

Unprecedented reduction of the uranyl ion $[\text{UO}_2]^{2+}$ into a polyoxo uranium(IV) cluster: Synthesis and crystal structure of the first f-element oxide with a $\text{M}_6(\mu_3\text{-O})_8$ core

Jean-Claude Berthet,* Pierre Thuéry and Michel Ephritikhine

Received (in Cambridge, UK) 16th March 2005, Accepted 4th May 2005

First published as an Advance Article on the web 31st May 2005

DOI: 10.1039/b503830h

The smooth comproportionation reaction of the U(VI) and U(III) complexes $\text{UO}_2(\text{OTf})_2$ and $\text{U}(\text{OTf})_3$, afforded the hexanuclear U(IV) oxide cluster $[\text{U}_6(\mu_3\text{-O})_8(\mu_2\text{-OTf})_8(\text{py})_8]$, a rare example of a metal oxide with a $\text{M}_6(\mu_3\text{-O})_8$ core.

The occurrence of the actinyl species $[\text{AnO}_2]^{n+}$ (An = U, Np, Pu, Am) in the nuclear industry and the natural environment is a strong incitement to the understanding and control of their physicochemical properties and chemical behaviour.¹ The U=O bonds of the *trans* dioxo uranyl(VI) ion $[\text{UO}_2]^{2+}$ are so strong that they are often considered as chemically inert, and their activation aimed at the formation of new uranium complexes represents a challenging synthetic goal.^{2,3} In particular, attracting perspectives in the chemistry of uranium would be afforded by the use of the uranyl moiety as a convenient oxide precursor for the synthesis of new soluble homo and heteronuclear polyoxo aggregates. In the course of our studies on the chemistry of uranyl complexes in strictly anhydrous organic media,⁴ we found that $\text{UO}_2(\text{OTf})_2$ undergoes an unprecedented redox reaction with $\text{U}(\text{OTf})_3$ to afford a novel hexanuclear uranium oxide,⁵ $[\text{U}_6(\mu_3\text{-O})_8(\mu_2\text{-OTf})_8(\text{py})_8]$ (**1**), which is also a rare example^{6,7} of a metal oxide with a $\text{M}_6(\mu_3\text{-O})_8$ core.

Reaction of $\text{UO}_2(\text{OTf})_2$ with 2 equivalents of $\text{U}(\text{OTf})_3$ in a 1 : 1 mixture of pyridine and acetonitrile at 20 °C led to the immediate formation of a green solution which slowly deposited light green crystals of **1**·2py upon heating at 120 °C.† This compound was also synthesized in a reproducible manner from pyridine or pyridine-tetrahydrofuran, while the isomorphous complex **1**·Et₂O crystallized upon slow diffusion of diethyl ether into a pyridine solution of **1**.

The crystal structure of **1** in **1**·2py and **1**·Et₂O‡ exhibits an octahedral-like skeleton of uranium atoms which are held together by triply bridging oxygen atoms located above each of the eight triangular faces of the octahedron. The U2 and U4 atoms lie on the crystallographically imposed C₂ axis, which corresponds to a pseudo S₄ axis for the point symmetry of the complex core; a view of **1** along this axis is represented in Fig. 1. The eight bidentate triflate ligands are divided into two groups; four of them bridge the adjacent metal atoms in the equatorial plane (U1, U3 and the symmetry-related atoms), whereas the four others connect the apical U2 and U4 atoms to U1 and U1' for the former and U3 and U3' for the latter. All the uranium atoms are eight-coordinate (Fig. 2), since they complete their coordination sphere with one (U1 and U3) or two pyridine molecules (U2 and U4), and are in an

approximate square antiprismatic environment, in which one of the square faces is shared with the cube of μ_3 -oxygen atoms. The geometry of the U_6O_8 core is only slightly distorted from the ideal O_h point symmetry; the U–O(oxo) distances vary from 2.208(3) to 2.326(3) Å, with an average value of 2.25(3) Å (including both compounds **1**·2py and **1**·Et₂O, as all the other values reported below). This mean value is close to that of 2.24(7) Å for the μ_3 -oxo bridges reported in the literature.⁸ The neighbouring U...U distances are ranging from 3.6356(3) to 3.6994(5) Å and average 3.666(18) Å, which rules out any strong interaction between the U(IV) ions. The distances between opposite uranium centres are in the range 5.1297(4)–5.2789(6) Å. The U–O and U...U distances in the $\text{U}_6(\mu_3\text{-O})_8$ core of **1** are shorter as expected, by 0.1 and 0.2 Å respectively, than the corresponding distances in the $\text{U}_6(\mu_3\text{-OH})_8$

