

First uranium(IV) triflates

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The uranium(IV) triflates $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2]$, $[\text{U}(\text{Cp})_2(\text{OTf})_2(\text{py})]$, $[\text{U}(\text{Cp})_3(\text{OTf})]$, $[\text{U}(\text{cot})(\text{OTf})_2(\text{py})]$ and $[\text{U}(\text{OTf})_4(\text{py})]$ have been synthesized by protonation of amide or alkyl precursors with pyridinium triflate; the crystal structures of $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2(\text{OH}_2)]$ and $[\text{U}(\text{Cp})_3(\text{OTf})(\text{CNBu}^t)]$ have been determined.

Transition metal triflates (trifluoromethanesulfonates) are much considered as Lewis acid catalysts in a variety of organic reactions, as well as precursors in inorganic and organometallic synthesis.¹ While the utility of lanthanide triflates has been clearly recognized in recent years,² scant attention has been paid to the actinide counterparts; a few thorium(IV) triflates have been reported^{3,4} and the only uranium triflates are uranyl derivatives.⁵ Here, we present the first uranium(IV) triflates, $[\text{U}(\text{OTf})_4(\text{py})]$, and a series of cyclopentadienyl and cyclooctatetraene derivatives; these were conveniently synthesized by using the pyridinium triflate as a novel reagent for the protonolysis of U–C and U–N bonds. We also describe the crystal structures of $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2(\text{OH}_2)]$ and $[\text{U}(\text{Cp})_3(\text{OTf})(\text{CNBu}^t)]$.

We first tried to prepare the cyclopentadienyl complexes $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2]$ **1** and $[\text{U}(\text{Cp})_3(\text{OTf})]$ **2** since $[\text{U}(\text{Cp}^*)_2\text{X}_2]$ and $[\text{U}(\text{Cp})_3\text{X}]$ compounds are regarded, for most X groups, as models in organouranium chemistry. In an NMR test experiment, $[\text{U}(\text{Cp}^*)_2\text{Me}_2]$ was treated at 20 °C in toluene with 2 equiv. of HOTf; immediate evolution of gas was observed and the spectrum showed a new single signal at δ 20.1, corresponding to the Cp* groups. The solution was evaporated and crystallization of the red–brown powder from thf–pentane gave a few crystals of $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2(\text{OH}_2)]$; these were characterized by X-ray crystallography (*vide infra*). Difficulties were encountered when the above reaction was performed in a preparative scale; products resulting from protonation of Cp* ligands were also formed in variable yields. Other attempts to prepare **1** by treating the complexes $[\text{U}(\text{Cp}^*)_2\text{X}_2]$ (X = Me, NMe₂, Cl) with AgOTf in thf or benzene were unsuccessful; complicated mixtures were obtained and thf was quickly polymerized. We found that the best way to obtain complex **1** was the reaction of $[\text{U}(\text{Cp}^*)_2\text{Me}_2]$ with PyHOTf, which could be easily reproduced, and gave **1** in satisfactory yield. A solution of the pyridinium salt (219 mg) in thf (25 cm³) was slowly added to the bis(alkyl) complex (215 mg) in thf (20 cm³) at –70 °C; the mixture was stirred for 1 h at 20 °C and after evaporation to dryness, the red–brown powder was extracted in toluene and washed with pentane (78% yield). Similar treatment of $[\text{U}(\text{Cp}^*)_2(\text{NMe}_2)_2]$ also gave **1** in good yield. By following the same procedure, the organouranium compounds $[\text{U}(\text{Cp})_3\text{X}]$ (X = NEt₂, Buⁿ), $[\text{U}(\text{Cp})_2(\text{NEt}_2)_2]$ and $[\text{U}(\text{cot})\{\text{N}(\text{SiMe}_3)_2\}_2]$ were transformed into $[\text{U}(\text{Cp})_3(\text{OTf})]$ **2** (brown, 93%), $[\text{U}(\text{Cp})_2(\text{OTf})_2(\text{py})]$ **3** (orange, 60%) and $[\text{U}(\text{cot})(\text{OTf})_2(\text{py})]$ **4** (brown, 92%), respectively. It is noteworthy that **3** was stable towards ligand exchange reactions, whereas $[\text{U}(\text{Cp})_2\text{Cl}_2]$ and its Lewis base adducts could not be isolated.⁶ In the presence of an excess of Bu^tNC in thf–pentane, **2** was converted into $[\text{U}(\text{Cp})_3(\text{OTf})(\text{CNBu}^t)]$, the crystal structure of which was

determined (*vide infra*); interestingly, the triflate group of **2** was not displaced by the isocyanide molecule.

