

Product evolution in the Np(IV) fluorophosphate system

Travis H. Bray^a, Tyler A. Sullens^a, Tatiana Y. Shvareva^a, Richard E. Sykora^b,
Richard G. Haire^c, Thomas E. Albrecht-Schmitt^{a,*}

^aDepartment of Chemistry and Biochemistry and the E. C. Leach Nuclear Science Center, Auburn University, Auburn, AL 36849, USA

^bDepartment of Chemistry, University of South Alabama, Mobile, AL 36688, USA

^cChemical Sciences Division, Transuranium Research Laboratory, Oak Ridge National Laboratory, MS 6375, Oak Ridge, TE 37831, USA

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Abstract

The reaction of ²³⁷NpO₂ with Cs₂CO₃, Ga₂O₃, H₃PO₄, and HF under mild hydrothermal conditions leads to the formation of NpFPO₄ after 4 days at 180 °C. Heating at 180 °C for an additional 6 days leads to the crystallization of Cs₂Np₂F₇PO₄ and NpF₄. The Ga₂O₃ forms a GaPO₄ matrix in which crystals of NpFPO₄, Cs₂Np₂F₇PO₄, and NpF₄ grow. Single crystal X-ray data reveal that the structure of NpFPO₄ consists of Np(IV) centers bound by both fluoride and phosphate to yield [NpF₂O₆] distorted dodecahedra. These are linked by corner-sharing with fluoride and both corner- and edge-sharing with phosphate to yield a dense, three-dimensional network. The structure of Cs₂Np₂F₇PO₄ is complex and contains both distorted dodecahedral [NpO₂F₆] and tricapped trigonal prismatic [NpO₂F₇] environments around Np(IV) that are linked with each other through corner- and edge-sharing, and with the phosphate groups to create a three-dimensional structure. There are small channels extending down the *a*-axis in Cs₂Np₂F₇PO₄. Crystallographic data: NpFPO₄, orthorhombic, space group *Pnma*, *a* = 8.598(2), *b* = 6.964(1), *c* = 6.337(1) Å, *Z* = 4, *V* = 379.44(13) Å³, R(F) = 3.53% for 40 parameters and 465 reflections with *I* > 2σ(*I*) (*T* = 193 K); Cs₂Np₂F₇PO₄, monoclinic, space group *P2₁/c*, *a* = 8.8727(4), *b* = 16.2778(7), *c* = 7.8009(4) Å, β = 112.656(1), *Z* = 4, *V* = 1039.73(8) Å³, R(F) = 2.27% for 146 parameters and 2465 reflections with *I* > 2σ(*I*) (*T* = 193 K).

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1. Introduction

Np(IV) phosphates were first prepared to determine the solubility of a wide range of Np compounds for designing separation and purification processes for the actinides [1]. Reports on the intentional preparation of pure Np(IV) phosphates come surprisingly late with the indication that NaNp₂(PO₄)₃ and Na₂Np(PO₄)₂ are isostructural with other tetravalent actinide analogs [2]. A thorough investigation of the *An*⁴⁺ (*An* = Th, U, Np) phosphate system showed that the only orthophosphate that could be prepared is Th₃(PO₄)₄ [3]. Furthermore, while the pyrophosphates, α-*MP*₂O₇, (*M* = U, Th, and Np) can be prepared, the oxyphosphates were only found for (*MO*)₂P₂O₇

(*M* = Np, U) [3]. Recent interest in Np(IV) phosphates has been primarily motivated by the potential utility of phosphate phases, particularly monazites, for long-term storage hosts for transuranium elements [4]. In addition, the complexation of higher oxidation states of Np by phosphate in solution may be of environmental importance [5].

A recent search of the Inorganic Crystal Structure Database (ICSD) for single crystal structures of Np(IV) phosphates revealed their surprising absence [6], although powder diffraction data are noted in the ICDD files. Despite the aforementioned importance of these compounds, the lack of information on these Np phases occurs in part because of the practice of using the substantially less radioactive elements, Th and U, as surrogates for Np. The use of Th and U to represent Np chemistry is questionable, especially if the potential for redox processes exists [7]. As a

*Corresponding author. Fax: +1 334 844 6959.

