ dodecahedron. The average Np-F distance is ~0.02 Å shorter than the U-F distance in [NH₄]₄UF₈ and is a result of the actinide contraction. The successful characterization of [NH₄]₄NpF₈ by XAFS spectroscopy indicates that this technique could be used to extract the An-F distances in other [NH₄]₄AnF₈ salts (An = Pa, Pu, Am).

Acknowledgments. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

References

-
- ¹ N.P. Freestone, J.H. Holloway. Actinide Fluorides in Synthesis of Lanthanide and Actinide compounds. G. Meyer, L. R. Morss, Editor. Topics in f-Element Chemistry, 2 (1991).
 - ² R.A. Penneman, Structure and Bonding, 13 (1973) 1.
 - ³ C.B. Yeaman, G.W.C. Silva, G.S. Cerefece, K.R. Czerwinski, T. Hartmann, A.K. Burrell, A.P. Sattelberger, J. Nucl. Mater. 374 (2008) 75.
 - ⁴ G.W.C. Silva, C.B. Yeaman, A.P. Sattelberger, T. Hartmann, G.S. Cerefece, K.R. Czerwinski, Inorg. Chem. 48 (2009) 10635.
 - ⁵ G.W.C. Silva, P.F. Weck, E. Kim, C.B. Yeaman, G.S. Cerefece, A.P. Sattelberger, K.R. Czerwinski, J. Am. Chem. Soc. 134 (2012) 3111.
 - ⁶ R.A. Penneman, F.H. Kruse, R.S. George, J.S. Coleman, Inorg. Chem. 3 (1964) 309.
 - ⁷ L.B. Asprey, F.H. Kruse, R.A. Penneman, Inorg. Chem. 6 (1967) 544.
 - ⁸ H. Abazli, J. Jove, M. Pages, Cr. Acad. Sci.C Chim. 288 (1979) 157.
 - ⁹ A. Rosenzweig, D.T. Cromer, Acta Crystallogr. B 26 (1970) 38.
 - ¹⁰ R.R. Ryan, R.A. Penneman, A. Rosenzweig, Acta Crystallogr. B. 25 (1969) 1958.

-
- ¹¹ M.R. Antonio, L. Soderholm. X-ray Absorption Spectroscopy of the Actinides, in *The Chemistry of the Actinide Transactinide Elementse*, Editors, Morss, L. R., Edelstein, N. M., Fuger, J., 3rd ed, Springer, Dordrecht, Netherland, 2006.
- ¹² F. Poineau, C.B. Yeaman, G.W.C. Silva, G.S. Cerefice, A.P. Sattelberger, K.R. Czerwinski, J. Radioanal. Nucl. Chem. 292 (2012) 989.
- ¹³ J.G. Tobin, C.H. Booth, W. Siekhaus, D.K. Shuh, J. Vac. Sci. Technol. A 33 (2015) 33001.
- ¹⁴ S.M. De Sio, R.E. Wilson, Inorg. Chem. 53 (2014) 1750.
- ¹⁵ M. Newville, P. Livins, Y. Yacoby, E.A. Stern, J.J. Rehr, Phys. Rev. B 47 (1993) 14126.
- ¹⁶ T. Ressler, J. Synchrotron Rad. 5 (1998) 118.
- ¹⁷ J.J. Rehr, R.C. Albers, Rev. Mod. Phys. 72 (2000) 621.
- ¹⁸ B. Ravel, J. Synchrotron Rad. 8 (2001) 314.
- ¹⁹ T.K. Keenan, Inorg. Nucl. Chem. Lett. 3 (1967) 463.
- ²⁰ T.K. Keenan, Inorg. Nucl. Chem. Lett. 2 (1966) 153.
- ²¹ L.B. Asprey, R.G. Haire, Inorg. Nucl. Chem. Lett. 9 (1973) 1121.
- ²² R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.
- ²³ L. Martel, J.F. Vigier, D. Prieur, S. Nourry, A. Guiot, K. Dardenne, J. Boshoven, J. Somers, J. Phys. Chem. C 118 (2014) 27640.
- ²⁴ M.A. Denecke, K. Dardenne, C.M. Marquardt, Talanta 65 (2005) 1008.
- ²⁵ A. Cousson, Acta Crystallogr. C 41 (1985) 804.
- ²⁶ A. Cousson, H. Abazali, A. Tabuteau, M. Pages, Crystallogr. B 38 (1982) 1801.
- ²⁷ A. Cousson, H. Abazali, M. Pages, Acta Crystallogr. C 39 (1983) 318.
- ²⁸ A. Cousson, H. Abazali, M. Pages, Acta Crystallogr. B 35 (1982) 2668.
- ²⁹ A. Cousson, H. Abazali, J. Jove, J. Less-Common Met. 109 (1985) 155.
- ³⁰ J. Yeon, M.D. Smith, A.S. Sefat, T.T. Tran, P.S. Halasyamani, H.C. zur Loye, Inorg. Chem. 52 (2013) 8303.
- ³¹ J. Olchowka, C. Volkringer, N. Henry, T. Loiseau, J. Fluorine. Chem. 159 (2014) 1.

Graphical Abstract

Np(IV)

$\text{Np-F} = 2.26(1) \text{ \AA}$