Simple Preparations of the Anhydrous and Solvent-Free Uranyl and Cerium(IV) Triflates $UO_2(OTf)_2$ and $Ce(OTf)_4$ − Crystal Structures of $UO_2(OTf)_2(py)_3$ and $[\{UO_2(py)_4\}_2(\mu\text{-}O)][OTf]_2$

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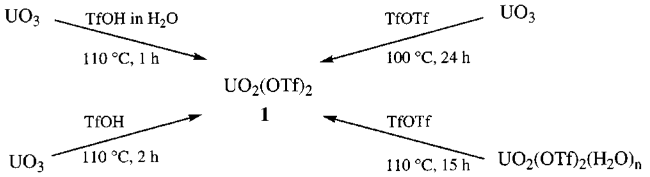
Treatment of UO_3 with pure triflic acid TfOH at 110 °C or with boiling triflic anhydride TfOTf afforded $[UO_2(OTf)_2]$ (**1**) in high yields. The latter was also prepared by the reaction of UO_3 with TfOH in water, or by dehydration of $[UO_2(OTf)_2(H_2O)_n]$ in boiling TfOTf. Anhydrous $[Ce(OTf)_4]$ (**2**) was similarly obtained from the commercially hydrated compound. X-ray analysis revealed that in $[UO_2(OTf)_2(py)_3]$ (**3**), the triflate ligands are monodentate whereas they are dissociated in $[\{UO_2(py)_4\}_2(\mu\text{-}O)][OTf]_2$ (**4**).

Introduction

Complexes of the uranyl moiety UO_2^{2+} are very familiar in actinide chemistry since considerable attention has been paid to their structure, physico-chemical properties and catalytic behaviour in a number of organic transformations.[1] It is interesting to note that most of these studies have been performed on compounds which were isolated from aqueous media. The development of anhydrous uranyl chemistry has long been impeded by the lack of easily available starting materials[2] and hence it is only very recently that a convenient preparation of $[UO_2Cl_2(THF)_3]$ has been reported.[3] In view of the major interest of metallic triflates in both organic[4] and inorganic syntheses,[5] and following our recent work on uranium triflates,[6] we decided to prepare the anhydrous and solvent-free uranyl and cerium (IV) triflates $[UO_2(OTf)_2]$ (**1**) and $[Ce(OTf)_4]$ (**2**). This will also be useful for further studies on the high oxidation-state chemistry of the f-block elements. Here we present convenient and large scale preparations of **1** and **2**; we also describe the X-ray crystal structures of the pyridine adduct $[UO_2(OTf)_2(py)_3]$ (**3**) (py = pyridine) and the μ-oxo derivative $[\{UO_2(py)_4\}_2(\mu\text{-}O)][OTf]_2$ (**4**).

Results and Discussion

Synthesis of the hydrated uranyl triflate $[UO_2(OTf)_2(H_2O)_n]$ was first performed by treating UO_3 with two equivalents of triflic acid in water.[7] Difficulties were encountered in the dehydration of this complex by the Kumagawa method, forming the acetonitrile adduct $[UO_2(OTf)_2(NCMe)_n]$ which was then used for the synthesis of inclusion compounds with crown-ethers. The anhydrous and solvent-free uranyl triflate **1** can be prepared by a number of different routes, as described in Scheme 1.



Scheme 1. Syntheses of the uranyl triflate **1**

A pale yellow solution was rapidly obtained by treating a suspension of uranium trioxide in water with a 10-fold excess of freshly distilled triflic acid. After evaporation and drying under vacuum at 200 °C, compound **1** was isolated as a pale yellow powder; the yields varied from 65 to 90%. This synthesis of **1** is analogous to that of UO_2Cl_2 by reaction of UO_3 with HCl.[8] However, thermal dehydration of uranyl triflate is straightforward whereas that of $[UO_2Cl_2(H_2O)_n]$ requires further treatment with dry HCl at 300 °C.[8] This was previously exploited in the preparation of anhydrous lanthanide(III) triflates,[9] and is related to the final sublimation of the triflic acid monohydrate $[TfO][H_3O]$. The synthesis of **1** can be described by Equation (1) and (2).

