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Practical Synthetic Routes to Solvates of $U(OTf)_3$: X-ray Crystal Structure of $[U(OTf)_3(MeCN)_3]_n$, a Unique U(III) Coordination Polymer

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The reaction of UH_3 or U metal with triflic acid results in the formation of a mixture of species including $U(OTf)_4$ and leads to the reproducible isolation of the mononuclear U(IV) hydroxo complex $[U(OTf)_3(OH)(py)_4]$ (**1**) and the U(IV) dinuclear μ-oxo-complex $[\{U(OTf)_2(py)_3\}_2\{\mu\text{-O}\}\{\mu\text{-OTf}\}_2]$ (**2**). The X-ray crystal structures of these complexes have been determined. Analytically pure complex **1** can be prepared in a 17–27% yield providing a good precursor for the synthesis and study of the reactivity of the hydroxo complexes with different coordination environments. Two practical synthetic methods for the preparation of Lewis base adducts of $U(OTf)_3$ are described. Analytically pure $[U(OTf)_3(py)_4]$ (**4**) was easily and reproducibly prepared (50–60% yield) by protonolysis of the amide $U\{N(SiMe_3)_2\}_3$ with pyridinium triflate in pyridine. Salt metathesis of $UI_3(thf)_4$ with potassium triflate in acetonitrile resulted in the complete substitution of the iodide counterions by triflate producing the acetonitrile solvate $[U(OTf)_3(MeCN)_3]_n$ (**3**). The solid-state structure of **3** shows the formation of a unique U(III) coordination polymer in which the metal ions are connected by three triflates acting as bidentate bridging ligands to form a 1D chain.

Introduction

A decade ago, the report of the efficient synthesis and detailed characterization of $UI_3(thf)_4$ and $U[N(SiMe_3)_2]_3$[1−3] provided a convenient entry into trivalent uranium chemistry. An increasing number of U(III) coordination complexes with diverse ligands such as neutral N donors,[4−8] neutral S donors,[9] anionic N donors,[10−17] and alkoxides[18−21] have been prepared using $UI_3(thf)_4$ as the starting material. Triflate salts are an attractive alternative to halides in coordination and organometallic chemistry and should lead to different coordination, solubility, and reactivity properties of trivalent uranium complexes. Indeed, uranium triflates have already proven to be useful precursors for the synthesis of coordina-

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tion and organometallic uranium complexes.[22,23] However, the synthetic procedure previously described for the preparation of $U(OTf)_3$ involves the reaction of U(0) or UH_3 with triflic acid, which is highly corrosive and difficult to obtain in an anhydrous form.[24] Moreover, while the reaction of aqueous triflic acid with plutonium metal was reported to form the Pu(III) aquo complex $[Pu(H_2O)_9][OTf]_3$ in very high yield,[25] in the case of uranium, this synthetic procedure was shown to be very sensitive to operating conditions (such as temperature and the presence of traces of water in the triflic acid). In our hands, it led to the reproducible isolation of the U(IV) oxo and hydroxo complexes which have been structurally characterized. Herein, we describe an efficient synthesis of $U(OTf)_3$ involving the protonation of $U[N(SiMe_3)_2]_3$ with pyridinium triflate, a procedure which had already proven very efficient and selective in the preparation of U(IV) organometallic derivatives.[26] Moreover, the acetonitrile solvate of $U(OTf)_3$ can also be easily prepared from the iodide salt $UI_3(thf)_4$ by salt metathesis.[27] Triflate salts of trivalent f-elements have found large applications as catalysts in organic synthesis[28] or as precursors in the preparation of coordination complexes.[29] While the solid-state structures of hydrated lanthanide triflates have been established, crystallographic information on the solid-state structures of anhydrous triflates remains scarce.[30] Here, we report the crystal structure of the neutral acetonitrile solvate of $U(OTf)_3$ in which all three triflates are bound to the U(III) ion in a bridging fashion resulting in the construction of an unique coordination polymer.

Experimental Section

General Details. ^{19}F NMR spectra were recorded on Varian Mercury-400 spectrometer in deuterated CD_3CN (distilled from CaH_2) at 298 K, calibrated against C_6F_6 and externally referenced to $CFCl_3$. Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany.

