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Synthesis and Crystal Structures of Volatile Neptunium(IV) β -Diketonates

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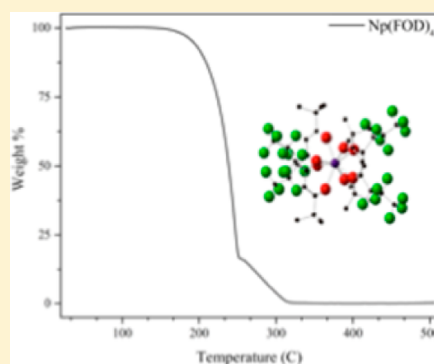
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Supporting Information

ABSTRACT: Production of certified reference materials in support of domestic nuclear forensics programs require volatile precursors for introduction into electromagnetic isotopic separation instruments. β -Diketone chelates of tetravalent actinides are known for their high volatility, but previously developed synthetic approaches require starting material (NpCl_4) that is prohibitively difficult and hazardous to prepare. An alternative strategy was developed here that uses controlled potential electrolysis to reduce neptunium to the tetravalent state in submolar concentrations of hydrochloric acid. Four different β -diketone ligands of varying degrees of fluorination were reacted with an aqueous solution of Np^{4+} . Products of this reaction were characterized via X-ray diffraction and infrared spectroscopy, and were found to be neutral 8-coordinate complexes that adopt square antiprismatic crystal geometry. Synthesis of Np β -diketonates by this approach circumvents the necessity of using NpCl_4 in tetravalent Np coordination compound synthesis. The volatility of the complexes was assessed using thermogravimetric analysis, where the temperature of sublimation was determined to be in the range of 180° to 205 °C. The extent of fluorination did not appreciably alter the sublimation temperature of the complex. Thermal decomposition of these compounds was not observed during sublimation. High volatility and thermal stability of Np β -diketonates make them ideal candidates for gaseous introduction into isotopic separation instruments.



1. INTRODUCTION

One of the key deterrents to global proliferation of nuclear material is a strong domestic nuclear forensics program.¹ The foremost obstacle to nuclear weapon acquisition by subnational (terrorist) groups is availability of highly enriched fissionable materials. The most probable way a subnational group planning a nuclear terrorist act may obtain fissionable material is through theft or clandestine cooperation with a known nuclear state. The ability to trace the origin and history of materials is one of the greatest deterrents in those scenarios. Among the most important analytical techniques used in nuclear forensic analyses is isotope dilution mass spectrometry (IDMS).^{1–3} IDMS provides quantitation of nuclides through the addition of a tracer. The tracer used is often an analytical standard or certified reference material (CRM).³ However, recent reports by interagency groups have highlighted the need for new sources of several CRMs important to the nuclear forensics community.⁴ To aid in satisfying this need, producing a new supply of neptunium (Np) CRM is critical to the domestic nuclear forensic infrastructure.

Useful Np CRMs contain known ratios or concentrations of certain Np isotopes. Production of such materials thus requires

isotopic separation, commonly performed via electromagnetic isotope separation instruments.⁵ In these instruments, Np-bearing volatile compounds are introduced as a gas into an ion source, and ultimately separated according to their masses.⁶ A complication is a requirement that the source Np-containing material be volatile. UF_6 , used to enrich ^{235}U for nuclear fuel production, is the most commonly used volatile actinide material used for electromagnetic isotopic separations. NpF_6 exhibits similar volatility to UF_6 ; however fluorine is corrosive to the internals of the instrument.⁷ Other halogens are not monoisotopic, which complicates separation processes. Alternatives to halogens for increasing the volatility of actinides for introduction into isotopic separation instruments may be β -diketonate coordination complexes. β -Diketonate complexes of the rare earths are known for their high volatility.^{8–14} Relative to the rare earths, few actinide β -diketonate complexes have been synthesized; however, a high degree of volatility has been observed in the reported compounds.^{15–17} This characteristic

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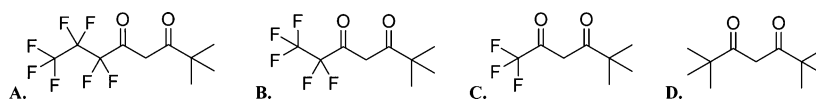


Figure 1. Chemical structures of (A) 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (FOD), (B) 1,1,1,2,2-pentafluoro-6,6-dimethylheptane-3,5-dione (PDHD), (C) 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (TDHD), and (D) 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD).

makes β -diketonate complexes a candidate for investigations as volatile isotopic separation precursor materials.

Synthetic routes for tetrakis complexes of Np^{4+} with 2,2,6,6-tetramethylheptane-3,5-dione (TMHD), 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (FOD), and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (TDHD) have been previously reported.^{15,16} Replication of these synthetic routes is currently prohibitively difficult due to the starting material that is required; for example, the prior reported synthesis of $\text{Np}(\text{TMHD})_4$ and $\text{Np}(\text{FOD})_4$ requires $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$, and $\text{Np}(\text{TDHD})_4$ requires Cs_2NpCl_6 . Preparation of the neptunium salts is relatively facile; $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{NpCl}_6$ is made by reacting tetraethylammonium chloride to NpCl_4 in 8–12 M HCl, and Cs_2NpCl_6 can be made by adding CsCl to NpCl_4 in 6 M HCl.^{18,19} However, the major difficulty in these procedures stems from synthesis of precursor NpCl_4 , which is required to make the neptunium salts. NpCl_4 is synthesized by passing CCl_4 over NpO_2 at elevated temperatures ($>600^\circ\text{C}$), followed by vacuum sublimation at even higher temperatures to obtain pure product material.²⁰ Stemming from the complexities involved with handling radioactive materials, repetition of this procedure requires unique dedicated facilities and infrastructure, rigorous work control documents, and significant oversight. These complications make repeating the historic synthesis prohibitively difficult or impossible, further evidenced by the fact that there is no longer a known commercial or governmental agency producing NpCl_4 .