$$UO_3 + (2 + x)\,TfOH \xrightarrow{H_2O} UO_2(OTf)_2.xL \qquad (1)$$

$$UO_2(OTf)_2.xL \xrightarrow[\text{vacuum}]{200\,°C} \underset{\mathbf{1}}{UO_2(OTf)_2} + xL \qquad L = [TfO][H_3O] \qquad (2)$$

While UO_3 was found to react with HCl only in the presence of moisture,[8] it also reacted in suspension in pure TfOH to give **1,** which was recovered in almost quantitative yield after evaporation and prolonged heating at 200 °C under vacuum. However, direct reaction of metal oxides with anhydrous triflic acid may sometimes lead to the

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formation of complexes solvated with the excess acid,[9] which can easily induce polymerization of THF,[10] a common solvent in uranium chemistry. Thus, the reaction of UO_3 with TfOH in aqueous solution should be preferred for the synthesis of **1**.

Nevertheless, the most convenient and efficient synthesis to **1** proved to be the reaction of uranium trioxide with triflic anhydride. A suspension of UO_3 in pure TfOTf was quantitatively transformed, after 24 h at 100 °C, into **1** which was easily recovered after evaporation of excess anhydride. The superiority of this synthetic route, shown in Equation (3), is related to the facile elimination of excess TfOTf, which is a poor coordinating reagent and has a lower boiling point (81−83 °C, 745 Torr) than triflic acid (162 °C, 760 Torr). In addition, reaction (3) does not generate side products, whereas sublimation of triflic acid hydrate, formed from reaction (2), requires a higher temperature (200 °C) and is time consuming.

$$UO_3 + TfOTf \xrightarrow{100\ ^\circ C} \underset{\mathbf{1}}{UO_2(OTf)_2} \qquad (3)$$

Uranyl triflate **1**, like the other uranyl salts, is very hygroscopic and a practical dehydration method would be highly desirable. Triflic anhydride can also be used as a dehydrating agent and **1** was conveniently obtained by heating a suspension of $[UO_2(OTf)_2(H_2O)_n]$ in pure TfOTf at 110 °C for 15 h, according to Equation (4). Triflic acid is the only side product released during the process and was evaporated off with the excess anhydride.

$$UO_2(OTf)_2(H_2O)_n + n\,TfOTf \xrightarrow{110\ ^\circ C} \underset{\mathbf{1}}{UO_2(OTf)_2} + 2n\,TfOH \qquad (4)$$

Irrespective of its mode of preparation, compound **1** was obtained in a pure state, as shown by the elemental analyses and the IR spectra, which confirm the absence of hydrated species.

In a similar way, with TfOTf as a dehydrating agent, the anhydrous cerium(IV) triflate $Ce(OTf)_4$ (**2**) was isolated as a pale yellow powder from the commercially available bright yellow compound $[Ce(OTf)_4(H_2O)_n]$ (n = 2−5) [Equation (5)]. After drying for 15 h at 100 °C, no reduction to Ce^{III} species was observed; the purity of **2** was established by elemental analyses as well as from IR and NMR spectra. $[Ce(OTf)_4(H_2O)_{1.5}]$ was previously prepared by successive treatment of cerium(IV) ammonium nitrate with potassium carbonate and triflic acid in water but could not be further dehydrated because of its decomposition above 120 °C into a trivalent cerium(III) species.[11] In addition to its applications in organic synthesis as a strong Lewis acid and oxidizing agent, compound **2** would be considered as a valuable precursor for the preparation of new cerium(IV) derivatives, while $CeCl_4$ is not stable, and its chemistry could be compared to that of its 5f analogue $U(OTf)_4$.[6b]

$$Ce(OTf)_4(H_2O)_n + n\,TfOTf \xrightarrow{20\ ^\circ C} \underset{\mathbf{2}}{Ce(OTf)_4} + 2n\,TfOH \qquad (5)$$