Magnetization of the crystalline complex $[U(OTf)_3(OH)(py)_4].py$ was recorded with a SQUID magnetometer (Quantum Design) at 10 kOe at 300 K. The value of the magnetic susceptibility was corrected for the underlying diamagnetic increment ($\chi_{dia} = 517 \times 10^{-6}$ cm^3 mol^{-1}) by using tabulated Pascal constants.[31]

All manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques and a Braun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. The solvents were purchased from Aldrich in their anhydrous forms, conditioned under argon, and vacuum distilled from K (tetrahydrofuran, isopropyl ether, pyridine) or CaH_2 (acetonitrile). Depleted uranium turnings were purchased from the "Societé Industrielle du Combustible Nucleaire" of Annecy (France). Starting materials were purchased from Aldrich, and used without further purification unless otherwise stated. Triflic acid (99^{+}% purity) packaged in sealed ampules was purchased from Aldrich. $UI_3(thf)_4$ and $U[N(SiMe_3)_2]_3$ were prepared as described by Clark and co-workers.[2]

Isolation of $[U(OTf)_3(OH)(py)_4]$ (1) and $[\{U(OTf)_2(py)_3\}_2\{\mu\text{-}O\}\{\mu\text{-}OTf\}_2]$ (2). Triflic acid (4 × 1.2 mL ampules) was carefully transferred into a flask equipped with a Youngs valve in the glovebox and then attached to a high vacuum ramp with airtight Teflon joints. The acid was then distilled twice under reduced pressure. Freshly prepared uranium turnings (0.40 g, 1.68×10^{-3} mmol) were then heated to 70 °C under a 1 bar atmosphere of H_2 for 1 h, followed by a further hour at 120 °C, or until all the U metal had been transformed into a black powder of UH_3.[32] The freshly distilled triflic acid was then slowly added to a flask containing the UH_3, cooled to −78 °C, by vacuum transfer over a period of 2 to 3 h (we found that an excess of triflic acid was necessary to enable the reaction to be stirred and the UH_3 to react). Upon completion of the addition of the triflic acid, the reaction was left to warm slowly to room temperature under a N_2 bubbler and stirred at room temperature for a further 12 h (or overnight). The olive green suspension that formed was stirred at ambient temperature until there were no visible traces of UH_3 left (~20 h). After this, a green-blue suspension had formed. It was heated gently to 60 °C for 1 h to ensure that the residual UH_3 had reacted; then, all of volatiles were removed under reduced pressure, and the solid was dried under vacuum at 50 °C for approximately 18 h. The flask containing the green-blue solid was subsequently taken into the glovebox and added carefully in solid portions to 60 mL of pyridine to remove traces of triflic acid as pyridinium triflate (note that this is an exothermic reaction). After the green suspension was heated to 60 °C for 1 h, a green-grey powder was isolated by filtration and washed with a further 2 × 10 mL of pyridine (1.28 g). The green filtrate that resulted was reduced to approximately one-quarter of the original volume and cooled to −18 °C; after several days, emerald green crystals were isolated, washed with minimal volumes of cold pyridine, and dried in vacuo to yield $[U(OTf)_3(OH)(py)_4]$ (**1**) in a 17% yield, 285 mg. (The yield of this compound increases to between 23 and 27% if the triflic acid is transferred outside of the glovebox under a N_2 flush prior to distillation).

NMR/CD_3CN/298 K δ_F-{^1H}: −85.66. Anal. Calcd for $[U(OTf)_3(OH)(py)_4]\cdot 4.75py$ $C_{24.25}H_{22.25}F_9N_{4.75}O_{10}S_3$: C, 29.77; H, 2.29; N, 6.16; S, 8.90. Found: C, 29.68; H, 2.14; N, 6.46; S, 8.81.

A portion of the isolated green-grey powder was then extracted into hot pyridine (20 mg in 5 mL) and layered with *n*-hexane. After several weeks, a few single green crystals were isolated; an X-ray diffraction analysis confirmed the product to be $[\{U(OTf)_2(py)_3\}_2\{\mu\text{-}O\}\{\mu\text{-}OTf\}_2]$ (**2**).

A second portion of the powder (50 mg) was suspended in pyridine (10 mL), and an excess of Ph_3PO (3−4 equiv based on $U(OTf)_4$, ~50 mg) was added. A mint green solution immediately formed; after 2 h of agitation, all volatiles were removed under reduced pressure, and 2 mL of thf was added. Slow vapor diffusion of $^{i}Pr_2O$ into this solution over several weeks resulted in mint green crystals of the previously reported[22] compound $[U(OTf)_4(Ph_3PO)_3]$

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Table 1. Crystallographic Data for **1**, **2** and **3**

	[U(OTf)$_3$(OH)(py)$_4$]•py (**1**)	[{U(OTf)$_2$(py)$_3$}$_2${μ-O}{μ-OTf}$_2$] (**2**)	[U(OTf)$_3$(MeCN)$_3$]$_n$ (**3**)
fw	1097.75	1009.64	808.40
cryst syst	monoclinic	monoclinic	triclinic
space group	P2(1)/*c*	*P*2/*c*	$P\bar{1}$
a (Å)	20.3563(17)	14.055(4)	5.868(2)
b (Å)	11.6181(10)	13.973(4)	10.587(3)
c (Å)	16.2844(14)	18.653(6)	19.064(5)
α (deg)	90	90	97.498(4)
β (deg)	94.580(2)	110.751(5)	94.104(4)
γ (deg)	90	90	91.772(5)
V (Å^3), Z	3839.0(6), 4	3425.7(18), 4	1170.2(6), 2
λ	0.71073	0.71073	0.71073
D$_{calc}$ (g cm^{-3})	1.899	1.958	2.294
μ(Mo Kα) (mm^{-1})	4.493	5.024	7.318
temp (K)	193(2)	223(2)	193(2)
R_1, R_2^{a}	0.0285, 0.0440	0.0583, 0.1402	0.0175,0.0436