For new investigations of Np β -diketonate coordination complexes, an alternative synthetic approach is needed. The limiting factor in the prior synthesis of these compounds is the source of Np^{4+} , NpCl_4 . While NpCl_4 cannot easily be made, Np^{4+} can be produced in aqueous solution via controlled potential electrolysis.²¹ Creating Np^{4+} “in situ” via electrochemistry offers the possibility for a new synthesis of Np β -diketonate coordination complexes by first generating Np^{4+} in acidic aqueous solution and then reacting it with β -diketone ligands to form the coordination complex. Preparation of Np β -diketonates in this manner uses techniques that are both inexpensive and readily available in the modern radiochemistry laboratory, thus expanding future opportunity for lower-valent Np coordination chemistry studies. The efficacy of preparing Np β -diketonates in this manner is examined in this work. A series of four β -diketones with varying degrees of fluorination were studied (Figure 1) in an attempt to prepare complexes with varying degrees of volatility. It is hypothesized that a greater degree of fluorination should correlate to a higher volatility.

The vaporization ability and thermal stability of these compounds were investigated through thermogravimetric analysis (TGA). The desired goal of this study is to synthesize a volatile compound that is suitable for gaseous introduction into an ion source for eventual CRM production. However, the new synthetic method for Np β -diketonates presented provides a platform for future tetravalent f-element coordination compound studies.

2. EXPERIMENTAL SECTION

2.1. Materials. 2,2,6,6-Tetramethyl-3,5-heptanedione (TMHD) and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (FOD) were supplied by Sigma-Aldrich at $\geq 98\%$ purity and used as received. 1,1,1,2,2-Pentafluoro-6,6-dimethylheptane-3,5-dione (PDHD) was purchased from Aurum Pharmatech at 97% purity, and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (TDHD) was purchased from Alfa Aesar at 95%; both were used as received. Trace Select hydrochloric acid and $\geq 99.9\%$ purity methanol were purchased from Sigma-Aldrich and used without further purification. All other chemicals used were of reagent grade, and HPLC grade water was used to prepare solutions when necessary. A stock of ^{237}Np was obtained in the form of NpO_2 from the Idaho National Laboratory. This NpO_2 was dissolved in 4 M nitric acid and purified using Eichrom TEVA columns to remove daughter ^{233}Pa .²² The Np was eluted from the TEVA column in 0.5 M HCl. Final purity of the Np solution was ensured by assay using HPGE and ICP-MS. **Note!** ^{237}Np is both an α - and γ -emitting radioisotope. All manipulations of Np were performed inside of a transuranic rated glovebox by personnel trained in the handling of radioactive materials.

2.2. Electrochemical Oxidation State Adjustment. Because Np^{4+} is sensitive to oxygen, all synthetic experiments were performed in an inert (Ar) atmosphere radiological glovebox. An aliquot of the stock Np solution in 0.5 M HCl was added to one side of a cylindrical glass cell with a built in cylindrical counter electrode compartment separated by an electrolysis diaphragm made of fritted glass. Controlled potential electrolysis experiments were performed using a platinum gauze (80 mesh, 120×20 mm) working electrode, a coiled platinum wire (1 mm diameter, 30 mm long) as the counter electrode, and an Ag/AgCl reference electrode. The sample was electrolyzed with a stirring rate of approximately 500 rpm by a magnetic stirrer. A Digi-Ivy DY2300 potentiostat was used for all electrochemical measurements. The concentration of Np present in the electrolytic cell was determined by controlled potential coulometry prior to synthesis.²³ Np^{4+} was prepared by applying a potential of -0.07 V vs Ag/AgCl to the stirred Np solution for approximately 2 h. During electrolysis some Np^{3+} was formed. A pure solution of Np^{4+} resulted by electrolyzing at $+0.1$ V for 15 min. Final determination by absorption spectrophotometry confirmed that the impurity of Np^{3+} was less than 1%. The oxidation states were determined by monitoring the 1223, 980, 960, and 768 nm peaks in the solution's absorption spectra (corresponding to NpO_2^{2+} , NpO_2^+ , Np^{4+} , and Np^{3+}).²⁴ All spectrophotometric measurements were made using an Ocean Optics light source, optical fibers, cuvette holders, and spectrometers (DH-2000-BAL, NIR512, CUV-UV, and FLAME-S-VIS-NIR-ES, respectively).

2.3. Synthesis. Compounds of $\text{Np}(\text{FOD})_4$, $\text{Np}(\text{PDHD})_4$, $\text{Np}(\text{TDHD})_4$, and $\text{Np}(\text{TMHD})_4$ were synthesized similarly. A typical procedure is described for $\text{Np}(\text{FOD})_4$. FOD was dissolved in methanol in a 4:1 molar ratio of $\text{Np}:\text{FOD}$. The previously prepared solution of Np^{4+} (typically 1–3 mM) was added dropwise to the methanolic solution of FOD while stirring. An aqueous solution of 25% sodium hydroxide was then added dropwise to the Np/FOD mixture while monitoring pH (litmus paper). Addition of NaOH is terminated upon reaching pH of approximately 5.5. During addition of NaOH, a green oil appeared in solution. The oil was extracted into toluene, which was then separated from the aqueous/methanol mixture and dried with anhydrous MgSO_4 . The toluene was allowed to slowly evaporate, yielding the final product as green crystals. Due to concerns of radioactive contamination and worker safety, it was not possible to perform melting point or elemental analysis on these compounds. FTIR spectra of the compounds were recorded inside an Ar atmosphere glovebox using a Bruker ALPHA FTIR using a