In the solid state, compounds **1** and **2** are likely to adopt a polymeric structure with OTf bridges; such a structure has previously been found in some uranyl alkylsulfonate compounds which form infinite chains with bidentate bridging RSO_3 groups.[12,13] Compounds **1** and **2** are soluble in coordinating solvents like pyridine, THF and diethyl ether, giving stable Lewis base adducts.

The X-ray crystal structure of the mononuclear complex $[UO_2(OTf)_2(py)_3]$ (**3**) is shown in Figure 1 together with selected bond lengths and angles. The uranium atom is found in the most common pentagonal bipyramidal configuration of uranyl complexes with the equatorial plane defined by three nitrogen atoms of the pyridine ligands and two oxygen atoms of the triflate groups that are monodentate and nonadjacent. The U−O(triflate) bond lengths of 2.370(2) and 2.394(2) Å are identical to those found in $[UO_2(OTf)_2(H_2O)_3\cdot 2benzo\text{-}15\text{-}crown\text{-}5]$ [2.38(1) and 2.392(9) Å][14] and in the monomeric sulfonato complexes $[UO_2(O_3SR)_2(H_2O)_3]$ (R = *p*-tolyl or mesityl) which vary from 2.355(6) to 2.406(7) Å.[13] The structural parameters of the OTf ligand are unexceptional. The structure of $[UO_2(OTf)_2(THF)_3]$, which could not be solved with good accuracy because of the poor quality of the crystals, shows the same arrangement of the equatorial ligands as in the above pyridine adduct **3** or the bromide analogue $[UO_2Br_2(THF)_3]$.[15]

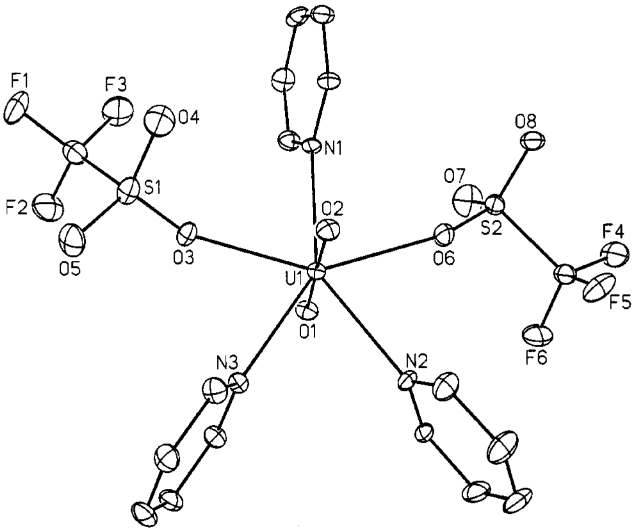

Figure 1. X-ray crystal structure of $UO_2(OTf)_2(py)_3$ (**3**) with thermal ellipsoids at the 40% probability level; selected bond lengths (Å) and angles (°): U−O(1) 1.744(2), U−O(2) 1.747(2), U−O(3) 2.370(2), U−O(6) 2.394(2), U−N(1) 2.529(2), U−N(2) 2.541(2), U−N(3) 2.518(2); O(1)−U−O(2) 178.49(9), N(1)−U−O(3) 72.82(7), N(1)−U−O(6) 73.00(8), N(3)−U−O(3) 73.47(7), N(2)−U−O(6) 71.06(8), N(2)−U−N(3) 69.71(8)

During one of the crystallizations of the bright yellow needles of **3**, a few round, yellow-green crystals were also deposited. X-ray analysis revealed that the μ-oxo complex $[\{UO_2(py)_4\}_2(\mu\text{-}O)][OTf]_2$ (**4**) had been formed, almost certainly after partial hydrolysis of **3** with adventitious traces

