Synthesis of the Uranium Triflates $U(OTf)_3$ and $U(OTf)_4$ – Crystal Structure of $[U(OTf)_2(OPPh_3)_4][OTf]$

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Reactions of pure triflic acid (TfOH) with UH_3 at 20 °C and with U or UCl_3 at 120 °C afforded $U(OTf)_3$ (**1**), which was transformed into $U(OTf)_4$ (**2**) by reaction with TfOH at 180 °C; **2** was also synthesized by treating UCl_4 with TfOH at 120 °C. The yields were in excess of 90%. The crystal structure of $[U(OTf)_2(OPPh_3)_4][OTf]$ (**3**) was determined, which revealed a seven-coordinate uranium(III) centre bound by monodentate and bidentate triflate ligands.

The widespread interest in metal triflates in both organic and inorganic chemistry[1] prompted us to consider the potential of such complexes of uranium. We recently reported on the first uranium(IV) triflates, $U(OTf)_4(NC_5H_5)$ (OTf = OSO_2CF_3), as well as on some organometallic derivatives. These were prepared by a novel synthetic route, namely the protonolysis of alkyl and amide precursors with pyridinium triflate.[2] Following these first results, it soon became apparent that further studies of uranium triflates would be considerably expedited if we had at our disposal sufficient quantities of the base-free complexes $U(OTf)_3$ (**1**) and $U(OTf)_4$ (**2**). Here, we present simple, large-scale syntheses of **1** and **2** from classical starting materials; Lewis base adducts of **1** and **2** have also been prepared and the crystal structure of one of the first uranium(III) triflates, $[U(OTf)_2(OPPh_3)_4][OTf]$ (**3**), has been determined.

Syntheses of the U^{III} and U^{IV} triflates are summarized in Scheme 1. **1** and **2** were prepared by treating triflic acid (TfOH) with either U, UH_3 or UCl_3 in the absence of solvent; **2** was also synthesized from UCl_4. It was essential that the acid was freshly distilled in order to achieve a clean and straightforward reaction. Treatment of UH_3 with excess TfOH at 20°C afforded **1** as an ochre powder within a few minutes, the reaction being accompanied by the vigorous evolution of dihydrogen gas. Reactions of activated uranium turnings or uranium trichloride were much slower, requiring 3 d at 120°C to reach completion. After evaporation of the excess TfOH and drying in vacuo, **1** was obtained in almost quantitative yield as a very fine green powder. Uranium(III) triflate (**1**) proved to be remarkably stable at 120°C in suspension in pure TfOH and its oxidation, signified by a colour change from ochre to pale green-blue, occurred only when the temperature was raised to 170−180°C; after 10 h, the acid was evaporated and **2** was isolated in quantitative yield. Of course, **2** could be prepared directly, without isolating **1**, by heating U, UH_3 or UCl_3 in TfOH at 180°C. To the best of our knowledge, these reactions of U or UH_3 with TfOH represent the first syntheses of metal triflates from the metal or metal hydride.[1a,3] Alternatively, compound **2** could be synthesized by reaction of TfOH with UCl_4 at 120°C; rapid HCl evolution occurred and the pale green-blue powder of **2** was recovered in 91% yield after evaporation of the excess TfOH.

Irrespective of their mode of preparation, compounds **1** and **2** were obtained in a pure state, as established from their elemental analyses. However, the samples retained a trace of triflic acid, even if they were thoroughly dried in vacuo at 150°C for several days; this was evidenced by the formation of pyridinium triflate (< 1%) upon their dissolution in pyridine. The strong Lewis acids **1** and **2** were found to be quite soluble in coordinating solvents such as pyridine and dimethoxyethane (DME), giving stable adducts. Use of tetrahydrofuran (THF) as a solvent was not practical since it was readily polymerized at ambient temperature.

Addition of stoichiometric amounts of $OPPh_3$ to solutions of **1** and **2** in DME led to the immediate formation of $U(OTf)_3(OPPh_3)_4$ (**3**) and $U(OTf)_4(OPPh_3)_2$ (**4**), which were isolated in yields of 85% as red and pale-green powders, respectively. These $OPPh_3$ adducts, as well as the pyridine adducts of **1** and **2**, were found to be soluble in THF and no polymerization of the solvent was observed.