Table 1. Observed Wavenumbers and Band Assignments of Np(FOD)₄, Np(PDHD)₄, Np(TDHD)₄, and Np(TMHD)₄

wavenumber (cm ⁻¹)				
Np(FOD) ₄	Np(PDHD) ₄	Np(TDHD) ₄	Np(TMHD) ₄	functional group
1590 (m, sh)	1592 (m)	1587 (m)	1595 (s)	ν(C–O)
1507 (m)	1513 (w)	1516 (m)	1516 (w)	ν(C–O) + ν(C–C) + δ(C–H)
1345 (m)	1326 (m)	1303 (m)	1300 (m), 1253 (m), 1194 (s), 1146 (s), 1108 (s)	ν(C–(CH ₃))
1219 (m), 1185 (m), 1154 (m), 1105 (sh)	1194 (s), 1169 (m, sh), 1123 (s)	1189 (s), 1151 (s), 1111 (s)		ν(C–F)
1070 (m, sh)	1029 (m, sh)	1062 (sh)		σ(CH ₃)
754 (w), 687 (w)	728 (m), 692 (w)			ν(C–CF ₂)
740 (m)		687 (m)		ν(C–CF ₃)
686 (w)			723 (w), 690 (m)	ν(C–C–O)
537 (w)	583 (w)	576 (m)	573 (m)	ring + ν(M–O)
471 (w)	467 (w, sh)	470 (m)	462 (w)	ν(M–O)

Platinum ATR sampling module, running OPUS spectroscopy software.

2.4. X-ray Diffraction. Single crystals of Np(TMHD)₄, Np(TDHD)₄, Np(FOD)₄, and Np(PDHD)₄ were mounted on a 50 μm MiTeGen loop in Paratone oil, mounted on a 3-circle Bruker APEXII diffractometer, and frozen under a cold nitrogen stream (Oxford Cryosystems Cryostream). An arbitrary sphere of data were recorded for each sample with counting times of 40 s for Np(TDHD)₄, Np(FOD)₄, and Np(PDHD)₄ and 60 s for Np(TMHD)₄. Data were integrated within the APEXII software, and a semiempirical absorption correction, as well as Lorentz and polarization corrections, were applied through SADABS.²⁵ The program suite SHELX-14 was used for space-group determination (XPREP), direct methods structure solution (XS) or intrinsic phasing (XT), imaging and peak assignment (XP), and least-squares refinement (XL).²⁶ Details of the refinements can be found in Table 1. All space group assignments were checked using PLATON.²⁷ The final refinements included anisotropic displacement parameters for ordered atoms. Disordered atoms were modeled with isotropic displacement parameters. Hydrogen atoms were located in geometrically calculated positions with U_{iso}(H) tied to that of the carbon to which they are bonded. Atomic coordinates, bond distances, and additional structural information are provided in the [supplementary crystallographic data](#) and the [Supporting Information](#).

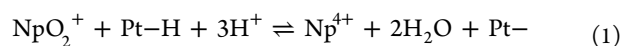
2.5. Thermogravimetric Analysis (TGA). Crystalline compounds of Np(TMHD)₄, Np(TDHD)₄, Np(FOD)₄, and Np(PDHD)₄ were crushed to ensure uniform sample distribution and then placed in Pt/Rh crucibles with yttrium oxide (Y₂O₃) liners. Decomposition onset temperatures and sample mass losses were observed using a Netzsch differential scanning calorimeter/thermogravimetric analyzer (DSC/TGA), model STA 449 F3 Jupiter, installed in a glovebox under high purity argon atmosphere. A rhodium furnace heated the sample from ambient to 500 °C at a rate of 10 °C min⁻¹, in an atmosphere composed of zero grade compressed air, at a flow rate of 20 mL min⁻¹ to the sample furnace. High purity argon at a flow rate of 50 mL min⁻¹ was used to protect instrument balance.

3. RESULTS AND DISCUSSION

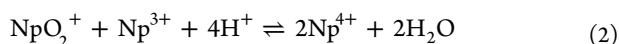
3.1. Synthesis of Np β-Diketonates. Currently there is a dearth of information in the literature regarding organometallic and coordination complexes of neptunium. This is due mainly to the radioactivity associated with ²³⁷Np (α emitter, t_{1/2} = 2.144 × 10⁶ years).²⁴ Regardless, there have been some prior investigations of the preparation of neptunium cyclopentadienyl, cyclooctatetraenyl, and β-diketonate compounds.^{28–31} The best established route to prepare tetravalent neptunium tetracyclopentadienyl is through refluxing NpCl₄ with KC₅H₅. This method was also used for preparation of Np cyclooctatetraene compounds.^{15,32} In fact, all previous literature

methods to produce both organometallic and coordination Np⁴⁺ complexes require reactive Np⁴⁺ starting material; by far the most common is NpCl₄. This is a major source of complication because the two most common preparation methods for NpCl₄ are hazardous and require extensive dedicated facilities to perform. Fried and Davidson developed a preparation wherein NpO₂ is reacted with CCl₄ at 773 K.²⁰ The product NpCl₄ is purified from remainder product materials through vacuum sublimation and condensation. A second synthetic method can be performed by reacting NpO₂(OH) with hexachloropropene (CCl₃CCl=CCl₂), followed by sublimation at 923 K to purify the final product.³³ Likewise, this procedure also requires significant hazard mitigation to perform. While the risks associated with the radioactive nature of Np cannot be avoided, a new method for the production of a viable Np⁴⁺ starting material such that Np⁴⁺ β-diketonates can be synthesized is highly desirable.