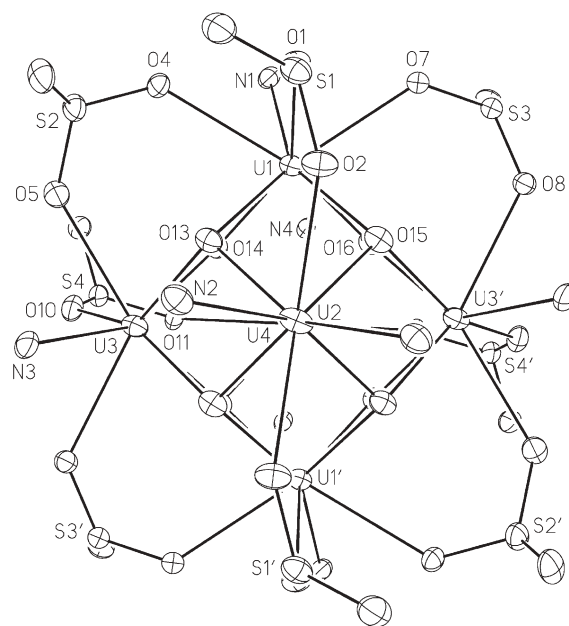


Fig. 1 View of complex **1** in **1**·2py down the C₂ axis. The H atoms, the C atoms of the pyridine ligands and the CF₃ groups of the triflate ligands have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected average bond lengths (including both **1**·2py and **1**·Et₂O) [Å]: <U(1)–O(oxo)> 2.26(3), <U(1)–O(OTf)> 2.512(18), U(1)–N(1) 2.635(13), <U(2)–O(oxo)> 2.239(18), <U(2)–O(OTf)> 2.587(14), <U(2)–N(2)> 2.663(15), <U(3)–O(oxo)> 2.27(4), <U(3)–O(OTf)> 2.51(3), U(3)–N(3) 2.641(1), <U(4)–O(oxo)> 2.248(19), <U(4)–O(OTf)> 2.566(3), U(4)–N(4) 2.669(11). Symmetry code †: 1 – x, y, 2.5 – z.

*berthet@drecam.cea.fr

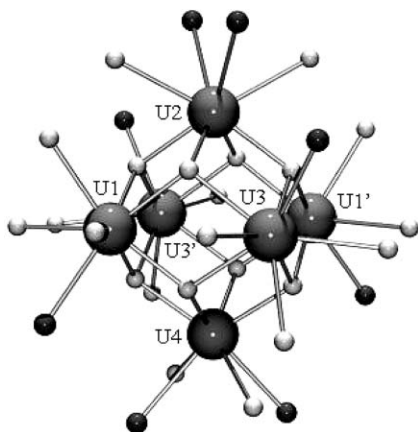


Fig. 2 View of the core of complex **1** and its environment of coordinating atoms at the periphery. Dark- and light-coloured atoms represent nitrogen and oxygen atoms, respectively. Symmetry code \prime : $1 - x, y, 2.5 - z$.

framework of the uranium phosphate compound $[U_6(\mu_3\text{-OH})_8(\mu_2\text{-O}_2\text{P(OPh)}_2)_{12}]$ and the $U_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ core of the sulfate complex $[U_6O_4(OH)_4(SO_4)_6]$.^{9,10} The mean U–O bond length of the bridging triflate ligands is equal to 2.53(4) Å and is identical to that measured in the tetranuclear compound $[\{U(\text{OTf}(\text{terpy})_2(\mu\text{-O})(\mu\text{-OTf})U(\text{terpy})\}_2(\mu\text{-OTf})_2(\mu\text{-O}))][\text{OTf}]_4$.¹¹ The U–N distances, which average 2.652(18) Å, are in the range of the U–N(py) distances found in uranium(IV) complexes, which is 2.54–2.70 Å.¹²

The ¹H NMR spectra of **1**·2py in acetonitrile exhibit three broad resonances which indicate that the coordinated and free pyridine molecules are rapidly exchanging in solution. The single signal in the ¹⁹F NMR spectrum at 20 °C suggests that the triflate ligands are scrambling over the whole U_6 octahedron; broadening of this resonance occurred at lower temperature, but the slow-limit spectrum could not be obtained.