E-mail address: albreth@auburn.edu (T.E. Albrecht-Schmitt).

part of ongoing studies on actinide phosphates [8], the preparation, structures, and properties of Np(IV) phosphates are of interest. Herein, the three-dimensional frameworks of two Np(IV) fluorophosphates, NpFPO₄ and Cs₂Np₂F₇PO₄, are reported.

2. Experimental

2.1. Materials

²³⁷NpO₂ (99.9%, ORNL), Ga₂O₃ (99.99%, Alfa-Aesar), Cs₂CO₃ (99.99%, Alfa-Aesar), H₃PO₄ (98%, Aldrich), and HF (48 wt.%, Aldrich) were used as received. Distilled and Millipore filtered water with a resistance of 18.2 MΩ cm was used in all syntheses. Reactions were run in Parr 4749 autoclaves with custom-made 10-mL PTFE liners. All studies were conducted in a lab dedicated to studies on transuranium elements using procedures previously described [7].

2.1.1. NpFPO₄ and Cs₂Np₂F₇PO₄

NpO₂ (0.0100 g, 0.037 mmol), Ga₂O₃ (0.0070 g, 0.037 mmol), H₃PO₄ (0.0150 g, 0.153 mmol), Cs₂CO₃ (0.0360 g, 0.110 mmol), HF (0.2 mL), and 0.5 mL of water were loaded into a 10-mL PTFE-lined autoclave. The autoclave was sealed and placed into a box furnace that had been pre-heated to 180 °C. The reaction solutions were cooled at a rate of 9 °C/h to 23 °C. After 4 days of heating, the solid products consisted of green blocks of NpFPO₄ in a GaPO₄ matrix. The yield was considered to be nearly 100%: NpFPO₄ was the only Np-containing product and soluble Np in the mother liquor was not detected using UV–vis–NIR spectroscopy. After a total of 10 days at 180 °C, green, roughly hexagonal tablets of Cs₂Np₂F₇PO₄ and large acicular crystals of NpF₄ were isolated from a GaPO₄ matrix, and NpF₄ was the major product.

2.1.2. Crystallographic studies

Single crystals of NpFPO₄ (0.094 × 0.034 × 0.032 mm) and Cs₂Np₂F₇PO₄ (0.079 × 0.060 × 0.034 mm) were selected using a digital microscope with remote viewing capabilities, and were transferred to Krytox oil. Crystals suitable for diffraction studies were mounted on glass fibers with epoxy and optically aligned on a Bruker SMART APEX CCD X-ray diffractometer using a digital camera. Intensity measurements were performed using graphite monochromated MoKα radiation from a sealed tube and monocapillary collimator. SMART (v 5.624) was used for preliminary determination of the cell constants and data collection control. The intensities of reflections of a sphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω . A total of 1800 frames were collected with an exposure time per frame of 30 s for each compound.

Determination of integrated intensities and global refinement were performed with the Bruker SAINT

(v 6.02) software package using a narrow-frame integration algorithm. A face-indexed analytical absorption correction was initially applied using XPREP, where individual shells of unmerged data were corrected analytically. These files were subsequently treated with a semiempirical absorption correction by SADABS [9]. The program suite, SHELXTL (v 6.12), was used for a space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [10]. The final refinements included anisotropic displacement parameters for all atoms and secondary extinction. Selected crystallographic details are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters for NpFPO₄ and Cs₂Np₂F₇PO₄ are given in Tables 2 and 3, respectively. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; Email: crysdata@fiz-karlsruhe.de) on quoting depository numbers CSD 416757 and 416758.

2.1.3. UV–vis–NIR spectroscopy

Absorption spectra of the mother liquors were collected using a Shimadzu UV3101 spectrophotometer.

3. Results and discussion

3.1. Synthesis

The evolution of product formation in the Np(IV) fluorophosphate system is of interest from several standpoints. First, the dissolution of NpO₂ in acid often leads to the formation of solutions containing NpO₂⁺ [11]. While it is possible that NpO₂⁺ could form and then disproportionate to yield Np⁴⁺ and NpO₂²⁺ [12], Np(VI) was not detected in our solutions. We have previously reported that HF can reduce U(VI) under hydrothermal conditions, but