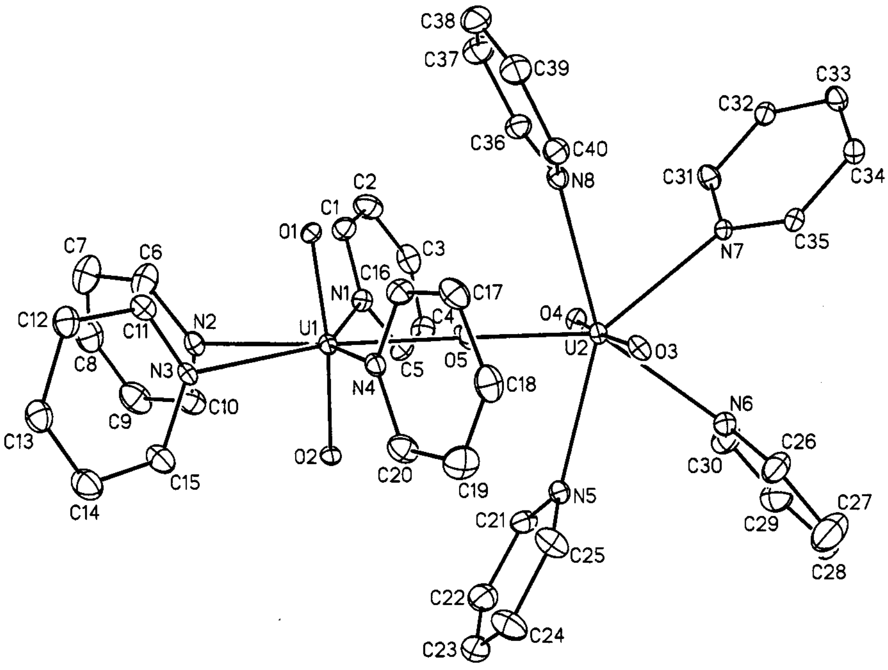

Figure 2. X-ray crystal structure of $[\{UO_2(py)_4\}_2(\mu\text{-}O)][OTf]_2$ (**4**) with thermal ellipsoids at the 15% probability level; selected bond lengths (Å) and angles (°): U(1)−O(1) 1.765(5), U(1)−O(2) 1.778(4), U(1)−N(1) 2.615(5), U(1)−N(2) 2.609(6), U(1)−N(3) 2.589(5), U(1)−N(4) 2.579(5), U(1)−O(5) 2.105(5), U(2)−O(3) 1.779(4), U(2)−O(4) 1.777(4), U(2)−N(5) 2.572(6), U(2)−N(6) 2.610(6), U(2)−N(7) 2.601(6), U(2)−N(8) 2.582(6), U(2)−O(5) 2.085(5); O(1)−U(1)−O(2) 173.1(2), N(1)−U(1)−N(2) 68.33(18), N(2)−U(1)−N(3) 71.88(17), N(3)−U(1)−N(4) 68.33(17), N(4)−U(1)−O(5) 74.81(17), N(1)−U(1)−O(5) 77.27(18), O(3)−U(2)−O(4) 171.5(2), N(5)−U(2)−N(6) 68.1(2), N(6)−U(2)−N(7) 73.35(19), N(7)−U(2)−N(8) 69.73(18), N(8)−U(2)−O(5) 74.3(2), N(5)−U(2)−O(5) 75.7(2), U(1)−O(5)−U(2) 173.7(2)

