which can be obtained in a transient fashion by electrochemical or photochemical reduction of hexavalent $[UO_2]^{2+}$ parent compounds. A number of ligands were found to provide a limited stabilization of the one-electron-reduced species, and have enabled a series of voltammetric and spectroscopic experiments in solution.[6] Recently, extended X-ray absorption fine structure (EXAFS) studies were carried out on the tricarbonatodioxouranates $[UO_2(CO_3)_3]^{n-}$ ($n = 4$, 5) in water, which showed that a minor geometrical rearrangement occured in the $[UO_2(CO_3)_3]^{4-} \rightarrow [UO_2(CO_3)_3]^{5-}$ reduction.[7] In addition to these results, structural data on $[UO_2(CO_3)_3]^{n-}$ ($n = 4$, 5),[8] $[UO_2(H_2O)_5]^{n+}$ ($n = 1$, 2)[9] and bare $[UO_2]^{n+}$ ions ($n = 1$, 2)[8] were predicted from theoretical calculations using a variety of methods. In this context, the isolation of a pentavalent uranyl derivative, and the comparison of its crystal structure with that of its $[UO_2]^{2+}$ parent compound are highly desirable.

In the course of our studies on the synthesis and structure of anhydrous uranyl triflate compounds,[10] we serendipitously obtained crystals of $[UO_2(OPPh_3)_4](OTf)$; here we present the crystal structure of this pentavalent uranyl compound, and compare it with that of the uranium(VI) analogue $[UO_2(OPPh_3)_4](OTf)_2$.

$[UO_2(OPPh_3)_4](OTf)_2$ (**1**) was readily obtained as a pale-yellow powder in almost quantitative yield upon addition of four equivalents of $OPPh_3$ to a solution of $UO_2(OTf)_2$ in acetonitrile. Large crystals of **1** were isolated after crystallization from a mixture of acetonitrile and diethyl ether. The X-ray crystal structure of **1** consists of discrete $[UO_2(OPPh_3)_4]^{2+}$ and $[OTf]^-$ ions in a 1:2 ratio;[11] a view of the cation is shown in Figure 1. The geometrical parameters are classical of hexavalent uranyl complexes; the linear $\{UO_2\}$ fragment is perpendicular to the equatorial plane defined by the uranium center and the four oxygen atoms of the $OPPh_3$ ligands. The mean U=O bond length of 1.76(1) Å and the average equatorial U−O bond length of 2.29(1) Å are identical to those found in $[UO_2\{OP(NMe_2)_3\}_4](I_3)_2$.[12]

In one attempt to crystallize complex **1**, small red-orange, cube-shaped crystals were deposited in a small quantity along with the yellow crystals of the $[UO_2]^{2+}$ compound. X-ray diffraction analysis revealed that these crystals were of a new complex, the pentavalent uranyl derivative $[UO_2(OPPh_3)_4](OTf)$ (**2**).[11] The unexpected formation of **2** requires elucidation; all attempts to produce it by reduction of **1** with UV light or various reducing agents are inconclusive at this time, and further work is in progress for controlling the synthesis of **2**. Nevertheless, complex **2** was found to be kinetically stable under an inert atmosphere, which demonstrates that such $[UO_2]^+$ complexes can be isolated in the crystalline form, without suffering disproportionation.

Crystals of **2** are composed of discrete cation–anion pairs; a view of one of the two independent $[UO_2(OPPh_3)_4]^+$ ions is represented in Figure 2. The cations of **1** and **2** adopt the same perfectly square bipyramidal configuration; in **2**, the uranium center is located at a center of symmetry. The U=O bond lengths of 1.817(6) and 1.821(6) Å are slightly longer than the Np=O bond (1.797(2) Å) in the isostructural $[NpO_2(OPPh_3)_4]^+$ ion,[2] in agreement with the variation in

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Isolation of a Uranyl [UO₂]⁺ Species: Crystallographic Comparison of the Dioxouranium(V) and (VI) Compounds [UO₂(OPPh₃)₄](OTf)ₙ (n = 1, 2)

Jean-Claude Berthet,* Martine Nierlich, and Michel Ephritikhine

The occurrence of the actinyl(V) species $[AnO_2]^+$ (An = U, Np, Pu, Am) in the nuclear industry and in the natural environment is a particular reason for the current studies of their physicochemical properties.[1] While various $[NpO_2]^+$ compounds have been isolated and crystallographically characterized,[2–5] there is scant structural information available for the other $[AnO_2]^+$ species, and in particular for $[UO_2]^+$, which is reputed to be unstable towards rapid disproportionation. Much effort has been devoted to the formation, detection, and characterization of these species,