^{a} Structure was refined on F_0^2 using all data: $R_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

(30−40%). NMR/CD$_3$CN/298 K δ_F-{^{1}H}: "U(OTf)$_4$.py" −82.9 (major product); [{U(OTf)$_2$(py)$_3$}$_2${μ-O}{μ-OTf}$_2$] (**2**) −73.5 (minor product).

Similar mixtures of species were obtained from the reaction of uranium metal and triflic acid.

Preparation of [U(OTf)$_3$(MeCN)$_3$]$_n$ (3) from UI$_3$(thf)$_4$. An acetonitrile solution of potassium triflate (1.0 g, 5.29 mmol, 25 mL) was added dropwise to a stirred acetonitrile solution of UI$_3$(thf)$_4$ at ambient temperature (1.5 g, 1.65 mmol, 30 mL) over a period of 90 min. The green solution was then stirred at this temperature for a further 18 h, after which time a green solid had precipitated from the reaction mixture. The precipitated material was subsequently isolated, washed with MeCN (3 × 10 mL), recrystallized twice from hot MeCN, and washed with ^{i}Pr$_2$O to produce **3** as a turquoise-green powder after drying in vacuo (60% yield, 802 mg). Single crystals suitable for X-ray diffraction studies were grown by slow diffusion of ^{i}Pr$_2$O into a 1.5×10^{-2} M MeCN solution of the complex. NMR/CD$_3$CN/298 K δ_F-{^{1}H}: −80.06. Anal. Calcd for [U(OTf)$_3$(MeCN)$_3$]•0.0.3KI $C_9H_9F_9N_3O_9S_3UK_{0.3}I_{0.3}$: C, 12.59; H, 1.05; N, 4.89; S, 11.21; I, 4.43. Found: C, 12.30; H, 1.06; N, 4.91; S, 11.29; I, 5.09.

Preparation of U(OTf)$_3$(py)$_4$ (4) from U{N(SiMe$_3$)$_2$}$_3$. In a typical preparation, 670 mg pyridinium triflate in pyridine (2.92 mmol, 10 mL) was added dropwise to a stirred solution of U{N(SiMe$_3$)$_2$}$_3$ in pyridine at room temperature (700 mg, 0.97 mmol, 15 mL) over a period of an hour. After the addition was complete, the solution was stirred for a further 16 h at this temperature, and then cooled to −18 °C. After several days, the green powder that precipitated was isolated, washed with 3 × 8 mL pyridine, recrystallized from hot pyridine (12 mL), and dried under reduced pressure for 2 h to yield **4** as an olive green powder in a 55% yield (745 mg). The number of pyridine molecules in the bulk compound were determined to be four in several samples by ^{1}H NMR spectroscopy by addition of a known concentration of the neutral chelating ligand *N*,*N*,*N′*,*N′*-tetrakis(2-pyrazylmethyl)-1,3-trimethylenediamine (tpztn)[33] and integration of the liberated pyridine resonances.

NMR/CD$_3$CN/298 K δ_F-{^{1}H}: −79.95

The elemental analysis correspond to the formula U(OTf)$_3$(py)$_{3.5}$ is probably the result of the prolonged drying period. Anal. Calcd for $C_{20.5}H_{17.5}O_9N_{3.5}S_3F_9U$: C, 25.60; H, 1.82; N, 5.10; S, 9.99. Found: C, 25.30; H, 1.79; N, 5.20; S, 9.81.

Derivatization of 4 with Ph$_3$PO. Ph$_3$PO (4 equiv, 56 mg, 0.20 mmol) as a solid in 3 portions was added to a pyridine solution of U(OTf)$_3$(py)$_4$ (50 mg, 0.05 mmol, 3 mL); the solution immediately changed color from green to dark red. All volatiles were then removed under reduced pressure, and the red oil was recrystallized from thf/^{i}Pr$_2$O (1:3) and washed with minimal volumes of cold thf to yield the previously described complex,[24] U(OTf)$_3$(Ph$_3$PO)$_4$, as analytically pure dark red single crystals in a 72% yield (65 mg).

Anal. Calcd for $C_{75}H_{60}O_{13}P_4S_3F_9U$: C, 50.08; H, 3.36. Found: C, 50.01; H, 3.39.

The structure was confirmed by X-ray analysis.

X-ray Crystallography. All diffraction data were taken using a Bruker SMART CCD area detector three-circle diffractometer (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å). To prevent oxidation, the crystals were coated with a light hydrocarbon oil and quickly transferred to a stream of cold nitrogen on the diffractometer.