Table 1
Crystallographic data for NpFPO₄ and Cs₂Np₂F₇PO₄

Formula	NpFPO ₄	Cs ₂ Np ₂ F ₇ PO ₄
Formula Mass	350.97	967.79
Color and habit	Green block	Green tablet
Crystal System	Orthorhombic	Monoclinic
Space group	<i>Pnma</i> (no. 62)	<i>P2₁/c</i> (no. 14)
<i>a</i> (Å)	8.598(2)	8.8727(4)
<i>b</i> (Å)	6.964(1)	16.2778(7)
<i>c</i> (Å)	6.337(1)	7.8009(4)
<i>V</i> (Å ³)	379.4(1)	1039.73(8)
<i>Z</i>	4	4
<i>T</i> (K)	193	193
λ (Å)	0.71073	0.71073
Maximum 2 θ (deg.)	56.48	56.60
ρ_{calcd} (g cm ⁻³)	6.144	6.183
μ (Mo <i>K</i> α) (cm ⁻¹)	277.16	270.30
<i>R</i> (<i>F</i>) for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0353	0.0227
<i>R_w</i> (F_o^2) ^b	0.0976	0.0590

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b R_w(F_o^2) = \frac{\left[\sum [w(F_o^2 - F_c^2)^2] \right]^{1/2}}{\sum wF_o^4}$$

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for NpFPO₄

Atom (site)	x	y	z	U_{eq} (Å ²) ^a
Np(1)	0.45116(6)	3/4	0.14279(8)	0.0070(3)
P(1)	0.6003(5)	3/4	-0.3203(6)	0.0110(7)
F(1)	0.7135(9)	3/4	0.1933(13)	0.0148(17)
O(1)	0.4897(13)	3/4	-0.5049(18)	0.0143(19)
O(2)	0.5657(8)	0.9234(12)	-0.1689(11)	0.0112(15)
O(3)	0.7718(11)	3/4	-0.3894(16)	0.013(2)

Table 3
Atomic coordinates and equivalent isotropic displacement parameters for Cs₂Np₂F₇PO₄

Atom (site)	x	y	z	U_{eq} (Å ²) ^a
Np(1)	0.14644(3)	0.577904(12)	0.17201(3)	0.00784(8)
Np(2)	0.45409(3)	0.741629(13)	0.49805(3)	0.00726(8)
Cs(1)	-0.03199(5)	0.82970(2)	0.08366(5)	0.01638(10)
Cs(2)	-0.35359(5)	0.99230(2)	-0.23771(6)	0.01908(10)
P(1)	0.72866(18)	0.62731(9)	0.8809(2)	0.0092(3)
O(1)	0.9087(5)	0.6460(2)	0.0045(6)	0.0121(8)
O(2)	0.7051(5)	0.5344(2)	0.8390(6)	0.0131(8)
O(3)	0.6783(5)	0.6733(3)	0.6953(6)	0.0118(8)
O(4)	0.6218(5)	0.6527(2)	0.9864(6)	0.0126(8)
F(1)	0.0994(5)	0.5517(2)	0.4170(5)	0.0179(8)
F(2)	0.0466(4)	0.5277(2)	-0.1265(5)	0.0133(7)
F(3)	0.1788(4)	0.7055(2)	0.3172(5)	0.0125(7)
F(4)	0.2857(4)	0.6495(2)	0.0214(5)	0.0140(7)
F(5)	0.3965(4)	0.5998(2)	0.4142(5)	0.0124(7)
F(6)	0.3465(4)	0.6928(2)	0.7004(5)	0.0122(7)
F(7)	0.5649(4)	0.6955(2)	0.2966(5)	0.0112(6)

organic amines have always been present in these cases [13]. One explanation for the absence of oxidation in these reactions is that NpFPO₄ may be sufficiently insoluble and precipitate before oxidation of Np(IV) occurs, as it is a slow process [14]. A subsequent reaction of NpFPO₄ with fluoride in the presence of Cs⁺ could also lead to the formation of Cs₂Np₂F₇PO₄, which upon further reaction would yield NpF₄. Nucleation sites for crystals of NpF₄, NpFPO₄, and Cs₂Np₂F₇PO₄ are provided by the GaPO₄ matrix that forms. The acicular crystals of NpF₄ that grow from this matrix were quite long (several mm in length), although they were unfortunately highly twinned. Crystals of NpFPO₄ and Cs₂Np₂F₇PO₄ were found both on the surface and within the GaPO₄ matrix.