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[*] Dr. J.-C. Berthet, Dr. M. Nierlich, Dr. M. Ephritikhine
Service de Chimie Moléculaire
Bat. 125, DSM, DRECAM, CNRS URA 331, CEA Saclay
91191 Gif-sur-Yvette (France)
Fax: (+33) 169-06-66-40
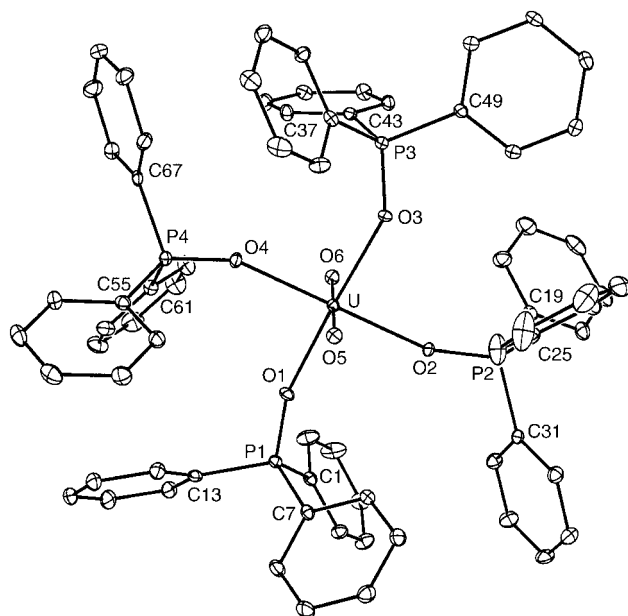E-mail: berthet@drecam.cea.fr

Figure 1. View of the [UO₂(OPPh₃)₄]²⁺ ion in **1**, with displacement ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: U-O1 2.2835(17), U-O2 2.2979(17), U-O3 2.3057(16), U-O4 2.3012(17), U-O5 1.7632(16), U-O6 1.7603(15), O1-P1 1.5250(18), O2-P2 1.5169(16), O3-P3 1.5214(18), O4-P4 1.5185(16); O1-U-O2 89.96(6), O2-U-O3 87.84(6), O3-U-O4 91.99(6), O1-U-O4 90.22(6), O5-U-O6 179.75(8), U-O1-P1 160.05(11), U-O2-P2 157.29(9), U-O3-P3 145.54(10), U-O4-P4 151.60(9).

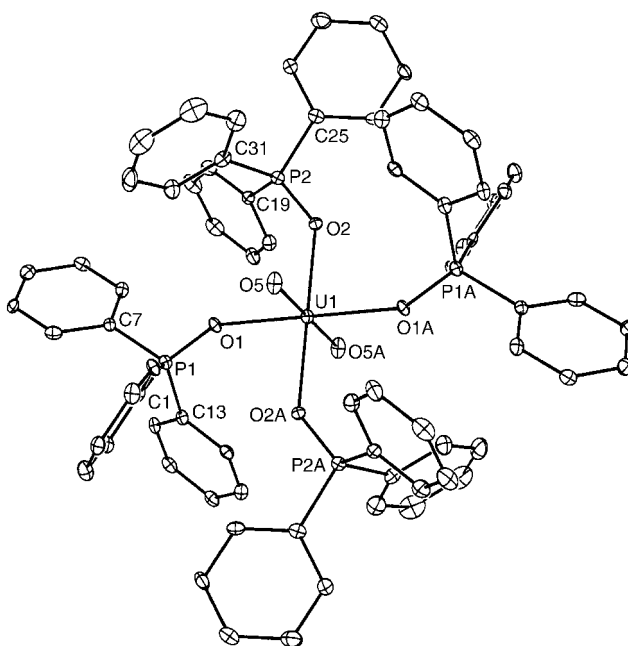**Figure 2.** View of one of the two independent [UO₂(OPPh₃)₄]⁺ ions in **2**, with displacement ellipsoids set at 30% probability. Atoms labeled A are related to those not labeled by a center of symmetry (symmetry code: −x, −y, 1−z). Selected bond lengths [Å] and angles [°] (the corresponding values in the second independent cation are given in brackets): U1-O1 2.427(5) [2.455(6)], U1-O2 2.439(5) [2.431(5)], U1-O5 1.821(6) [1.817(6)], O1-P1 1.502(6) [1.500(6)], O2-P2 1.504(6) [1.496(5)]; O1-U1-O2 88.93(18) [88.57(18)], O1-U1-O5 90.3(2) [89.9(2)], U1-O1-P1 144.5(3) [144.2(3)], U1-O2-P2 137.8(3) [139.8(3)].