The cell parameters were obtained with intensities detected on three batches of 15 frames with a 5 s exposure time for **1**, 60 s for **2**, and 120 s for **3**. The crystal-detector distance was 5 cm. For three settings of Φ and 2θ, narrow data frames were collected with 0.3° increments in ω and with a 5 s exposure time for **1**, 60 s for **2**, and 120 s for **3**. A full hemisphere of data was collected for each complex. At the end of data collection, the first 50 frames were recollected to establish that crystal decay had not taken place during the collection. Unique intensities with $I > 10\sigma(I)$ detected on all frames using the Bruker SMART program[34] were used to refine the values of the cell parameters. The substantial redundancy in the data allows empirical absorption corrections to be applied using multiple measurements of equivalent reflections with the SADABS Bruker program.[34] Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure (Table 1). Complete information on crystal data and data collection parameters is given in the Supporting Information.

The structures were solved by direct methods using the SHELXTL 5.03 package.[35] For the three complexes, all atoms, including hydrogen atoms for complex **3**, were found by difference Fourier syntheses. All non-hydrogen atoms were anisotropically refined on F^2, and hydrogen atoms were isotropically refined. All hydrogens in complex **2** and hydrogen atoms of the cocrystallized pyridine

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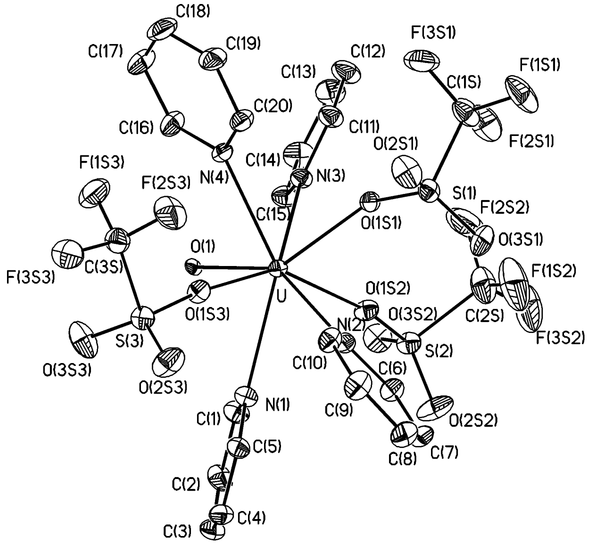

Figure 1. Side view of the crystal structure of the complex [U(OTf)$_3$(OH)(py)$_4$] (**1**) with thermal ellipsoids at 30% probability.

molecule in complexes **1** were included in calculated positions with isotropical thermal coefficients.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

U−O(1)	2.040(2)
U−O(1S3)	2.340(2)
U−O(1S2)	2.343(3)
U−O(1S1)	2.372(2)
U−N(4)	2.579(3)
U−N(2)	2.604(3)
U−N(1)	2.607(3)
U−N(3)	2.616(3)
O(1)−U−O(1S3)	85.59(9)
O(1)−U−O(1S2)	103.67(9)
O(1S3)−U−O(1S2)	147.29(9)
O(1)−U−O(1S1)	144.79(8)
O(1S3)−U−O(1S1)	108.66(9)
O(1S2)−U−O(1S1)	81.85(9)
O(1)−U−N(4)	79.58(9)
O(1S3)−U−N(4)	72.36(9)
O(1S2)−U−N(4)	139.78(9)
O(1S1)−U−N(4)	74.80(9)
O(1)−U−N(2)	143.83(9)
O(1S3)−U−N(2)	74.16(9)
O(1S2)−U−N(2)	80.68(9)
O(1S1)−U−N(2)	71.18(9)
N(4)−U−N(2)	120.31(10)
O(1)−U−N(1)	72.72(9)
O(1S3)−U−N(1)	79.30(9)
O(1S2)−U−N(1)	73.93(10)
O(1S1)−U−N(1)	140.35(9)
N(4)−U−N(1)	141.55(10)
N(2)−U−N(1)	74.23(10)
O(1)−U−N(3)	72.17(9)
O(1S3)−U−N(3)	140.70(9)
O(1S2)−U−N(3)	71.12(9)
O(1S1)−U−N(3)	77.15(9)
N(4)−U−N(3)	72.02(9)
N(2)−U−N(3)	140.04(10)
N(1)−U−N(3)	121.70(9)