3.1.1. Structure of NpFPO₄

The structure of NpFPO₄ consists of Np(IV) centers bound by both fluoride and phosphate to yield [NpF₂O₆] distorted dodecahedra, as is shown in Fig. 1. The PO₄³⁻ anions play a fascinating role in this structure in that they chelate one Np center and through two μ_3 and two μ_2 oxo atoms, bind an additional four Np sites. The fluoride anions are μ_2 and simply bridge between two Np(IV) ions. The [NpF₂O₆] units share two edges and two corners with

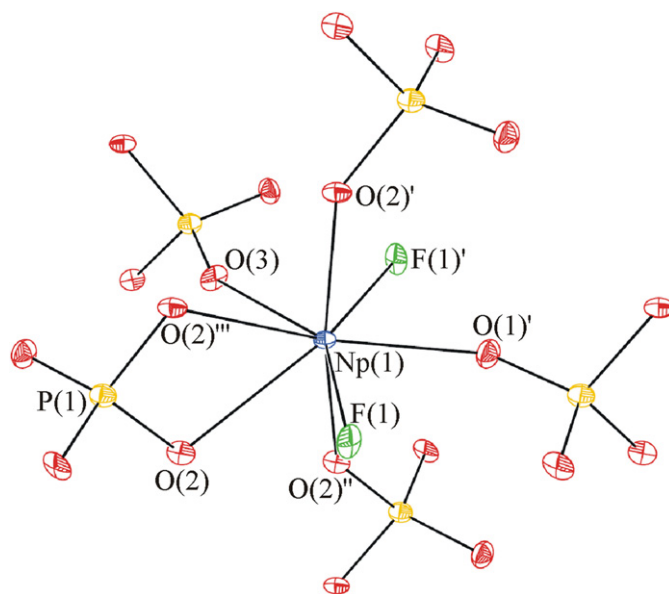


Fig. 1. A view of the fundamental building units in NpFPO₄ that consist of Np(IV) centers bound by both fluoride and phosphate to yield [NpF₂O₆] distorted dodecahedra. [50% probability ellipsoids are depicted.]

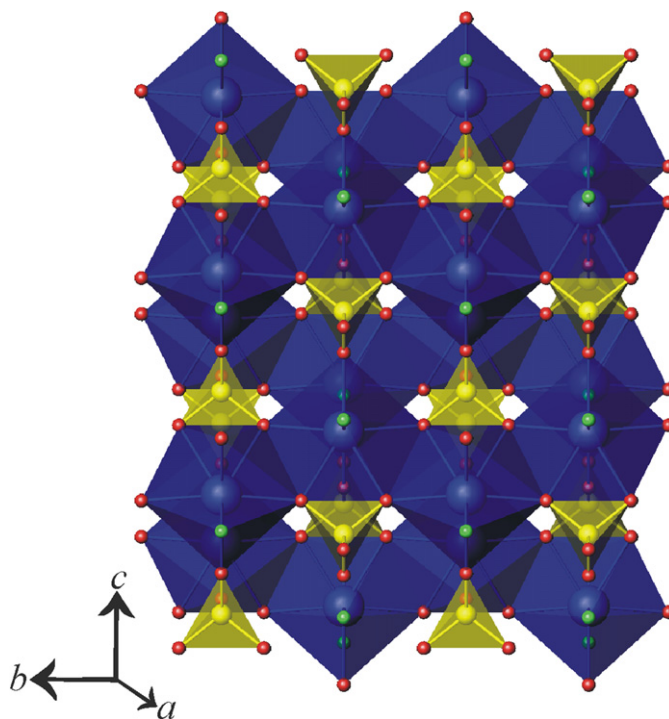


Fig. 2. A depiction of the tightly-packed structure of NpFPO₄. [NpF₂O₆] distorted dodecahedra are shown in blue, phosphate anions in yellow, oxygen atoms are red, and fluoride anions in green.

identical polyhedra to assemble into a dense three-dimensional network that is shown in Fig. 2.