Complexes with a $M_6(\mu_3\text{-X})_8$ or $M_6(\mu_3\text{-X})_n(\mu_3\text{-Y})_{8-n}$ cluster core form a large class of complexes with a variety of d transition metals and bridging heteroatoms,^{6,7,13} including the series of compounds $[M_xM_o_6(\mu_3\text{-X})_8]$ (X = S, Se, Te) known as Chevrel phases.¹⁴ However, such species are rather uncommon with the f-elements; only a few lanthanide clusters with similar geometry have been reported,¹⁵ whereas in the actinide family, they are restricted to the aforementioned uranium sulfate and phosphate complexes.^{9,10,16} It is noteworthy that in the series of $M_6(\mu_3\text{-O})_8$ clusters, **1** is the first which is not an organometallic species, the other few examples being cyclopentadienyl complexes of d transition metals which were prepared either by hydrolysis of monomeric precursors or by oxidation of very reactive metal complexes.^{6,7} These reactions, in addition to the reductive coupling of oxo-halide precursors,¹⁷ constitute in fact the classical synthetic routes to polyoxo aggregates.^{6,7} To the best of our knowledge,^{7,18} the synthesis of an oxide cluster involving a redox reaction between a high-valent metal oxide and a low-valent complex of the same metal, has no precedent.

The mechanism of formation of **1** is still unclear; the ¹⁹F NMR spectra of the reaction mixture exhibit broad resonances, suggesting the presence of exchanging triflate ligands in solution, and are not informative. The failure to produce **1** by reduction of

$UO_2(\text{OTf})_2$ with classical reducing reagents indicates that $U(\text{OTf})_3$ does not act only as a one-electron reducing reagent. It seems likely that the formation of **1** results from the comproportionation reaction depicted by eqn. (1), and we are currently working to elucidate the mechanism, through $\{^1\text{H}\}$ NMR observation of the intermediates involved in analogous reactions of $UO_2(\text{OTf})_2$ and $U(\text{III})$ organometallic species.



These results clearly evidence the possibility of using the $[UO_2]^{2+}$ ion in redox reactions with other low-valent metal compounds to give new homo- or heteropolynuclear complexes with stable oxide frameworks. It seems surprising that, despite the high oxophilicity of the f-elements, polyoxo aggregates are quite uncommon and have been most generally obtained by oxidation of low-valent species by adventitious traces of oxygen or water.^{11,19} In parallel to the ligand-controlled hydrolysis of the f element ions giving oxo/hydroxo polynuclear complexes,²⁰ the smooth synthesis of such polyoxo uranium complexes in anhydrous media is also very attractive for both fundamental and applied aspects, in particular in the field of catalysis and materials.

Jean-Claude Berthet,* Pierre Thuéry and Michel Ephritikhine

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA Saclay, 91191 Gif-sur-Yvette, France.

E-mail: berthet@dreacam.cea.fr; ephri@dreacam.cea.fr;

Fax: +33(0)169086640; Tel: +33(0)169086436

Notes and references

† *Synthesis and characterizing data:* In a glove-box under argon, a flask was charged with $UO_2(\text{OTf})_2$ (200 mg, 0.35 mmol) and $U(\text{OTf})_3$ (482.4 mg, 0.70 mmol) in a 1 : 1 mixture of acetonitrile and pyridine (10 mL). The deep green solution was heated at 120 °C for 48 h, and deposited green crystals of **1**·2py which were filtered off, washed with the mixture of solvents by Soxhlet technique, and dried under vacuum. Yield : 177 mg (85% based on uranyl). Elemental analysis (%) calc. for $C_{58}H_{50}F_{24}N_{10}O_{32}S_8U_6$: C 19.68, H 1.42, N 3.96; found: C 19.48, H 1.39, N 3.90. ¹H NMR (200 MHz, $[\text{H}_8]\text{thf}$, 23 °C): δ = 8.54, 8.18 and 7.09 (broad signals of pyridine). ¹⁹F NMR (188 MHz, $[\text{H}_8]\text{acetonitrile}$, 23 °C): δ = 10.5 (δ 0 for $\text{CF}_3\text{CO}_2\text{D}$). IR (nujol mulls in KBr pellets): $\nu(\text{cm}^{-1})$ = 1604(w), 1446(s), 1366(m), 1319(s), 1212(s), 1187(m), 1067(w), 1041(w), 1024(s), 1019(s), 800(w), 757(w), 703(m), 632(m), 557(m), 513(m).