Rather than utilizing difficult to produce starting material such as NpCl₄, the rich redox chemistry of Np can be exploited to selectively produce Np⁴⁺ in acidic aqueous solution by using electrochemical techniques. Np can exist in the +4 through +6 oxidation states in acidic aqueous solution. When dissolved in hydrochloric acid, the major species of neptunium is the +5 oxidation state; however through the process of disproportionation, +4 and +6 are also present.²⁴ In the +5 and +6 states, Np exists as a linear dioxocation (NpO₂⁺ and NpO₂²⁺).²⁴ For synthesis of Np β-diketonate compounds, the oxidation state of neptunium in solution must be controlled to the +4 state. Chemical methods have often been employed to adjust the oxidation state of neptunium; however introducing impurities to the Np sample in this regard complicates the synthesis procedures following redox conversion. Electrolytic methods do not require the addition of special reagents to control the oxidation state of Np, and the selectivity for a specific oxidation state can be precisely and easily controlled through adjustment of the electrolysis potential. A platinum working electrode was used to reduce Np⁵⁺ to Np⁴⁺ through an adsorbed hydrogen atom on the Pt electrode surface at a potential of −0.07 V (vs Ag/AgCl reference electrode). Np⁵⁺ is reduced via eq 1:



A fraction of the Np⁴⁺ produced in this potential range is further reduced to Np³⁺ at the electrode surface, which further reduces Np⁵⁺ by eq 2:



A 5 mL solution containing approximately 4.1 mM NpO_2^+ in 0.5 M HCl was placed in a cylindrical glass H-cell, and a constant potential of -0.07 V was applied while the current was monitored. Electrolysis was allowed to proceed for approximately 2 h. During this time, a peak maximum at ~ 1500 s in the resulting current–time curve was observed (Figure 2). A discussion of the unique current profile of this system has been previously reported.²¹

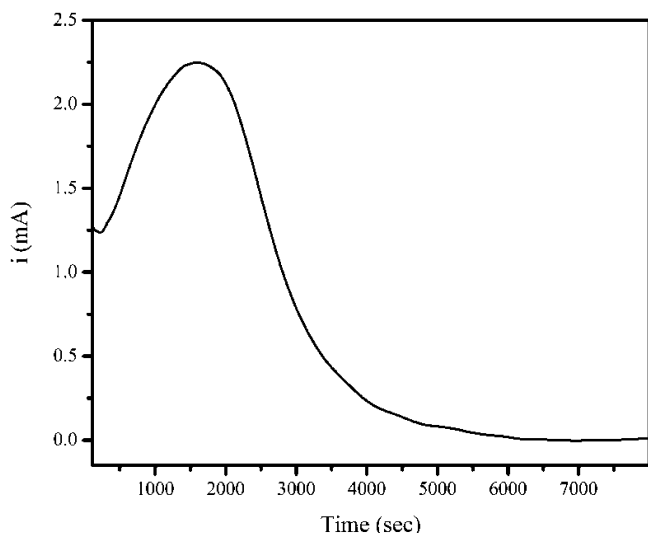


Figure 2. Current–time curve for the reduction of 4.1 mM NpO_2^+ by controlled potential electrolysis using a platinum gauze electrode. Applied potential of -0.07 V versus Ag/AgCl. Total solution volume of 5 mL.

After 2.5 h, the sample was fully reduced to Np^{4+} with a minor impurity of Np^{3+} . The impurity was removed by applying a potential of $+0.10$ V for 15 min, which oxidizes remaining Np^{3+} to Np^{4+} . The final oxidation state of the Np solution was confirmed by absorbance spectroscopy. Np^{4+} slowly reacts with atmospheric O_2 resulting in oxidation to Np^{5+} . To prevent this from occurring, an inert (Ar) atmosphere glovebox was used. However, the oxidation occurs at rates slow enough that this reduction can be performed in the open atmosphere; though, over a period of 48 h, measurable quantities of Np^{5+} can be found in solution.

The freshly prepared stock of Np^{4+} in HCl was used as starting material to synthesize four Np β -diketonates with varying degrees of fluorination: $\text{Np}(\text{FOD})_4$, $\text{Np}(\text{PDHD})_4$, $\text{Np}(\text{TDHD})_4$, and $\text{Np}(\text{TMHD})_4$. These compounds were prepared by the metathesis reaction between the Np^{4+} and the deprotonated β -diketone. When the β -diketone is deprotonated, the proton is removed from the α -carbon, which exhibits high acidity due to its proximity to the two adjacent carbonyl groups. The presence of electron withdrawing groups such as F (in FOD, PDHD, and TDHD) further increases the acidity of the proton at the α -carbon position (pK_a of FOD, PDHD, TDHD, and TMHD are approximately 6.74, 6.62, 6.78, and 11.6 respectively, calculated using Advanced Chemistry Development (ACD/Laboratories) Software V11.02). The negative charge of the deprotonated ligand is delocalized, forming neutral six-membered chelate rings with Np^{4+} . Varying the degree of fluorination should result in variable volatility

between the different complexes. It is theorized that fluorine atoms in the outer periphery of the Np complex reduce van der Waals interactions as well as intermolecular hydrogen bonding. As such, coordination of Np with the proper β -diketone can be used to “tune” introduction into an ion source such that the maximum degree of ionization and most efficient use of the material can be obtained. Crystals were grown of all four Np β -diketonates by slow evaporation from toluene.

The crystals were characterized by FTIR using an attenuated total reflectance (ATR) sampling module. The resulting spectra are shown in Figure 3. Six-membered metal chelate rings, as pictured in Figure 4, are expected to form upon coordination of the β -diketone to Np^{4+} .