of water in the solvent. Compound **4** was obtained in larger quantities by crystallization of $[UO_2(OTf)_2(H_2O)_n]$ from pyridine/diethyl ether. The crystals of **4** are composed of discrete OTf anions, which display the expected geometry, and of $[\{UO_2(py)_4\}_2(\mu\text{-}O)]$ dications, the structure of which is shown in Figure 2 with selected bond lengths and angles. The pentagonal bases of each uranyl moiety, composed of the four nitrogen atoms of the pyridine ligands and the common oxygen atom of the μ-oxo group, are nearly orthogonal, intersecting at an angle of 88.3(1)°. The U(1)−O(5)−U(2) bridge is almost linear [173.7(2)°] with short metal−oxygen bond lengths which average 2.09(1) Å, reflecting a π interaction between the bridging oxygen and the metal.[16] This geometry of pseudo-D_{2d} symmetry is the best for the minimization of steric interactions between the two metallic fragments. It is interesting to note that, while linearly oxo-bridged binuclear compounds of early transition metals, lanthanides(III) and actinides(IV) are well documented,[17] compound **4** represents, to the best of our knowledge and from a search of the data of the Cambridge Crystallography Centre, the first example of such a uranyl complex. The other oxo bridged derivatives of uranyl exhibit a higher nuclearity ensured by μ_3-O bridges.[18]

In both **3** and **4**, the U−O bond lengths of the UO_2 moieties are unexceptional, ranging from 1.744(2) Å to 1.780(3) Å, as are the U−N(py) bond lengths which vary from 2.518(2) to 2.614(3) Å. These values compare well with those found in $[UO_2(NO_3)_2(py)_2]$ [$\langle U{-}O\rangle = 1.751(15)$ Å, U−N = 2.543(15) Å],[19a] $[UO_2(C_{15}H_{11}O_2)_2(py)]$ [$\langle U{-}O\rangle = 1.75(1)$ Å, U−N = 2.569(6) Å][19b] and $[UO_2(C_8H_{13}O_3)_2(py)]$ [$\langle U{-}O\rangle = 1.76(2)$ Å, U−N = 2.595(24) Å].[19b] It is noteworthy that, in contrast to **3**, the OTf groups of **4** are totally dissociated, having been replaced with pyridine ligands. This distinct behaviour is difficult to explain. More generally, the triflate ligands in $[UO_2(OTf)_2(H_2O)_3\cdot 2\text{benzo-15-crown-5}]$[14] and all the crystallographically characterized triflates of U^{III} and U^{IV} − $[U(OTf)_2(OPPh_3)_4][OTf]$,[6b] $[U(OTf)_4(OPPh_3)_3]$,[6c] $[U(C_5H_5)_3(OTf)(CN\mathit{t}Bu)]$,[6a] $[U(C_5Me_5)_2(OTf)_2(H_2O)]$,[6a] and $[U(C_8H_8)(OTf)_2(OPPh_3)_2]$[6c] − were found not to have been displaced by strong oxygen and nitrogen Lewis bases. This clearly indicates that the uranium−triflate bond, whatever the metal oxidation state, is not as weak as could be expected.

Experimental Section

All preparations were carried out under argon (less than 2 ppm oxygen and water) using standard Schlenk- and vacuum-line techniques, or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. $[D_8]$THF was dried over Na-K alloy. IR spectra were obtained on a Perkin−Elmer 1725X spectrometer. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The yellow powder of UO_3 was supplied by the Commissariat à l'Energie Atomique. $[Ce(OTf)_4(H_2O)_n]$ was supplied by Aldrich. Triflic acid (98 or 99%, Aldrich) and triflic anhydride (99%, Aldrich) were distilled before use. $[UO_2(OTf)_2(H_2O)_n]$ was synthesized as previously reported.[7]