Results and Discussion

Several attempts to prepare pure U(OTf)$_3$ salts following a previously reported synthetic method involving the reaction of U metal or UH$_3$ with anhydrous triflic acid under rigorously anhydrous conditions and even at temperatures lower than 60° C resulted in our hands in the formation of a mixture of species. The green-blue solid obtained from this reaction was treated with anhydrous pyridine in order to eliminate traces of triflic acid resulting in the partial dissolution of the solid. Subsequent slow cooling of the green solution to −18 °C led to the reproducible isolation of the mononuclear hydroxo complex [U(OTf)$_3$(OH)(py)$_4$] (**1**) in a 17−27% yield as emerald-green crystals. The crystal structure of (**1**) is shown in Figure 1 and selected interatomic distances and angles are given in Table 2. The metal is eight coordinate by three oxygens of the monodentate triflate, four pyridine nitrogens, and one hydroxo group. The coordination geometry of the U(IV) ion is a slightly distorted square antiprism with N(4), N(2), O(1S1), and O(1S3) forming one square base (deviation from the mean plane = 0.042 Å) and N(1), O(1), N(3) and O(1S2) forming the next square plane (deviation from the mean plane = 0.038 Å). The angle between the two square planes is 3.2°. The U−O(1) distance of 2.040(2) Å is short when compared to the distances found in the mononuclear bis-hydroxo U(IV) complex, [U(tpa)$_2$(OH)$_2$]I$_2$ (tpa = tris[(2-pyridyl)methyl]amine) (2.1269(12) and 2.1465(13) Å),[36] in the U(IV) triamidoamine complex [U(NN$'_3$)(OH)(CH$_2$PMe$_3$)] (NN$'_3$ = N(CH)$_2$CH$_2$NSiMe$_2$-Bu^t)$_3$) (2.145(6) Å)[37] or in terminal phenoxides in U(IV) complexes[18,38] (ranging from 2.132(8) to 2.146(4) Å). However, the U−O(1) distance is longer than those usually found for terminal oxo species (ca. 1.8 Å[39]). The assignment as a U(IV)−OH species was confirmed by the determination of the magnetic moment of **1**. The measured magnetic moment of $\mu_{\text{eff}} = 3.35\ \mu_{\text{B}}$ at 300 K although smaller than the theoretically determined free ion moment of $\mu_{\text{eff}} = g(J(J+1))^{1/2} = 3.58\ \mu_{\text{B},}$ rules out the presence of a U(V)═O species (theoretically determined $\mu_{\text{eff}} = 2.54\ \mu_{\text{B}}$). The formation of complex **1** could be explained by the presence of residual water traces in the triflic acid even after several distillations. Indeed, the yield of the hydroxo complex varied significantly depending on the quality of the triflic acid used and on the manipulation. We expect that the yield of the hydroxo complex could be easily increased even further by using undistilled triflic acid. Although the formation of hydroxo complexes of U(IV) is probably often involved in the hydrolysis of uranium(III) complexes, very few examples of these species have been reported in the literature. Several U(IV) metallocene hydroxides of the type [(Cp)$_3$U(OH)] have been prepared,[40] but their solid-state structures have not been determined. Accidental oxidation has led to the structural determination of two complexes containing terminal hydroxo groups: a mononuclear triamidoamine U(IV) mono-hydroxo complex[37] and a mononuclear bis-hydroxo U(IV) complex of tris[(2-pyridyl)methyl]amine (tpa).[36] However, it was

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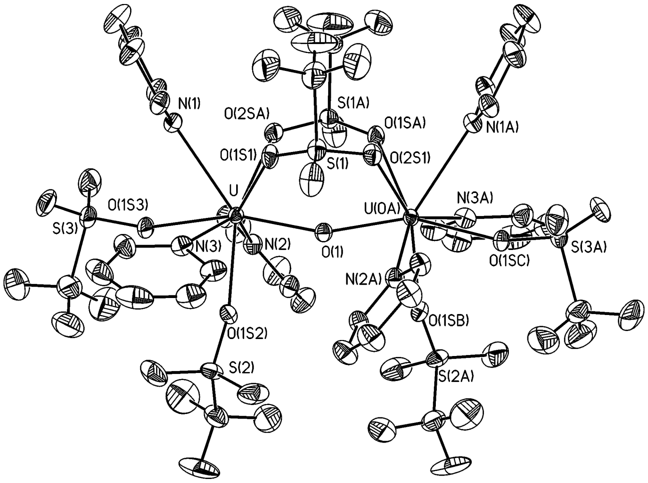

Figure 2. Side view of the crystal structure of the complex [{U(OTf)$_2$(py)$_3$}$_2${μ-O}{μ-OTf}$_2$] (**2**) with thermal ellipsoids at 30% probability.

reported impossible to reproduce the syntheses of these species. Conversely, complex **1** can be prepared in reasonable amounts providing a good precursor for the synthesis and study of the reactivity of hydroxo complexes with different coordination environments.