The Np–O bond distances range from 2.227(9) to 2.515(8) Å, and the two Np–F distances are 2.278(8) and 2.292(8) Å. It is important to note here, and for that matter in most oxyfluorides, that it is usually not possible to

distinguish between the O atoms and F atoms based on standard X-ray scattering or bond distances. This is a pervasive problem in fluoride chemistry, especially when hydrolysis is involved. One argument for it being a F^- and not an OH^- is a lack of an appropriate hydrogen bonding distance. Furthermore, semi-quantitative SEM-EDX measurements clearly show the presence of F in the crystals. The P–O bond distances are normal with two longer bonds of 1.571(8) Å ($\times 2$) to the μ_3 -O atoms, and two shorter bonds of 1.508(11) and 1.537(10) Å to the μ_2 -O atoms. Selected bond distances for $NpFPO_4$ are given in Table 4.

The structure of $NpFPO_4$ is also illustrative of another problem with published single crystal structures described as containing Np(IV) [6]. In an earlier work we derived bond-valence parameters [15] for Np(V) and Np(VI) (7d), and we have found that these parameters work quite well, although they should be improved as more high-resolution structures become available. When we attempted to determine an appropriate bond-valence parameter for Np(IV)–O bonds, the distances available from the small number of known structures could not be used to derive a reliable value. There may simply be too few structures available at this time, and/or some of the previously reported Np(IV) compounds structures may be incorrect.

3.2. Structure of $Cs_2Np_2F_7PO_4$

The structure of $Cs_2Np_2F_7PO_4$, as its formula suggests, is much more complex than that of $NpFPO_4$. To start with there are two crystallographically unique Np centers in two different coordination environments. Both Np(IV) cations are bound by both fluoride and phosphate. Np(1) is found as a $[NpO_2F_6]$ distorted dodecahedron, while Np(2) in $[NpO_2F_7]$ is a tricapped trigonal prism, as depicted in Fig. 3. The method of fusing together these polyhedra is quite intricate. The $[NpO_2F_6]$ units share one edge with an adjacent $[NpO_2F_6]$ unit, one edge with a $[NpO_2F_7]$ polyhedron, and one corner with a second $[NpO_2F_7]$ unit. The $[NpO_2F_7]$ tricapped trigonal prisms share two opposite edges with neighboring $[NpO_2F_7]$ polyhedra, one edge with a $[NpO_2F_6]$ unit, and one corner with a different, but crystallographically equivalent, $[NpO_2F_6]$ unit. This joining of the $[NpO_2F_6]$ distorted dodecahedra and $[NpO_2F_7]$ tricapped trigonal prisms along with the PO_4 tetrahedra, that bridge between two Np(1) and two Np(2) centers, creates a three-dimensional framework structure that has

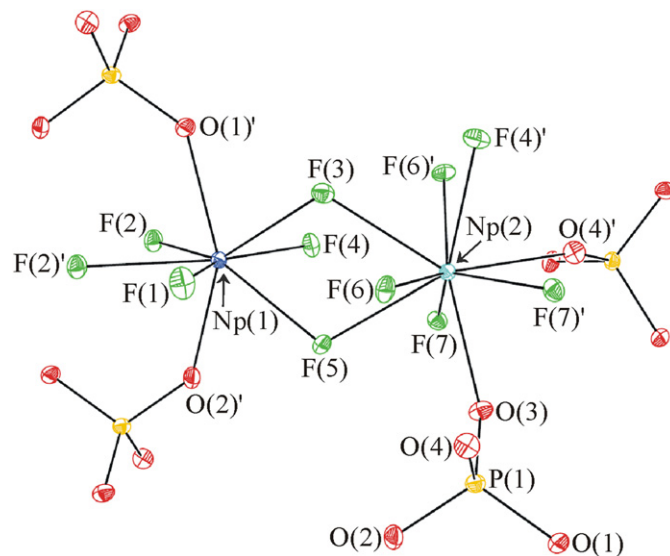


Fig. 3. A view of the fundamental building units in $Cs_2Np_2F_7PO_4$. Np(1) is present in a distorted dodecahedral environment, and Np(2) in tricapped trigonal prismatic environment. [50% probability ellipsoids are depicted].