Monitoring changes in the frequencies of the carbonyl ($\text{C}=\text{O}$) band in the range of $1600\text{--}1500\text{ cm}^{-1}$ of the neat ligand compared to those in the complex can provide strong indication of bonding in this mode. In Figure 3, the measured FTIR spectra of the neat ligands are compared to those of their coordination complex with Np^{4+} . In the coordinated complex, the frequency corresponding to the carbonyl splits into two, with one peak shifting to lower wavenumbers. This split results from a shift in structure of the β -diketone, where deprotonation of the α -carbon causes a delocalized structure that results in coordination with the central Np^{4+} atom. This is evidenced on the resulting FTIR spectra by the two observed peaks: one corresponding to ($\text{C}-\text{C}$) coupled with ($\text{C}-\text{O}$), and another from ($\text{C}-\text{O}$) coupled to ($\text{C}-\text{C}$). Such splits are observed in all four complexes analyzed, and suggest a shift from the double-bonded “keto” structure to a single bond ($\text{C}-\text{O}$) coordinated with the central Np atom. These results are consistent with those observed for other metal β -diketonates of similar structure.⁸ Prior literature reports have assigned the frequency bands around 450 cm^{-1} to the ($\text{M}-\text{O}$) band coupled to the ($\text{C}-\text{C}(\text{CH}_3)$) frequency.¹⁴ In this work, every compound analyzed had a characteristic band associated with that frequency range. Additional assignments of the observed frequencies are tabulated in Table 1, and are in agreement with similar assignments observed in prior studies.

3.2. Crystallography. **3.2.1. Structure of $\text{Np}(\text{TMHD})_4$.** $\text{Np}(\text{TMHD})_4$ crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (Figure 5, Table 2). The unit cell contains two crystallographically unique Np centers, both of which are coordinated by four unique TMHD ligands. The Np centers adopt square antiprismatic geometries with average Np–O bond lengths ranging from 2.317(2) to 2.328(2) Å. Evidence of the anionic nature of the TMHD ligands is found in the average C–C bond lengths and C–C–C bond angle of the central α -carbons of 1.396(5) Å and $123(1)^\circ$, respectively, which is consistent with sp^2 hybridization. Selected bond lengths and angles as well as a thermal ellipsoid plot for the structure are located in the Supporting Information.

3.2.2. Structure of $\text{Np}(\text{TDHD})_4$. $\text{Np}(\text{TDHD})_4$ crystallizes in the centrosymmetric monoclinic space group $C2/c$ (Figure 6, Table 2). The asymmetric unit consists of a Np center located on a 2-fold axis coordinated by two TDHD ligands. The overall coordination geometry about the Np center is square antiprismatic with Np–O bond distances ranging from 2.309(3) to 2.339(3) Å. Evidence of the anionic nature of the TDHD ligands is found in the average C–C bond lengths and C–C–C bond angle of the central α -carbons of 1.39(2) Å and $121(1)^\circ$, respectively, which is consistent with sp^2 hybridization. Selected bond lengths and angles as well as a