The ^{19}F NMR of the products of the reaction of UH$_3$ with triflic acid showed the presence of two additional species. Further extraction of these products in hot pyridine (after preliminary separation of **1**) resulted in the isolation of a small amount of crystals of the dimeric complex [{U(OTf)$_2$(Py)$_3$}$_2${μ-O}{μ-OTf}$_2$] (**2**). The crystal structure of **2**, in which two identical moieties are joined by one μ-oxo group and two bridging triflate groups to form a centrosymmetric dimer is shown in Figure 2, and selected interatomic distances and angles are given in Table 3. The U(IV) ion in **2** is eight coordinate by two oxygens of two monodentate triflates, three pyridine nitrogens, two oxygens of the bridging triflates, and one bridging oxo group. The value of the U−O(1) distance (2.098(2) Å), the U−O triflate distances (2.325(7) − 2.506(6) Å), and the U#1−O(1)−U angle (159.2(5)°) are similar to the values found in the recently described trinuclear and tetranuclear U(IV) μ-oxo complexes containing triflate bridges and displaying a linear arrangement of the metal ions.[23]

To further characterize the species formed in the reaction of UH$_3$ with triflic acid, an excess of Ph$_3$PO was added to a suspension of the raw reaction mixture resulting in the isolation of X-ray quality crystals of the previously reported[22] complex [U(OTf)$_4$(Ph$_3$PO)$_3$] as a major reaction product.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**^{a}

U−O(1)	2.0987(17)
U−O(1S2)	2.325(7)
U−O(1S3)	2.335(6)
U−O(2S1)#1	2.413(6)
U−O(1S1)	2.506(6)
U−N(3)	2.563(9)
U−N(2)	2.594(8)
U−N(1)	2.659(8)
O(1)−U#1	2.0987(17)
O(1)−U−O(1S2)	83.3(3)
O(1)−U−O(1S3)	154.0(3)
O(1S2)−U−O(1S3)	78.9(2)
O(1)−U−O(2S1)#1	80.7(2)
O(1S2)−U−O(2S1)#1	145.6(2)
O(1S3)−U−O(2S1)#1	103.8(2)
O(1)−U−O(1S1)	73.9(2)
O(1S2)−U−O(1S1)	125.0(2)
O(1S3)−U−O(1S1)	132.1(2)
O(2S1)#1−U−O(1S1)	79.1(2)
O(1)−U−N(3)	110.7(2)
O(1S2)−U−N(3)	71.7(2)
O(1S3)−U−N(3)	81.5(3)
O(2S1)#1−U−N(3)	142.6(3)
O(1S1)−U−N(3)	70.9(3)
O(1)−U−N(2)	83.6(2)
O(1S2)−U−N(2)	75.4(2)
O(1S3)−U−N(2)	73.6(3)
O(2S1)#1−U−N(2)	72.6(2)
O(1S1)−U−N(2)	146.3(2)
N(3)−U−N(2)	141.9(3)
O(1)−U−N(1)	133.1(3)
O(1S2)−U−N(1)	140.6(2)
O(1S3)−U−N(1)	70.3(2)
O(2S1)#1−U−N(1)	68.0(2)
O(1S1)−U−N(1)	66.7(2)
N(3)−U−N(1)	79.8(3)
N(2)−U−N(1)	116.7(2)
U#1−O(1)−U	159.2(5)

^{a} Symmetry transformations used to generate equivalent atoms: #1 $-x$, y, $-z + {}^3/_2$.

In conclusion, in our hands, treatment of U metal or UH$_3$[32] with triflic acid always resulted in a mixture of U(IV) products. Traces of water in the triflic acid are probably responsible for the formation of oxo and hydroxo uranium(IV) species. Conversely, the reaction of Pu metal with aqueous triflic acid only results in formation of the Pu(III) aquo-complex, [Pu(H$_2$O)$_9$][OTf]$_3$, and oxidation to Pu(IV) is not observed. This is in agreement with the difference in redox potentials for the two trivalent actinides (0.98 V for the Pu(IV)/Pu (III) couple and −0.63 V for the U(IV)/U(III) couple[39]). To avoid the use of triflic acid, which is highly corrosive and difficult to obtain anhydrous and the concomitant formation of oxidized species, we have explored alternative synthetic procedures in order to obtain a practical preparation of U(OTf)$_3$. Salt metathesis[27] of UI$_3$(thf)$_4$ with potassium triflate in acetonitrile (equation 1) resulted in the complete substitution of the iodide counterions by triflate to yield the acetonitrile solvate [U(OTf)$_3$(MeCN)$_3$]$_n$ (**3**). Crystallization of U(OTf)$_3$ from acetonitrile resulted in the isolation of an unique coordination polymer of trivalent uranium. The crystal structure of the polymeric complex [U(OTf)$_3$(MeCN)$_3$]$_n$ (**3**) is shown in Figure 3. The coordination environment around the U(1) ion is shown in Figure 4, and selected interatomic distances and angles are listed in Table 4. The U(III) ion in **3** is nine coordinate by six oxygen atoms from the triflate and three nitrogens from the coordinated acetonitrile molecules. The coordination geometry around U(III) is a slightly distorted tricapped trigonal prism with the three capping positions occupied by the acetonitrile nitrogens. All three triflate anions are bound in a bidentate bridging fashion resulting in the construction of a 1D chain (along the *a* axis of the unit cell); the separation between neighboring U(III) ions is 5.868 Å. Each triflate ion forms an interchain hydrogen bond through the noncoordinating oxygen atom with the acetonitrile hydrogens of an adjacent chain as indicated by the C···O distances (C2···O2S2