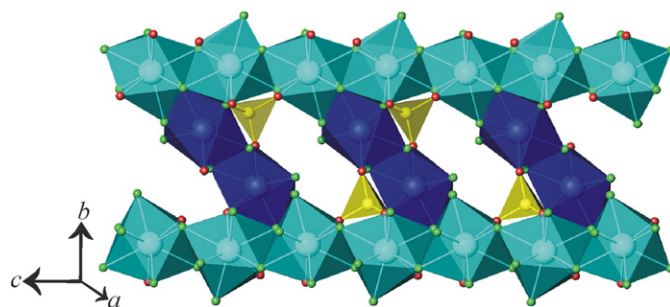


Fig. 4. An illustration of the $[NpO_2F_6]$ distorted dodecahedra (dark blue) and $[NpO_2F_7]$ tricapped trigonal prisms (light blue), PO_4^{3-} (yellow), and F^- anions (green) that form the structure of $Cs_2Np_2F_7PO_4$.

small channels extending along the a -axis, as is illustrated in Fig. 4. The Cs^+ cations are not specifically located within these channels, but rather fill other spaces within the framework. The structure can also be described as containing chains of $[NpO_2F_7]$ units that are joined by dimers of $[NpO_2F_6]$.

The two Np(1)–O bond distances are 2.274(4) and 2.294(4) Å. The remaining six Np(1)–F bond distances range from 2.150(3) to 2.355(3) Å. For both Np(1) and Np(2), all of the O and F atoms are bridging except F(1), which is terminal, and thus possesses the shortest bond distance. The Np(2)–O bond distances are 2.282(4) and 2.299(4) Å, which are similar in length to the Np(2)–F bond distances that vary from 2.280(3) to 2.401(3) Å. As in $NpFPO_4$, if the oxygen atoms were not a part of the phosphate anions, they would be essentially indistinguishable from the fluoride anions. However, semi-quantitative EDX measurements also support the presence of F in these crystals. The P–O bond distances are quite regular and range only from 1.532(4) to 1.545(4) Å. The two crystallographically unique Cs^+ cations form a large number of

Table 4
Selected bond distances (Å) for $NpFPO_4$

Distances (Å)			
Np(1)–O(1)	2.257(11)	Np(1)–F(1)	2.278(8)
Np(1)–O(2)	2.285(8)	Np(1)–F(1')	2.292(8)
Np(1)–O(2')	2.285(8)	P(1)–O(1)	1.508(11)
Np(1)–O(2)''	2.515(8)	P(1)–O(2)	1.571(8)
Np(1)–O(2)'''	2.515(8)	P(1)–O(2')	1.571(8)
Np(1)–O(3)	2.227(9)	P(1)–O(3)	1.537(10)

Table 5
Selected bond distances (Å) for Cs₂Np₂F₇PO₄

Distances (Å)			
Np(1)–O(1)	2.294(4)	Np(2)–F(4)	2.370(3)
Np(1)–O(2)	2.274(4)	Np(2)–F(5)	2.401(3)
Np(1)–F(1)	2.150(3)	Np(2)–F(6)	2.280(3)
Np(1)–F(2)	2.299(3)	Np(2)–F(6′)	2.395(3)
Np(1)–F(2′)	2.355(3)	Np(2)–F(7)	2.278(3)
Np(1)–F(3)	2.330(3)	Np(2)–F(7′)	2.382(3)
Np(1)–F(4)	2.320(3)	P(1)–O(1)	1.545(4)
Np(1)–F(5)	2.321(3)	P(1)–O(2)	1.544(4)
Np(2)–O(3)	2.282(4)	P(1)–O(3)	1.535(4)
Np(2)–O(4)	2.299(4)	P(1)–O(4)	1.532(4)
Np(2)–F(3)	2.377(3)		

long contacts with surrounding oxygen and fluorine atoms. If an arbitrary cut-off of 3.45 Å is chosen, then there are eight interactions ranging from 2.818(4) to 3.436(3) Å for Cs(1), and eight contacts occurring from 2.817(4) to 3.331(4) Å for Cs(2). Selected bond distances for Cs₂Np₂F₇PO₄ are given in Table 5.

4. Conclusions

The purpose of this work is not only to report on the syntheses and structures of two new Np(IV) fluorophosphates, but to also use these compounds as heralds for new synthetic and structural chemistry with Np(IV). There are only a handful of reported single crystal structures for Np(IV) compounds, and there may be problems with the metrics in some of these given our valence band considerations. These compounds provide standards for Np(IV)–O and Np(IV)–F bond distances that should be useful in future work.

Acknowledgments

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