The pyridinium triflate proved thus to be very efficient in the protonolysis reactions of U–C and U–N bonds. In contrast to triflic acid, this commercial powder is not hygroscopic, does not polymerize thf, can be stored for a long time and is easy to handle. This reagent was also useful to prepare a pyridine adduct of the homoleptic uranium(IV) triflate $[\text{U}(\text{OTf})_4]$ while more classical routes, by reacting UCl₄ with HOTf or AgOTf, were not straightforward. The complex $[\text{U}(\text{OTf})_4(\text{py})]$ **5** was synthesized in 76% yield by treating the metallacycle $[\text{U}\{\text{N}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)\}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (250 mg) with PyHOTf (319 mg) in pyridine (20 cm³). The solution was heated at 110 °C for 20 h and after partial evaporation and addition of diethyl ether, deposited a green microcrystalline powder. Complex **5** would be a useful precursor for the synthesis of organometallic derivatives. For example, its reactions with K₂cot or $[\text{U}(\text{cot})_2]$ in thf afforded **4** in almost quantitative yield (NMR experiments), providing a new access to monocyclooctatetraene uranium compounds; it is noteworthy that the chloride analogue $[\text{U}(\text{cot})\text{Cl}_2(\text{thf})_2]$ could not be obtained by similar treatment of UCl₄.⁷

Complexes **1**–**5** were characterized by elemental analyses (C, H, N or S) and ¹H NMR spectroscopy.† Besides a dimeric triflate bridged thorium compound,³ $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2(\text{OH}_2)]$ and $[\text{U}(\text{Cp})_3(\text{OTf})(\text{CNBu}^t)]$ are the only actinide(IV) triflates to have been crystallographically characterized; the bis(triflate) derivative is also, from the data of the CCDC, the first structurally characterized organouranium compound with a coordinated H₂O molecule. The structures are shown in Fig. 1 and 2 together with selected data.§ The monomeric complexes adopt, respectively, a bent-sandwich configuration with an unsymmetrical arrangement of OTf and H₂O ligands in the

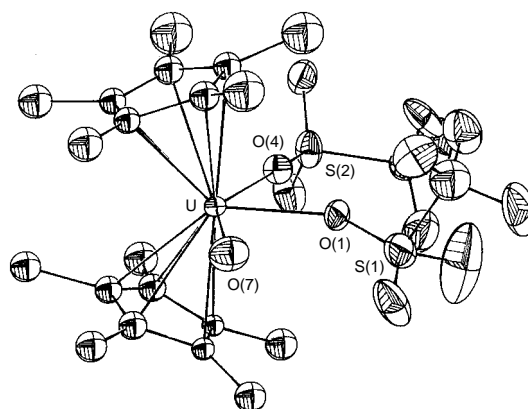


Fig. 1 X-Ray crystal structure of $[\text{U}(\text{Cp}^*)_2(\text{OTf})_2(\text{OH}_2)]$. Displacement ellipsoids are shown at the 33% probability level. Selected bond distances (Å) and angles (°): U–O(1) 2.36(1), U–O(4) 2.40(1), U–O(7) 2.57(2), O(1)–S(1) 1.48(1), O(4)–S(2) 1.45(1); O(1)–U–O(4) 74.8(6), O(1)–U–O(7) 70.2(6), O(4)–U–O(7) 145.0(6), U–O(1)–S(1) 154.3(9), U–O(4)–S(2) 173.7(9).

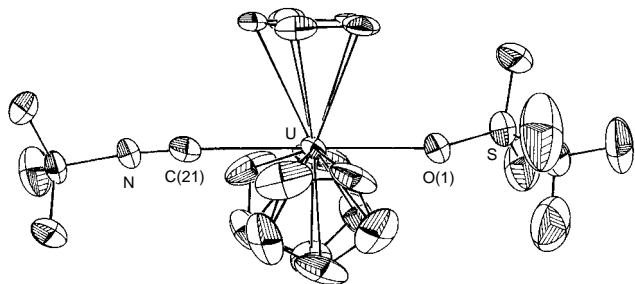


Fig. 2 X-Ray crystal structure of $[U(Cp)_3(OTf)(CNBu^4)]$. Displacement ellipsoids are shown at the 40% probability level. Selected bond distances (Å) and angles ($^\circ$): U–O(1) 2.485(9), U–C(21) 2.59(2), O(1)–S 1.456(9), C(21)–N 1.13(2); O(1)–U–C(21) 179.3(4), U–O(1)–S 157.7(6), U–C(21)–N 175(1).