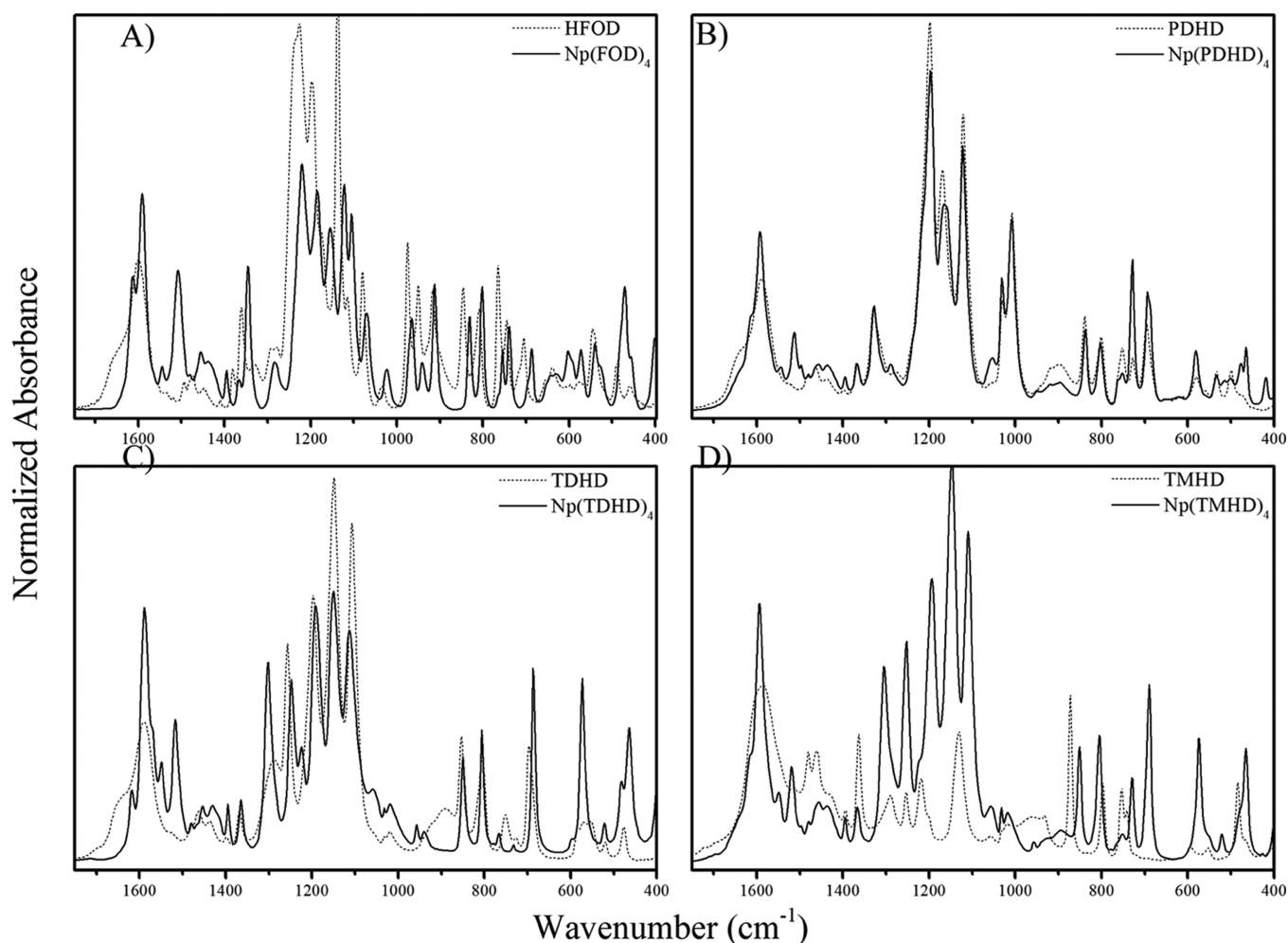


Figure 3. FTIR absorbance spectra of neat ligand compared to its coordination complex with Np^{4+} : (A) HFOD and $\text{Np}(\text{FOD})_4$, (B) PDHD and $\text{Np}(\text{PDHD})_4$, (C) TDHD and $\text{Np}(\text{TDHD})_4$, and (D) TMHD and $\text{Np}(\text{TMHD})_4$.

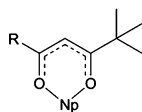


Figure 4. Metal chelate rings formed upon complexation of Np with β -diketonates, where R is the hepta-, penta-, or trifluorinated alkyl chain present on FOD, PDHD, or TDHD, or *t*-butyl for TMHD. Each Np^{4+} coordinates four β -diketonates, forming the neutral coordination complex.

thermal ellipsoid plot for the structure are located in the [Supporting Information](#).

3.2.3. Structure of $\text{Np}(\text{PDHD})_4$. $\text{Np}(\text{PDHD})_4$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, and there are two unique Np centers which both lie on independent 2-fold axes (Figure 7, Table 2). The Np centers are each coordinated by 4 PDHD ligands leading to a square antiprismatic geometry with average Np–O bond lengths ranging from 2.301(5) to 2.346(4) Å. Evidence that the PDHD ligands were anionic could be found by investigation of the

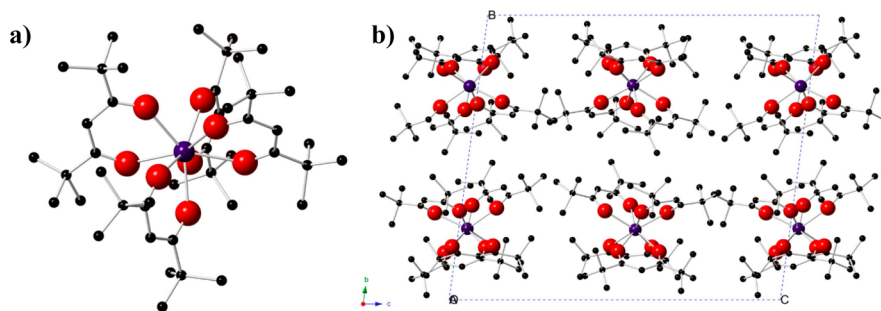


Figure 5. (a) Ball-and-stick model of $\text{Np}(\text{TMHD})_4$ showing the coordination environment around the $\text{Np}(\text{IV})$ center. This square antiprismatic geometry appears in all four compounds. (b) Packing diagram of $\text{Np}(\text{TMHD})_4$ viewed normal to the bc plane. Purple, red, and black spheres represent neptunium, oxygen, and carbon atoms, respectively. Hydrogen atoms have been omitted for clarity.

Table 2. Crystallographic Data for Np(TMHD)₄, Np(TDHD)₄, Np(PDHD)₄, and Np(FOD)₄

	Np(TMHD) ₄	Np(TDHD) ₄	Np(PDHD) ₄	Np(FOD) ₄
formula mass	970.4	1017.64	1217.68	1417.69
color and habit	purple, block	pale purple, plate	pale green, block	pale green, plate
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>P</i> 2/ <i>c</i> (No. 13)	<i>P</i> 2/ <i>c</i> (No. 13)
<i>a</i> (Å)	12.315(1)	20.808(4)	21.226(2)	22.006(2)
<i>b</i> (Å)	19.493(1)	11.437(4)	11.6771(9)	12.486(1)
<i>c</i> (Å)	21.186(1)	16.549(3)	18.875(1)	19.360(2)
α (deg)	82.579(1)	90	90	90
β (deg)	89.731(1)	94.635(3)	105.400(1)	106.129(2)
γ (deg)	71.617(1)	90	90	90
<i>Z</i>	4	4	4	4
<i>T</i> (K)	100	100	100	100
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} (g cm ^{−3})	1.347	1.722	1.793	1.843
μ (Mo K α) (mm ^{−1})	2.218	2.748	2.433	2.183
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0362	0.0416	0.0595	0.0618
$R_w(F_o^2)^b$	0.0822	0.0885	0.1787	0.1869

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b R(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}.$$

central α -carbons (C(4), C(13), C(22), C(31)), which had average C–C bond lengths ranging from 1.34(2) to 1.54(2) Å and average C–C–C bond angles of 122.4(9)°, consistent with sp^2 hybridization.

The disorder present in the fluoroalkyl chains of the ligands presented some challenges in accurately modeling the structure. The atoms F(8), F(11)–F(13), F(15)–F(18), F(20), C(10), C(11), C(19), C(25)–C(27), and C(28) were all found to be disordered over two sites, and each site was assigned 50% occupancy. This disorder is an alternate link of the acetate to the oxygen related by the 2-fold rotation, rather than that observed in the standard model. Complete details for modeling the disorder as well as an exhaustive list of bond lengths and angles may be found in the [supplementary crystallographic data](#). Selected bond lengths and angles as well as an atomic displacement ellipsoid plot for the structure are located in the [Supporting Information](#).