the radii of the [UO₂]⁺ and [NpO₂]⁺ ions.[13] The U=O bond lengths in **2** are also very close to those of the Np=O bonds determined by X-ray crystallography in the pentavalent neptunyl cations [NpO₂([18]crown-6)]⁺ (1.800(5) Å)[3] and [NpO₂(bipy)(H₂O)₃]⁺ (bipy = 2,2′-bipyridyl; mean bond length 1.81(5) Å),[5] but are 0.08 Å shorter than those determined by EXAFS in the uranium(v) anion [UO₂(CO₃)₃]⁵⁻ (1.90(2) Å).[7] Similarly, the Np=O bonds in the aforementioned neptunyl cations are approximately 0.05 Å shorter than those found in the anionic complexes [NpO₂(CO₃)₃]⁵⁻ (1.86(2) Å)[14] and [BaNpO₂(OAc)₃] (1.85(2) Å),[4] as determined by X-ray absorption and X-ray diffraction methods, respectively. These results are in accordance with theoretical calculations, which predicted that the variation in An=O bond lengths, by passing from the bare [AnO₂]⁺ cation to the [AnO₂(CO₃)₃]⁵⁻ anion, should be greater for An = U (0.17 Å) than for An = Np (0.11 Å).[8, 15] Since the nature of the equatorial ligands and the electronic charge of the complex would induce significant variations in the An=O bond lengths, the influence of the oxidation state on the geometrical parameters of [AnO₂]²⁺ and [AnO₂]⁺ compounds (An = U or Np) can only be evaluated correctly by comparing the structures of analogous complexes, as is the case for **1** and **2**.

The reduction of **1** to **2** leads to a lengthening of the U=O bond by 0.06 Å. This value can be compared with the variation of 0.03 Å in the ionic radii of the [UO₂]²⁺ and [UO₂]⁺ ions,[13] and with the difference of 0.1 Å between the U=O bond lengths in [UO₂(CO₃)₃]⁴⁻ and [UO₂(CO₃)₃]⁵⁻, as measured by EXAFS.[7] The theoretical study of the structure of these tricarbonatodioxouranates using multiconfigurational second-order perturbation theory (CASSCF/CASPT2) predicted bond lengths of 1.845 and 1.929 Å for the U^{VI}=O and U^V=O bonds, respectively, and values of 1.707 and 1.758 Å for the same bonds in the bare [UO₂]²⁺ and [UO₂]⁺ ions;[7] these differences of 0.08 and 0.05 Å are in agreement with the values determined from the structures of **1** and **2**. Most notably, the U=O bond lengths in **1** and **2** correspond quite perfectly to those calculated in [UO₂(H₂O)₅]²⁺ (1.756 Å) and [UO₂(H₂O)₅]⁺ (1.810 Å) using density functional theory and relativistic effective core potentials.[9] In the pairs of neptunyl and plutonyl derivatives [NpO₂(CO₃)₃]ⁿ⁻ (n = 4, 5)[15] and [AnO₂(H₂O)₅]ⁿ⁺ (An = Np, Pu; n = 1, 2),[9] spectroscopic studies and theoretical calculations showed commensurate differences (0.06–0.08 Å) between the An^{VI}=O and An^V=O bond lengths.[16]

The U−O(OPPh₃) bond lengths in the two independent cations of **2** range from 2.427(5) to 2.455(6) Å (average 2.44(2) Å), the average value being in good agreement with that of 2.438(4) Å found for the Np−O bonds in [NpO₂(OPPh₃)₄]⁺.[2] The mean U−O(OPPh₃) bond length in **2** is 0.14 Å longer than that determined in **1** and this difference, which is much greater than the difference in ionic radii between [UO₂]²⁺ and [UO₂]⁺,[13] results from the lower positive charge of the uranium(v) center of **2**, which induces a weaker interaction with the Lewis base. A similar situation was encountered with the organouranium compounds [U(η-C₈H₈){OP(NMe₂)₃}₃](BPh₄)ₙ (n = 1 or 2), where the difference between the mean U−O bond lengths is 0.2 Å,