X-ray analysis showed the crystals of **3** to be composed of discrete pairs of OTf anions and $U(OTf)_2(OPPh_3)_4$ cations; such a dissociation of OTf ligands has frequently been encountered, in particular from lanthanide triflates.[4] The structure of **3** is shown in Figure 1, together with selected bond lengths and angles. The uranium atom is surrounded by seven oxygen atoms, which form a distorted pentagonal bipyramid. The apical positions are occupied by two $OPPh_3$ ligands [O(1) and O(4)], while the equatorial positions are occupied by two $OPPh_3$ ligands [O(2) and O(3)], a bidentate triflate group [O(5) and O(6)], and a monodentate triflate group [O(8)]; the U and the five equatorial O atoms are

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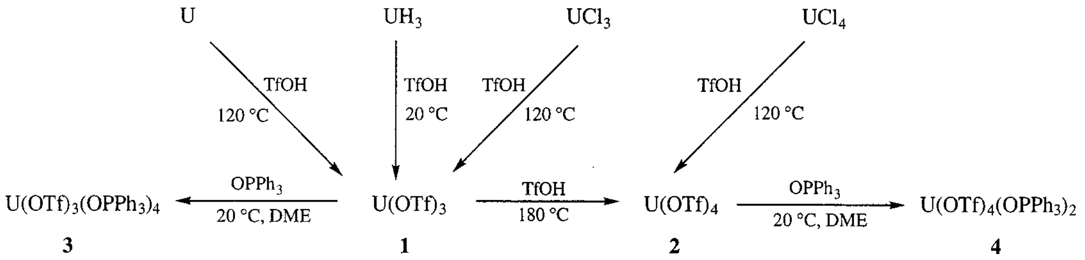

Scheme 1. Syntheses of the uranium triflates **1−4**

coplanar within ± 0.13 Å. The OPPh$_3$ ligands are arranged such that the steric interactions are minimized. The lengths of the U−O(OPPh$_3$) bonds are unexceptional, with an average value of 2.36(2) Å. The U−O(8) bond length to the monodentate OTf ligand [2.446(4) Å] may be compared with those measured in U(C$_5$Me$_5$)$_2$(OTf)$_2$(OH$_2$) [2.36(1) and 2.40(1) Å] and U(C$_5$H$_5$)$_3$(OTf)(CN*t*Bu) [2.485(9) Å].[2] This length is longer than those of typical U−O σ bonds (2.0−2.2 Å) and is even longer than the U−O(OPPh$_3$) bond lengths, confirming the weak nucleophilic character of the OTf group. More interestingly, **3** is the first structurally characterized f-block element compound containing an η^2-*O,O'*-bonded triflate ligand. Such examples of a bidentate triflate ligand have previously been encountered in d-transition metal complexes, but remain very rare.[5] The U−O(5) and U−O(6) lengths are 0.2 Å longer than the U−O(8) length; such a difference between the metal−oxygen bond lengths of mono- and bidentate OTf ligands has previously been observed, most notably in the titanium compound Ti(NCN)(O*i*Pr)(OTf)$_2$ [NCN = C$_6$H$_3$-(CH$_2$NMe$_2$)$_2$-2,6].[5a]