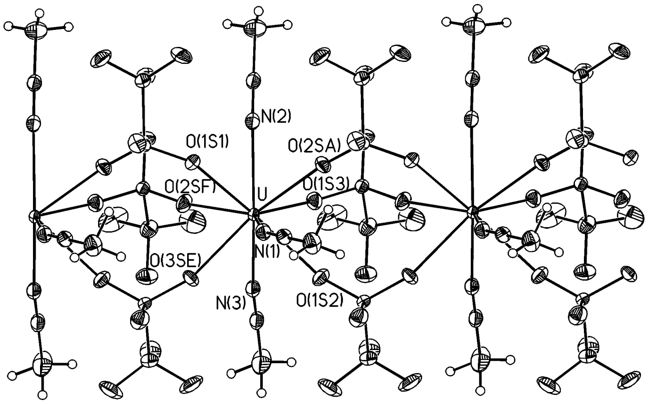

Figure 3. Side view of the crystal structure of $[U(OTf)_3(MeCN)_3]_n$ (**3**) with thermal ellipsoids at 30% probability.

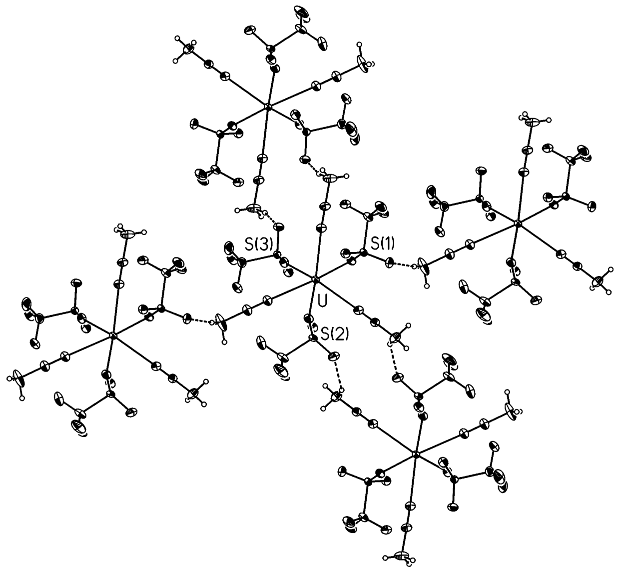

Figure 4. The hydrogen-bonded 2D network of $[U(OTf)_3(MeCN)_3]_n$ (**3**).

2.64(7) Å, C4···O3S3 2.38(7) Å, and C6···O3S1, 2.45(7) Å) and corresponding CHO angles (148(6)°, 165(5)°, 175(6)°). Each chain is hydrogen bonded to four adjacent chains resulting in a 2D hydrogen-bonded network (Figure 4).The mean value of the U−O distances (2.49(1) Å) is similar to values reported for monodentate triflates in the few examples of crystallographically characterized uranium(III) triflate complexes.[23] Isomorphous hydrate lanthanide triflates $[Ln(H_2O)_9][OTf]_3$ have been prepared and crystallographically characterized for all of the trivalent lanthanide ions[30] and more recently an analogous structure has been determined for trivalent plutonium.[25] In all of these examples, no triflate counterions are bound in the primary coordination sphere of the metal in the solid state. Conversely, there is scarce information on the solid-state structure of solvates of trivalent f-metal anhydrous triflates. $[U(OTf)_3(MeCN)_3]_n$ thus represents a rare example of crystallographically characterized solvate in which all the triflate anions are coordinated to the metal center in the solid state.

Although salt metathesis is often nonselective, elemental analyses performed on bulk samples of **3** are in agreement with the observed crystal structure and confirm the complete substitution of the iodide counterions by the triflate. The selectivity of this reaction is probably a result of the higher affinity of trivalent uranium for the triflate group associated with the lower solubility of the reaction products with respect to the starting materials. However, the bulk sample can contain small amounts (0.1−0.3 equiv) of coprecipitated potassium iodide which can be minimized by successive recrystallizations.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**[a]