while the difference between the U^{4+} and U^{3+} ionic radii is only 0.1 Å.[17] The U–O(OPPh$_3$) bonds in **2** are, to the best of our knowledge, the longest so far measured, longer than, for example, those found in [UO$_2$(OtBu)$_2$(OPPh$_3$)$_2$] (2.40(1) Å);[18] the average O–P bond length and U-O-P angle are respectively 0.02 Å longer and 12° smaller than those in **1**. The 0.14 Å difference between the mean equatorial U^{VI}–O and U^{V}–O bond lengths of **1** and **2** is greater than that of 0.07 and 0.1 Å determined by EXAFS for the pairs of complexes [UO$_2$(CO$_3$)$_3$]$^{n-}$ ($n = 4$, 5)[7] and [NpO$_2$(H$_2$O)$_5$]$^{n+}$ ($n = 1$, 2),[9] respectively. However, comparison of the crystal structures of **1** and **2** confirms that in cationic actinyl complexes, elongation of the equatorial An–O bonds is more important than that of the axial An=O bonds, while the reverse situation is the case for the anionic derivatives.

Experimental Section

1: A mixture of [UO$_2$(OTf)$_2$] (1.00 g, 1.76 mmol) and OPPh$_3$ (1.96 g, 7.04 mmol) in anhydrous acetonitrile (50 mL) was stirred for 10 min at 20 °C under an argon atmosphere. After filtration, the yellow solution was evaporated to dryness, which yielded a yellow powder (**1**) which was washed with toluene (2 × 25 mL) and dried under vacuum (2.8 g, 95 %).

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[11] Crystallographic data for **1**: C$_{74}$H$_{60}$F$_6$O$_{12}$P$_4$S$_2$U, $M_r = 1681.25$, triclinic, space group $P\bar{1}$, $a = 14.088(3)$, $b = 15.314(3)$, $c = 18.767(4)$ Å, $\alpha = 69.33(3)$, $\beta = 70.52(3)$, $\gamma = 78.55(3)$°, $V = 3556.5(12)$ Å^3, $\rho_{calcd} = 1.570$ g cm^{-3}, $Z = 2$, $T = 123$ K, μ(Mo$_{K\alpha}$) = 2.508 mm^{-1}, 24692 measured reflections, 12444 independent, $10857 > 2\sigma(I)$, 946 parameters, $R1 = 0.0336$, $wR2 = 0.0708$, GOF = 0.999. Crystallographic data for **2**: C$_{73}$H$_{60}$F$_3$O$_9$P$_4$SU,

$M_r = 1532.18$, triclinic, space group $P\bar{1}$, $a = 9.0570(18)$, $b = 13.888(3)$, $c = 27.487(6)$ Å, $\alpha = 96.55(3)$, $\beta = 93.05(3)$, $\gamma = 108.66(3)$°, $V = 3239.4(11)$ Å^3, $\rho_{calcd} = 1.571$ g cm^{-3}, $Z = 2$, $T = 123$ K, μ(Mo$_{K\alpha}$) = 2.704 mm^{-1}, 20161 measured reflections, 10150 independent, $7192 > 2\sigma(I)$, 823 parameters, $R1 = 0.0542$, $wR2 = 0.1070$, GOF = 1.102. The data were collected on a Nonius Kappa CCD diffractometer with Mo$_{K\alpha}$ radiation. The structures were solved by direct methods and refined against F^2 for all observed reflections with anisotropic thermal parameters for all non-hydrogen atoms. H atoms were introduced at calculated positions and constrained to ride on their parent carbon atom. Software used: SHELXTL (version 5.1), SHELXS 97, SHELXL 97 (G. M. Sheldrick, University of Göttingen). CCDC-196561 (**1**) and CCDC-196562 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[16] The difference between the An^{VI}=O and An^V=O bond lengths should not be equal to 0.14 Å, a value which has been considered after comparison of the crystal structures of some analogous [NpO$_2$]$^{2+}$ and [NpO$_2$]$^+$ derivatives, for example [MNpO$_2$(OAc)$_3$] (M = Ba or Na).[4] It seems that the Np^{VI}=O bond length of 1.71 Å in these complexes, which has been calculated from the crystal structure of the isostructural uranyl compound, is too short; a better value for this bond length is 1.75 Å (0.01 Å shorter than the typical U^{VI}=O bond).

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