equatorial girdle,⁸ and a nearly ideal trigonal bipyramidal structure with the Cp groups occupying the equatorial vertices.⁹ Coordination of H_2O and Bu^4NC to the U^{IV} centre is unexceptional, with U–O(7) and U–C(21) bond distances of 2.57(2) and 2.59(2) Å. In both compounds, the triflate ligands are monodentate and, as expected for this weakly nucleophilic group, the U–O bond lengths which average 2.42(6) Å are longer than usual U–O σ bond distances (2.0–2.2 Å). In the bis(triflate) compound, the U–O–S angles are inequivalent and rather obtuse, with U–O(1)–S(1) and U–O(4)–S(2) equal to 154.3(9) and 173.7(9) $^\circ$, respectively; similar structural features were previously noted in the yttrium complex $[Y\{C_6H_{12}N_3(CH_2CONH_2)_3\}(OTf)_2(H_2O)](OTf)$.¹⁰

In conclusion, the first uranium(IV) triflates were prepared by protonolysis of alkyl and amide precursors with pyridinium triflate; this convenient and efficient reaction should be of general interest for the synthesis of metal triflates. By comparison with their chloride analogues, uranium triflates should exhibit distinct structure and reactivity patterns, and open new perspectives in actinide chemistry.

Notes and References

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‡ *Characterising data*: 1H NMR (200 MHz, 30 $^\circ C$, $[^2H_8]thf$). **1**, δ 20.1 (s, Cp*); **2**, δ –2.45 (s, Cp); **3**, δ 11.2 (10 H, Cp), 8.85, 8.8 and 6.9 (5 H, py); **4**, δ 7.6, 7.4 and 6.9 (5 H, py), –37.5 (8 H, s, cot); **5**, δ 8.8, 7.85 and 7.3 (py). Elemental analyses (%) (calculated values in parentheses). **1**: C, 32.8 (32.75); H, 3.75 (3.75); S, 7.85 (7.95). **2**: C, 32.85 (33.0); H, 2.7 (2.6). **3**: C, 26.65 (27.4); H, 2.0 (2.0); N, 2.05 (1.9). **4**: C, 25.0 (25.0); H, 1.9 (1.8); N, 2.1 (1.95). **5**: C, 12.05 (11.85), H, 0.7 (0.55); N, 1.6 (1.55).

§ *Crystal data* for $[U(Cp^*)_2(OTf)_2(OH_2)]$: $C_{22}H_{32}F_6O_7S_2U$, $M = 824.64$, crystal dimensions: $0.5 \times 0.25 \times 0.15$ mm, monoclinic, space group Cc , $a = 18.464(3)$, $b = 10.847(3)$, $c = 17.323(4)$ Å, $\beta = 126.57(2)^\circ$, $U = 2787(3)$ Å³, $Z = 4$, $D_c = 1.965$ g cm^{–3}, $2 < 2\theta < 44^\circ$, ω – 2θ scan mode,

$\mu = 57.44$ cm^{–1}, $F(000) = 1592$, $T = -30$ $^\circ C$. 1988 reflections collected, 1787 unique, 1680 reflections with $I > 3\sigma(I)$. Data were corrected for absorption ($T_{min} = 0.571$, $T_{max} = 0.999$),¹¹ Lorentz polarization effects and decay (10% in 30 h, linearly corrected). The structure was solved by the heavy-atom method and refined by full-matrix least squares (F) with anisotropic thermal parameters for all non-C atoms. H atoms were not introduced. The final R values were $R = 0.030$ and $R_w = 0.047$ ($w = 1/(\sigma F)^2 = 4F^2/[\sigma F^2 + (pF^2)^2]^{1/2}$, $p = 0.04$). The absolute structure was determined ($R = 0.038$ and $R_w = 0.053$). For $[U(Cp)_3(OTf)(CNBu^4)]$, $C_{21}H_{24}NF_3O_3SU$, $M = 665.52$, crystal dimensions: $0.4 \times 0.35 \times 0.15$ mm, monoclinic, space group $P2_1/n$, $a = 8.533(1)$, $b = 19.545(4)$, $c = 13.890(3)$ Å, $\beta = 90.65(2)^\circ$, $U = 2316(1)$ Å³, $Z = 4$, $D_c = 1.908$ g cm^{–3}, $2 < 2\theta < 44^\circ$, ω – 2θ scan mode, $\mu = 67.75$ cm^{–1}, $F(000) = 1264$, $T = 22$ $^\circ C$. 3195 reflections collected, 2961 unique, 2018 reflections with $I > 3\sigma(I)$. Data were corrected for absorption ($T_{min} = 0.452$, $T_{max} = 0.999$),¹¹ Lorentz polarization effects and decay (19% in 39 h, linearly corrected). The structure was solved by the heavy-atom method and refined by full-matrix least squares (F) with anisotropic thermal parameters. H atoms were not introduced. The final R values were $R = 0.031$ and $R_w = 0.042$ ($w = 1/(\sigma F)^2 = 4F^2/[\sigma F^2 + (pF^2)^2]^{1/2}$, $p = 0.04$). For both compounds, diffraction data were recorded on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å). All calculations were performed on a VAX 4000-200 computer with the Enraf-Nonius MolEN package.¹² CCDC 182/879.

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