‡ *Crystal data for 1·2py:* $C_{58}H_{50}F_{24}N_{10}O_{32}S_8U_6$, $M = 3539.74$, monoclinic, $a = 25.2878(14)$, $b = 15.0388(9)$, $c = 26.581(3)$ Å, $\beta = 116.656(5)^\circ$, $V = 9034.3(13)$ Å³, space group $C2/c$, $Z = 4$, $T = 100(2)$ K, $\mu(\text{MoK}\alpha) = 11.035 \text{ mm}^{-1}$, 73593 measured reflections, 8545 independent, 5920 with $I > 2\sigma(I)$, 654 parameters, $R1 = 0.026$, $wR2 = 0.057$. *Crystal data for 1·Et₂O:* $C_{52}H_{50}F_{24}N_8O_{33}S_8U_6$, $M = 3455.66$, monoclinic, $a = 25.3194(5)$, $b = 15.0312(2)$, $c = 26.9908(5)$ Å, $\beta = 116.9200(10)^\circ$, $V = 9159.1(3)$ Å³, space group $C2/c$, $Z = 4$, $T = 100(2)$ K, $\mu(\text{MoK}\alpha) = 10.881 \text{ mm}^{-1}$, 78194 measured reflections, 8681 independent, 7212 with $I > 2\sigma(I)$, 615 parameters, $R1 = 0.026$, $wR2 = 0.071$. The data were collected on a Nonius Kappa-CCD diffractometer with Mo-K α radiation. Absorption effects were empirically corrected. CCDC 262836 (**1**·2py) and CCDC 262837 (**1**·Et₂O). See <http://www.rsc.org/suppdata/cc/b5/b503830/h/> for crystallographic data in CIF format.

- J. J. Katz, G. T. Seaborg and L. R. Morss, *The Chemistry of the Actinide Elements*, Chapman and Hall, London, Vol. 1 and 2, 1986.
- (a) K. W. Bagnall, J. G. H. du Preez, B. J. Gellatly and J. H. Holloway, *J. Chem. Soc., Dalton Trans.*, 1975, 1963; (b) P. C. Leverd, D. Rinaldo and M. Nierlich, *J. Chem. Soc., Dalton Trans.*, 2002, 829; (c) C. J. Burns and A. P. Sattelberger, *Inorg. Chem.*, 1988, **21**, 3692; (d) M. P. Wilkerson, C. J. Burns, H. J. Dewey, J. M. Martin, D. E. Morris, R. T. Paine and B. L. Scott, *Inorg. Chem.*, 2000, **39**, 5277; (e) D. C. Bradley, A. K. Chatterjee and A. K. Chatterjee, *J. Inorg.*