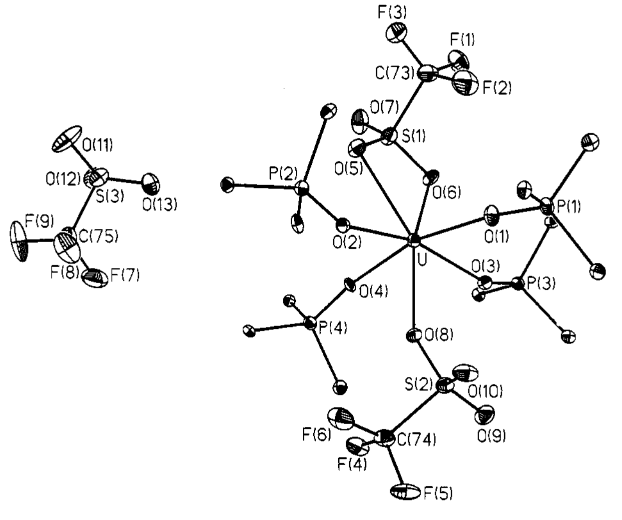

Figure 1. X-ray crystal structure of [U(OTf)$_2$(OPPh$_3$)$_4$][OTf] (**3**) with thermal ellipsoids drawn at the 30% probability level; for the sake of clarity, only the *ipso* carbon atoms (not labelled) of the phenyl rings are represented; selected bond lengths [Å] and angles [°]: U−O(1) 2.370(4), U−O(2) 2.352(4), U−O(3) 2.389(4), U−O(4) 2.348(4), U−O(5) 2.645(5), U−O(6) 2.614(4), U−O(8) 2.446(4); O(1)−U−O(4) 166.2(2), O(3)−U−O(6) 72.45(13), O(5)−U−O(6) 53.80(14), O(2)−U−O(5) 72.88(13), O(2)−U−O(8) 77.95(14), O(3)−U−O(8) 83.12(14)

In conclusion, the new uranium triflates **1** and **2** have been synthesized by treating triflic acid with the corresponding chlorides in a classical manner, or by two novel routes from uranium metal or its hydride. The reactions were easy to perform and, by adjusting the temperature, **1** and **2** were obtained selectively in good yields. The crystal structure of **3** revealed three distinct triflate groups, one being dissociated and the other two coordinating in monodentate and bidentate ligation modes

Experimental Section

All preparations were carried out under argon (less than 2 ppm oxygen and water). Activated uranium turnings were prepared according to ref.[6] except that HgI$_2$ was replaced by iodine. UH$_3$,[7] UCl$_3$,[8] and UCl$_4$[9] were prepared by published methods. Triflic acid (99%; Aldrich) was freshly distilled prior to use.

Uranium(III) Triflate (1). − From UH$_3$: Triflic acid (1 mL) was added to UH$_3$ (250 mg, 1.04 mmol) in a 50-mL round-bottomed flask. The black powder of the hydride was rapidly transformed into an ochre powder, which was accompanied by the vigorous evolution of H$_2$ gas (***CAUTION!***). In order to ensure that the reaction had reached completion, the mixture was further heated at 100 °C for 15 h. The excess TfOH was then distilled off and **1** was obtained as a green powder after drying in vacuo at 120 °C for 24 h (687 mg, 96%). − C$_3$F$_9$O$_9$S$_3$U (685): calcd. F 24.95, S 14.04; found F 24.73, S 13.85. − **From U or UCl$_3$:** A 200-mL flask was charged with activated uranium turnings (1050 mg, 4.41 mmol) and triflic acid (3 mL) and the mixture was heated for 3 d at 120 °C. The excess TfOH was then distilled off and **1** was dried in vacuum at 120 °C for 30 h (2840 mg, 94%). − C$_3$F$_9$O$_9$S$_3$U (685): calcd. F 24.95, S 14.04; found F 24.80, S 14.32. − According to the same procedure, **1** was obtained in 96% yield from UCl$_3$ (250 mg, 0.72 mmol) and TfOH (3 mL). − C$_3$F$_9$O$_9$S$_3$U (685): calcd. F 24.95, S 14.04; found F 24.68, S 13.80.

Uranium(IV) Triflate (2). − From UCl$_4$: A 100-mL flask was charged with UCl$_4$ (4.0 g, 10.5 mmol) and TfOH (8.5 mL) and the mixture was heated at 120 °C. The colour of the powder rapidly turned from green to pale green-blue, which was accompanied by the evolution of HCl vapour. The HCl was pumped off to avoid a build-up of pressure (***CAUTION!***). After 10 h, the excess TfOH was distilled off and the green-blue powder **2** was dried in vacuo at 150 °C for 60 h (8.0 g, 91%). − C$_4$F$_{12}$O$_{12}$S$_4$U (834): calcd. F 27.32, S 15.37; found F 27.10, S 15.25, Cl < 0.1%. − **From U, UH$_3$ or UCl$_3$:** The procedure was identical to that used for the preparation of **1** except that the reaction mixture was heated at 180 °C for 15 h (UH$_3$) or 3 d (U or UCl$_3$). The yields were almost quantitative and the samples were found to be analytically pure.

Tetrakis(triphenylphosphane oxide)uranium(III) Triflate (3): A mixture of **1** (250 mg, 0.36 mmol) and OPPh$_3$ (406 mg, 1.46 mmol) was dissolved in DME (30 mL). After 30 min, the red solution was concentrated to a volume of 5 mL and diethyl ether (30 mL) was added, whereupon **3** precipitated as a red powder. The product was collected by filtration, washed with toluene, and dried in vacuo (556 mg, 85%). − $C_{75}H_{60}F_9O_{13}P_4S_3U$ (1798): calcd. C 50.09, H 3.36, S 5.35; found C 49.92, H 3.20, S 5.51.