Uranyl Triflate $UO_2(OTf)_2$ (1). − From UO_3 and TfOH in Water: In the glove box, freshly distilled triflic acid (620 mL, 7 mmol) was added with a microsyringe into a 100 mL round-bottomed flask containing a suspension of UO_3 (210 mg, 0.7 mmol) in deoxygenated and demineralized water (15 mL). The trioxide was dissolved in a few minutes and the pale yellow solution was then refluxed for one hour to ensure complete reaction. Water was then evaporated off under vacuum and collected in a trap connected between the flask and the vacuum line and cooled in liquid nitrogen. The pale yellow residue was further heated at ca 200 °C under vacuum for 24 h and the white solid of $[TfO][H_3O]$ was eliminated by sublimation. During this step, the viscous drops that appeared on the upper walls of the flask were heated with a hot air stripper. Compound **1** was isolated as a pale yellow powder with yields varying from 65 to 90%; it turned bright yellow in air because of rapid hydration. − $C_2F_6O_8S_2U$ (568): calcd. C 4.22, F 20.06, S 11.28; found C 4.40, F 19.85, S 11.43. − IR (KBr in air): $\tilde{\nu}$ = 3593 (m), 3509 (m), 3217 (s) 1598 (s), 1262 (s), 1179 (s), 1034 (s), 950 (w), 905 (U=O, s), 769 (s), 643 (s), 581 (w), 519 (w), 478 (m); the IR spectrum of **1** in nujol between KBr plates shows no bands for water in the region 3600−3000 cm^{-1}.

From UO_3 and Pure TfOH: Triflic acid (ca 3 mL) was distilled into a 100 mL round-bottomed flask containing UO_3 (320 mg, 1.1 mmol) and the mixture was magnetically stirred for 2 h at 110 °C. The excess TfOH was distilled under vacuum into a trap cooled in liquid nitrogen and connected between the flask and the vacuum line. Compound **1** was obtained in 87% yield (550 mg) after drying for 24 h at 200 °C under vacuum. The IR spectra were identical to those described above.

From UO_3 and TfOTf: Freshly distilled triflic anhydride (ca 3 mL) was added in the glove box into a 100 mL round-bottomed flask containing UO_3 (205 mg, 0.7 mmol). The suspension was refluxed for 24 h whilst magnetically stirring. The excess TfOTf was distilled under vacuum into a trap connected between the flask and the vacuum line and cooled in liquid nitrogen. Further drying of the residue for 1 h at 100 °C under vacuum afforded **1** in 96% yield (340 mg). − $C_2F_6O_8S_2U$ (568): calcd. C 4.22, F 20.06, S 11.28; found C 4.37, F 19.81, S 11.37. The IR spectra were identical to those described above.

By Dehydration of $UO_2(OTf)_2(H_2O)_n$ with TfOTf: Triflic anhydride (ca 3 mL) was distilled under vacuum into a 100 mL round-bottomed flask containing the hydrated uranyl triflate $[UO_2(OTf)_2(H_2O)_n]$ (352 mg) and the bright yellow suspension was magnetically stirred at 110 °C for 15 h; the initial colour of the solid turned pale yellow. After cooling to room temperature, excess TfOTf was distilled off and **1** was obtained in almost quantitative yield (330 mg) after drying at 200 °C for 20 h under vacuum. − $C_2F_6O_8S_2U$ (568): calcd. C 4.22, F 20.06, S 11.28; found C 4.29, F 19.94, S 11.32. The IR spectra were identical to those described above.

Cerium(IV) Triflate $Ce(OTf)_4$ (2): Triflic anhydride (ca 3 mL) was distilled under vacuum into a 50 mL round-bottomed flask containing the hydrated cerium(IV) triflate $[Ce(OTf)_4(H_2O)_n]$ (500 mg). The yellow suspension was magnetically stirred for 1 h at 50 °C and then for 15 h at room temperature. The excess TfOTf was evaporated off and the pale yellow residue was dried under vacuum, first at room temperature for 10 h and then at 100 °C for 15 h. Compound **2** was obtained in almost quantitative yield (450 mg); its colour turned bright yellow upon exposure to air. − $C_4CeF_{12}O_{12}S_4$ (736): calcd. C 6.52, S 17.42; found C 6.39, S 17.25. Whereas the ^1H NMR spectrum of the commercially available $[Ce(OTf)_4(H_2O)_n]$ shows a broad signal at δ = 13.6 corresponding to H_2O, the spectrum of **2** in $[D_8]$THF confirms the absence of water and traces of triflic acid; polymerization of the solvent was not observed after 10 days. IR of $Ce(OTf)_4(H_2O)_n$ (KBr): $\tilde{\nu}$ = 3443 (s), 1660 (m), 1636 (m), 1244 (s), 1187 (m), 1031 (s), 771 (w), 640 (s), 582 (m), 524 (s). The IR spectrum of **2** in nujol between KBr plates shows no bands for H_2O; the IR spectrum of **2** in KBr pellet carried out in air is identical to that of $[Ce(OTf)_4(H_2O)_n]$.