- Nucl. Chem.*, 1959, **12**, 71; (f) P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris and B. L. Scott, *Inorg. Chem.*, 2001, **40**, 5491.
- 3 (a) V. Golovnyia and G. T. Bolotova, *Russ. J. Inorg. Chem.*, 1966, **11**, 1419; (b) H. Greiwing, B. Krebs and A. A. Pinkerton, *Inorg. Chim. Acta*, 1995, **234**, 127; (c) G. M. Shashidhara and T. R. Goudar, *J. Indian Chem. Soc.*, 2001, **78**, 360; (d) T. M. McCleskey, T. M. Foreman, E. E. Hallman, C. J. Burns and N. N. Sauer, *Environ. Sci. Technol.*, 2001, **35**, 547; (e) L. V. Moskaleva, S. Kruger, A. Spörl and N. Rösch, *Inorg. Chem.*, 2004, **43**, 4080.
- 4 (a) J. C. Berthet, M. Nierlich and M. Ephritikhine, *Chem. Commun.*, 2004, 870; (b) J. C. Berthet, M. Nierlich and M. Ephritikhine, *Dalton Trans.*, 2004, 2814; (c) J. C. Berthet, M. Nierlich and M. Ephritikhine, *Angew. Chem. Int. Ed. Engl.*, 2003, **42**, 1952; (d) J. C. Berthet, M. Lance, M. Nierlich and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 2000, 1969; (e) J. C. Berthet, M. Lance, M. Nierlich and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 1999, 2005.
- 5 P. B. Duval, C. J. Burns, D. L. Clark, D. E. Morris, B. L. Scott, J. D. Thompson, E. L. Werkema, L. Jia and R. A. Andersen, *Angew. Chem. Int. Ed.*, 2001, **40**, 3357.
- 6 (a) J. C. Huffman, J. G. Stone, W. C. Krusell and K. G. Caulton, *J. Am. Chem. Soc.*, 1977, **99**, 5829; (b) F. Bottomley, *Polyhedron*, 1992, **11**, 1707 and references therein; (c) T. Carofiglio, C. Floriani, A. Roth, A. Sgamellotti, M. Rosi, A. Chiesi-Villa and C. Rizzoli, *J. Organomet. Chem.*, 1995, **488**, 141; (d) G. Bai, H. W. Roesky, P. Lobinger, M. Noltemeyer and H.-G. Schmidt, *Angew. Chem. Int. Ed. Engl.*, 2001, **40**, 2156.
- 7 H. W. Roesky, I. Haiduc and N. S. Hosmane, *Chem. Rev.*, 2003, **103**, 2579 and references therein.
- 8 F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380.
- 9 L. M. Mokry, S. N. Dean and C. J. Carrano, *Angew. Chem. Int. Ed. Engl.*, 1996, **35**, 1497.
- 10 G. Lundgren, *Arkiv. Kemi.*, 1952, **5**, 349.
- 11 J. C. Berthet, M. Nierlich, Y. Miquel, C. Madic and M. Ephritikhine, *Dalton Trans.*, 2005, 369 and references therein.
- 12 J. C. Berthet, M. Nierlich and M. Ephritikhine, *Inorg. Chem.*, 2005, 1142 and references therein.
- 13 (a) M. L. Steigerwald, T. Siegrist and S. M. Stuczynski, *Inorg. Chem.*, 1991, **30**, 2256; (b) A. V. Firth and D. W. Stephan, *Inorg. Chem.*, 1997, **36**, 1260; (c) S. Jin, F. Popp, S. W. Boettcher, M. Yuan, C. M. Oertel and F. J. Disalvo, *J. Chem. Soc., Dalton Trans.*, 2002, 3096; (d) D. T. Hay, D. C. Swenson and L. M. Messerle, *Inorg. Chem.*, 2002, **41**, 4700; (e) B. K. Roland, H. D. Selby, M. D. Carducci and Z. Zheng, *J. Am. Chem. Soc.*, 2002, **124**, 3222; (f) G. Bai, H. W. Roesky, J. Li, T. Labahn, F. Cimpoesu and J. Magull, *Organometallics*, 2003, **22**, 3034.
- 14 (a) *Advanced Inorganic Chemistry*, ed. F. A. Cotton, G. Wilkinson, C. Murillo, A. Bochmann, J. Wiley and Sons, Inc., New York, 6th edn., 1999, pp. 671–674 and 967–968; (b) S. Jin and F. J. Disalvo, *Chem. Commun.*, 2001, 1586 and references therein.
- 15 (a) P. Toledano, F. Ribot and C. Sanchez, *C. R. Acad. Sci. Paris*, 1990, **311**, Série II, 1315; (b) R. Wang, M. D. Carducci and Z. Zheng, *Inorg. Chem.*, 2000, **39**, 1836; (c) D.-S. Zhang, B.-Q. Ma, T.-Z. Jin, S. Gao, C.-H. Yan and T. C. W. Mak, *New J. Chem.*, 2000, **24**, 61; (d) W. J. Evans, N. T. Allen, M. A. Greci and J. W. Ziller, *Organometallics*, 2001, **20**, 2936 and references therein; (e) A.-V. Mudring and A. Babai, *Z. Anorg. Allg. Chem.*, 2005, **631**, 261.
- 16 It must be noted that $[\text{U}_6(\mu_3\text{-OH})_8(\mu_2\text{-O}_2\text{P}(\text{OPh})_2)_{12}]$ is obtained from uranyl acetate, sodium diphenylphosphate and $[\text{TpVCl}_2(\text{dmf})]$ [Tp = hydridotris(pyrazolyl)borate] in aqueous acetonitrile; however, it is likely to result from classical hydrolysis of initially formed low-valent uranium species rather than from true activation of the uranyl ion, because of the requirement of water.
- 17 C. D. Abernethy, F. Bottomley, R. W. Day, A. Decken, D. A. Summers and R. C. Thompson, *Organometallics*, 1999, **18**, 870.
- 18 (a) E. Collange, L. Metteau, P. Richard and R. Poli, *Polyhedron*, 2004, **23**, 2605; (b) F. Bottomley and J. E. McKenzie-Boone, *J. Organomet. Chem.*, 1997, **534**, 23; (c) X. Zhou, H. Ma, Z. Wu, X. You, Z. Xu and X. Huang, *J. Organomet. Chem.*, 1995, **503**, 11; (d) F. Bottomley, J. Chen, K. F. Preston and R. C. Thompson, *J. Am. Chem. Soc.*, 1994, **116**, 7989.
- 19 (a) J. W. Gilje and H. Roesky, *Chem. Rev.*, 1994, **94**, 895; (b) L. Karmazin, M. Mazzanti and J. Pécault, *Inorg. Chem.*, 2003, **42**, 5900.
- 20 Z. Zheng, *Chem. Commun.*, 2001, 2521.