3.2.4. Structure of Np(FOD)₄. Np(FOD)₄ crystallizes in the centrosymmetric monoclinic space *P*2/*c* (Figure 8, Table 2). There are two crystallographically unique Np centers which both lie on 2-fold rotation axes. Each Np atom is coordinated

by eight oxygen atoms with average bond lengths ranging from 2.290(7) to 2.347(5) Å, which leads to a geometry that is best described as a square antiprism. Evidence that the FOD ligands were anionic could be found by investigation of central α -carbons (C(5), C(15), C(25), C(35)), which had average C–C bond lengths ranging from 1.37(1) to 1.43(2) Å and average C–C–C bond angles of 120(1)°, consistent with sp^2 hybridization.

The fluoroalkyl chains present in the diketone ligand gave rise to some difficulty in the refinement of the structure. Specifically, pains had to be taken to model the disorder present in the structure, which manifests itself in the diketone ligand coordinated to Np(2) defined by the central α -carbon C(35). The ligand appears to partially occupy sites shifted roughly 47° about a vertex defined by O(8), i.e., to the acetate oxygen that is related by the 2-fold axis, rather than that in the standard model. The occupancy of the disordered ligand was defined as 50% for both sites. The disorder present in the ligands coordinated to Np(1) was modeled by identifying disordered sites for F(2), F(3), F(4), F(6), F(7), F(8), F(10), F(11), F(12), F(13), C(18), C(19), and C(20) in the Fourier difference map and assigning each site 50% occupancy. Complete details for modeling the disorder as well as an exhaustive list of bond lengths and angles may be found in the [supplementary crystallographic data](#). Selected bond lengths and angles as well as a thermal ellipsoid plot for the structure are located in the [Supporting Information](#).

3.2.5. Coordination Geometry of Np Centers. As noted in the above sections, in all cases the Np(IV) centers adopt square antiprismatic geometries (Figure 9). This coordination motif is not surprising since the singly anionic ligand chelates the metal through the oxygen atoms and there are no severe steric influences that would preclude this geometry, which allows for maximum distance between the ligands. The average Np–O bond length observed in the four structures was 2.32(1) Å, and the average O–Np–O chelate angle was 71(1)°. Additional information for selected bond lengths and angles, including bond lengths and angles specific to each structure, may be found in the [Supporting Information](#) and the [supplementary crystallographic data](#).

3.3. Thermogravimetric Analysis (TGA). TGA was used to determine the relative volatilities and thermal stability of the four new β -diketonates synthesized. Np(FOD)₄, Np(PDHD)₄, Np(TDHD)₄, and Np(TMHD)₄ were heated from room temperature at a rate of 10 °C min^{−1} under atmospheric conditions. The relative volatility of each compound can be determined from the onset of mass loss. The results of this analysis are shown in Figure 10.

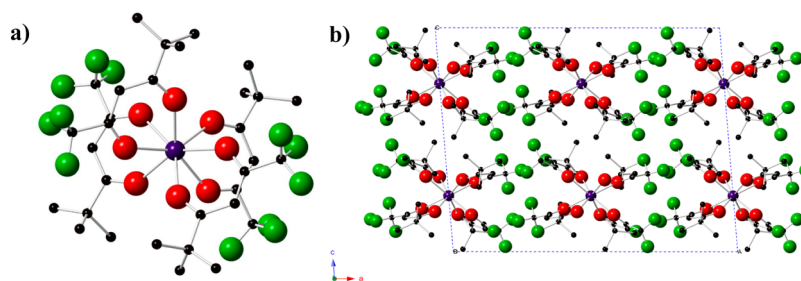


Figure 6. (a) Ball-and-stick model of Np(TDHD)₄ showing the coordination environment around the Np(IV) center. (b) Packing diagram of Np(TDHD)₄ viewed normal to the *ac* plane. Purple, red, green, and black spheres represent neptunium, oxygen, fluorine, and carbon atoms, respectively. Hydrogen atoms have been omitted for clarity.

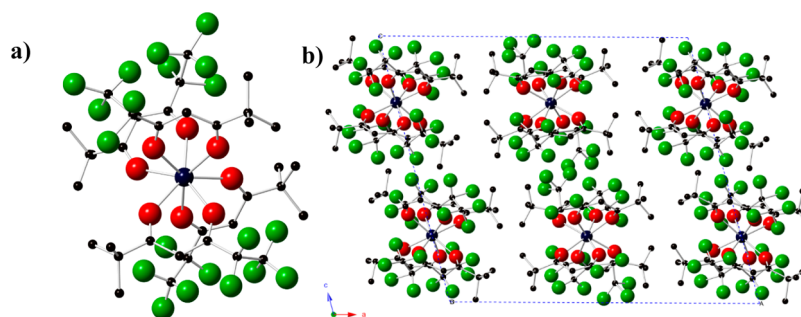


Figure 7. (a) Ball-and-stick model of $\text{Np}(\text{PDHD})_4$ showing the coordination environment around the $\text{Np}(\text{IV})$ center. (b) Packing diagram of $\text{Np}(\text{PDHD})_4$ viewed normal to the ac plane. Purple, red, green, and black spheres represent neptunium, oxygen, fluorine, and carbon atoms, respectively. Hydrogen atoms have been omitted for clarity.