U−O(2S3)#1	2.480(3)
U−O(2S1)#2	2.494(3)
U−O(3S2)#1	2.498(3)
U−O(1S3)	2.505(3)
U−O(1S2)	2.506(3)
U−O(1S1)	2.516(2)
U−N(2)	2.635(4)
U−N(3)	2.654(4)
U−N(1)	2.663(4)
O(2S3)#1−U−O(2S1)#2	139.13(10)
O(2S3)#1−U−O(3S2)#1	75.54(10)
O(2S1)#2−U−O(3S2)#1	139.42(9)
O(2S3)#1−U−O(1S3)	89.13(10)
O(2S1)#2−U−O(1S3)	75.04(9)
O(3S2)#1−U−O(1S3)	137.64(9)
O(2S3)#1−U−O(1S2)	137.13(9)
O(2S1)#2−U−O(1S2)	75.91(10)
O(3S2)#1−U−O(1S2)	88.50(10)
O(1S3)−U−O(1S2)	76.29(10)
O(2S3)#1−U−O(1S1)	77.34(9)
O(2S1)#2−U−O(1S1)	88.71(9)
O(3S2)#1−U−O(1S1)	78.69(9)
O(1S3)−U−O(1S1)	136.67(9)
O(1S2)−U−O(1S1)	138.72(9)
O(2S3)#1−U−N(2)	70.87(10)
O(2S1)#2−U−N(2)	68.28(10)
O(3S2)#1−U−N(2)	136.76(10)
O(1S3)−U−N(2)	68.57(10)
O(1S2)−U−N(2)	134.74(10)
O(1S1)−U−N(2)	68.11(9)
O(2S3)#1−U−N(3)	69.83(10)
O(2S1)#2−U−N(3)	132.31(10)
O(3S2)#1−U−N(3)	69.94(10)
O(1S3)−U−N(3)	67.71(10)
O(1S2)−U−N(3)	67.33(10)
O(1S1)−U−N(3)	138.97(10)
N(2)−U−N(3)	120.26(11)
O(2S3)#1−U−N(1)	136.77(10)
O(2S1)#2−U−N(1)	68.17(10)
O(3S2)#1−U−N(1)	71.27(10)
O(1S3)−U−N(1)	134.10(10)
O(1S2)−U−N(1)	69.01(10)
O(1S1)−U−N(1)	69.71(10)
N(2)−U−N(1)	118.53(11)
N(3)−U−N(1)	121.02(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 $x + 1, y, z$; #2 $x - 1, y, z$.

We therefore also explored an alternative synthetic route which led to the analytically pure pyridine solvate adduct $[U(OTf)_3(py)_4]$ (**4**). Complex **4** was easily and reproducibly prepared in a 50−60% yield by protonolysis of the amide $U\{N(SiMe_3)_2\}_3$ with pyridinium triflate in pyridine (equation 2).

$$[UI_3(thf)_4] + 3\ KOTf \xrightarrow{CH_3CN} [U(OTf)_3(MeCN)_3]_n + 3KI \quad (1)$$

$$[U\{N(SiMe_3)_2\}_3] + 3\ [Hpy][OTf] \xrightarrow{py} [U(OTf)_3(py)_4] + 3\ NH(SiMe_3)_2 \quad (2)$$

The formulation of complex **4** was confirmed by substitution of the labile pyridine molecules with Ph_3PO to produce the known compound $[U(OTf)_3(Ph_3PO)_4]$[24] as dark red X-ray quality crystals. Protonolysis reactions of complex $[U\{N(SiMe_3)_2\}_3]$have successfully been employed in the past for the synthesis of homoleptic U(III) aryloxide complexes.[18] The pyridinium salt [Hpy][OTf] previously used in the preparation of tetravalent triflate derivatives[22] has also been proven to be an effective protonolysis reagent for the U(III)−N bond.

Conclusion

The reaction of UH_3 with triflic acid in the presence of traces of water resulted in the reproducible isolation of a rare mononuclear hydroxo complex of tetravalent uranium which has been crystallographically characterized. This complex is an interesting precursor for reactivity studies. The versatile acetonitrile solvate $[U(OTf)_3(MeCN)_3]_n$ was easily prepared from $UI_3(thf)_4$ by salt metathesis with potassium triflate while the pyridine solvate $[U(OTf)_3(py)_4]$ was obtained by protonolysis of $[U\{N(SiMe_3)_2\}_3]$ with pyridinium triflate. These two practical methods allow the preparation of soluble derivatives of the versatile precursor $U(OTf)_3$ avoiding the use of triflic acid which is highly corrosive and difficult to purify providing convenient alternatives routes into U(III) coordination chemistry. The X-ray crystal structure of the acetonitrile solvate shows the formation of a unique U(III) coordination polymer in which the metal ions are connected by three triflate anions acting as bidentate bridging ligands in a 1D chain. This is a rare example of a crystallographically characterized $M(OTf)_3$ solvate complex of a trivalent f-element where all three triflates are bound to the metal ion. The versatility of these solvates to act as precursors of U(III) complexes was confirmed by their use in the preparation of the previously reported phosphineoxide adduct $[U(OTf)_3(Ph_3PO)_4]$[24] and by preliminary work on the preparation of triflate complexes of tetrapodal N-donor ligands.[41]

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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