X-ray Crystallography of 3: Single crystals were obtained by slow diffusion of diethyl ether into a solution of **3** in pyridine. A yellow crystal of approximate dimensions 0.30 × 0.20 × 0.15 mm was selected. Diffraction collection was carried out on a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 1° Φ-scans and later refined on all data. The data were recorded at 173 K. A 180° Φ-range was scanned with 2° steps with a crystal-to-detector distance fixed at 35 mm. Data were corrected for Lorentz-polarization and absorption[20] effects. The structure was solved by the heavy-atom method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-H atoms. H atoms were introduced at calculated positions and constrained to ride on their parent C atom. $C_{17}H_{15}F_6N_3O_8S_2U$ (805.47), monoclinic, space group $P2_1/n$, $a = 8.5920(17)$, $b = 15.733(3)$, $c = 18.687(4)$ Å, $\beta = 94.73(3)°$, $V = 2517.5(9)$ Å^3, $Z = 4$, $D_c = 2.125$ g cm^{-1}, Mo-$K\alpha$ ($\lambda = 0.71073$ Å), $\mu_{Mo} = 6.705$ mm^{-1}, $F(000) = 1520$, total reflections = 12022, independent reflections = 3361 ($R_{int} = 0.077$), observed reflections [$I > 2\sigma(I)$] = 2864, $R_1 = 0.0334$, $wR_2 = 0.0890$. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package.[21]

X-ray Crystallography of 4: During one of the crystallizations of **3**, a few single crystals of **4** were deposited. A yellow crystal of approximate dimensions 0.35 × 0.25 × 0.20 mm was selected. Diffraction collection was carried out on a Nonius diffractometer equipped with a CCD detector. The lattice parameters were determined from ten images recorded with 1° Φ-scans and later refined on all data. The data were recorded at 173 K. A 180° Φ-range was scanned with 2° steps with a crystal to detector distance fixed at 35 mm. Data were corrected for Lorentz-polarization and absorption [20] effects. The structure was solved by the heavy-atom method and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-H atoms. H atoms were introduced at calculated positions and constrained to ride on their parent C atom. Due to imperfect absorption corrections and rather poor quality of data, the U−O−U angles of the uranyl fragments deviate from linearity. $C_{42}H_{40}F_6N_8O_{11}S_2U_2$ (1487.0), monoclinic, space group $P2_1/c$, $a = 19.352(4)$, $b = 13.248(3)$, $c = 19.631(4)$ Å, $\beta = 91.12(3)°$, $V = 5031.9(17)$ Å^3, $Z = 4$, $D_c = 1.963$ g cm^{-1}, Mo-K_α ($\lambda = 0.71073$ Å), $\mu_{Mo} = 6.597$ mm^{-1}, $F(000) = 2824$, total reflections = 12163, independent reflections = 6686 ($R_{int} = 0.073$), observed reflections [$I > 2\sigma(I)$] = 4744, $R_1 = 0.047$, $wR_2 = 0.102$. All calculations were performed on an O2 Silicon Graphics Station with the SHELXTL package.[21]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-138645 **(3)** and -138646 **(4)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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