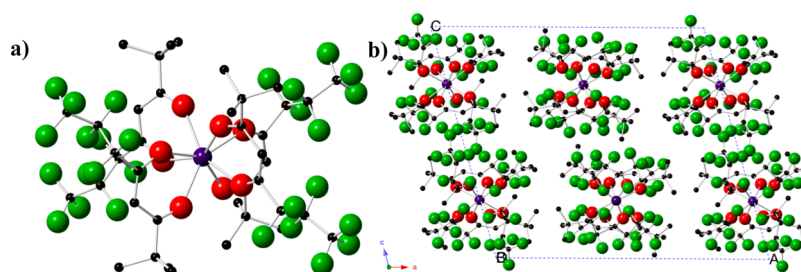


Figure 8. (a) Ball-and-stick model of $\text{Np}(\text{FOD})_4$ showing the coordination environment around the $\text{Np}(\text{IV})$ center. (b) Packing diagram of $\text{Np}(\text{FOD})_4$ viewed normal to the ac plane. Purple, red, green, and black spheres represent neptunium, oxygen, fluorine, and carbon atoms, respectively. Hydrogen atoms have been omitted for clarity.

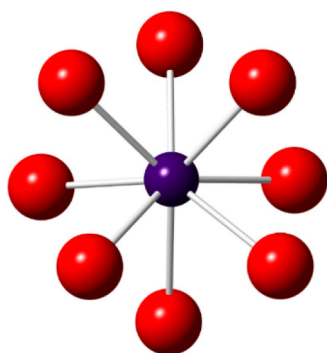


Figure 9. Ball and stick model depicting the square antiprismatic inner sphere coordination geometry of $\text{Np}(\text{FOD})_4$, which is representative of the Np centers present in all four compounds. The average $\text{Np}-\text{O}$ bond lengths and $\text{O}-\text{Np}-\text{O}$ chelate angles in all four structures were found to be $2.32(1)$ Å and $71(1)^\circ$, respectively. The purple sphere represents the neptunium atom, and the red spheres represent the oxygen atoms.

The fluorinated β -diketonates all begin to volatilize at nearly identical temperature (~ 182 °C), while the nonfluorinated $\text{Np}(\text{TMHD})_4$ volatilizes at a higher temperature of ~ 205 °C. Most interesting is that varying the degree of fluorination does not appear to appreciably alter the volatilization temperature of the compounds. Merely having fluorine present in the periphery of the compound reduces van der Waals and intermolecular hydrogen bonding to the extent that the compounds volatilize under similar conditions. TGA also provides information on thermal stability of these compounds. In Figure 9, it can be noted that all compounds except for $\text{Np}(\text{PDHD})_4$ volatilize completely, with nearly no mass remaining above 375 °C, whereas, with $\text{Np}(\text{PDHD})_4$, approximately 6% of the sample did not volatilize. This

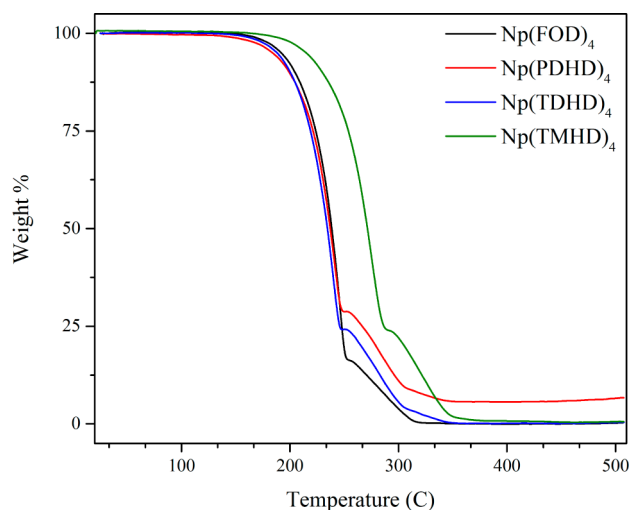


Figure 10. Thermogravimetric analysis of $\text{Np}(\text{FOD})_4$, $\text{Np}(\text{PDHD})_4$, $\text{Np}(\text{TDHD})_4$, and $\text{Np}(\text{TMHD})_4$. The samples were analyzed at a heat rate of 10 °C min^{-1} under atmospheric conditions.

suggests that, during heating, the compound partially decomposes to nonvolatile species. One last feature of the TGA curves is the shoulders that appear at $\sim 25\%$ weight for all the samples. Because this shoulder is associated with further weight loss, it is likely due to a large change in surface area of the compound. Such a large change would result from the compound melting. A more complete picture of this process may warrant more in depth analysis. However, high volatility of these compounds has been confirmed; when coupled with their thermal stability over the temperature range studied, it is shown that these compounds are reasonable for further investigations

of their ionization efficiency for future isotopic separation studies.

4. CONCLUSION

A new preparative method is demonstrated for the synthesis of tetravalent Np coordination complexes that does not require the use of NpCl_4 . This method uses electrochemical techniques to selectively reduce and control the Np oxidation state to +4, wherein a metathesis reaction is then employed to synthesize the Np β -diketonates. Characterization of the compounds via FTIR and single crystal X-ray diffraction studies confirmed their successful creation, thus demonstrating this new preparative method for Np^{4+} coordination complex synthesis. This synthetic method was then utilized to prepare tetravalent Np β -diketonates of TMHD, PDHD, TDHD, and TMHD. These β -diketonate compounds were targeted because of their anticipated high volatility. However, the TGA studies of these compounds identified that $\text{Np}(\text{FOD})_4$, $\text{Np}(\text{PDHD})_4$, and $\text{Np}(\text{TDHD})_4$ all volatilize at approximately the same temperature ($\sim 182^\circ\text{C}$), while $\text{Np}(\text{TMHD})_4$ volatilizes at a higher temperature of $\sim 205^\circ\text{C}$. It was also determined that $\text{Np}(\text{PDHD})_4$ decomposes while heating. Ultimately this study has confirmed a new method for synthesizing volatile Np β -diketonates suitable for introduction into an electromagnetic mass separator ion source.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b02290.

Selected bond lengths and angles of the Np compounds and images of their crystals (PDF)

Accession Codes

CCDC 1572816–1572819 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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