Bis(triphenylphosphane oxide)uranium(IV) Triflate (4): A mixture of **2** (250 mg, 0.30 mmol) and $OPPh_3$ (167 mg, 0.60 mmol) was dissolved in DME (30 mL). After 30 min, the pale-green solution was concentrated to a volume of 5 mL and diethyl ether (40 mL) was added. The green oily material was transformed into a fine powder after stirring for 12 h; the green product **4** was then filtered off, washed with diethyl ether and toluene, and dried in vacuo for 12 h at 20°C (350 mg, 84%). − $C_{40}H_{30}F_{12}O_{14}P_2S_4U$ (1390): calcd. C 34.54, H 2.17, S 9.22; found C 34.71, H 2.30, S 9.08.

X-ray Crystallography of 3: Single crystals were obtained from a mixture of the DME adduct of **1** and excess $OPPh_3$ in THF/diethyl ether. A red crystal of approximate dimensions $0.18 \times 0.12 \times 0.12$ mm was selected. Diffraction data were collected with 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 123 K. A 180° Φ range was scanned in 2° increments with the crystal-to-detector distance fixed at 26 mm. Data were corrected for Lorentz polarization and absorption[10] 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. $C_{75}H_{60}F_9O_{13}P_4S_3U$ (1798.32), triclinic, space group $P{-}1$, $a = 13.694(1)$, $b = 14.734(1)$, $c = 19.420(1)$ Å, $\alpha = 92.143(4)$, $\beta = 108.393(4)$, $\gamma = 91.460(4)$°, $V = 3713(3)$ Å^3, $Z = 2$, $D_c = 1.609$ g cm^{-1}, Mo-K_α ($\lambda = 0.71073$ Å), $\mu_{Mo} = 2.441$ mm^{-1}, $F(000) = 1790$, total reflections = 19977, independent reflections = 10109 ($R_{int} = 0.076$), observed reflections [$I > 2\sigma(I)$] = 7023, $R_1 = 0.044$, $wR_2 = 0.077$. All calculations were performed with an O2 Silicon Graphics Station using the SHELXTL package.[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-115885. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] G. A. Lawrance, *Chem. Rev.* **1986**, 86, 17. − [1b] S. Kobayashi, *Synlett* **1994**, 689.
[2] J. C. Berthet, M. Lance, M. Nierlich, M. Ephritikhine, *J. Chem. Soc., Chem. Commun.* **1998**, 1373.
[3] M. Labrouillère, C. Le Roux, H. Gaspard, A. Laporterie, J. Dubac, J. R. Desmurs, *Tetrahedron Lett.* **1999**, *40*, 285.
[4] [4a] H. C. Aspinall, J. L. M. Dwyer, N. Greeves, E. G. McIver, J. C. Woolley, *Organometallics* **1998**, *17*, 1884. − [4b] P. H. Smith, K. N. Raymond, *Inorg. Chem.* **1985**, *24*, 3469.
[5] [5a] J. G. Donkervoort, J. T. B. Jastrzebski, B. J. Deelman, H. Kooijman, N. Veldman, A. L. Spek, G. van Koten, *Organometallics* **1997**, *16*, 4174. − [5b] L. Giannini, A. Caselli, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, N. Re, A. Sgamellotti, *J. Am. Chem. Soc.* **1997**, *119*, 9198.
[6] L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin, B. D. Zwick, *Inorg. Chem.* **1994**, *33*, 2248.
[7] R. E. Rundle, *J. Am. Chem. Soc.* **1951**, *73*, 4172.
[8] J. J. Katz, I. Sheft, *Adv. Inorg. Chem. Radiochem.* **1960**, *2*, 195.
[9] J. A. Hermann, J. F. Suttle, *Inorg. Synth.* **1957**, *5*, 143.
[10] A. L. Spek, *MULABS PLATON*, University of Utrecht, The Netherlands, **1997**.
[11] G. M. Sheldrick, *SHELXTL-93: Program for the Refinement of Crystal Structures*, University of Gottingen, Germany, **1993**.

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