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Formation of Uranium(IV) Oxide Clusters from Uranocene [U(η^8-C_8H_8)$_2$] and Uranyl [UO_2X_2] Compounds

Jean-Claude Berthet,* Pierre Thuéry, and Michel Ephritikhine

CEA Saclay, DSM, IRAMIS, UMR 3299, CEA/CNRS SIS2M, 91191 Gif-sur-Yvette, France

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Uranocene [U(η^8-C_8H_8)$_2$] reacted in refluxing pyridine with 2 equiv of the uranyl(VI) compound [$UO_2(OTf)_2$] or [$UO_2I_2(THF)_3$] (OTf = O_3SCF_3; THF = tetrahydrofuran) or 1 equiv of the uranyl(V) complex [$UO_2(py)_{2.3}K(OTf)_2$] to afford the hexanuclear uranium(IV) oxide cluster [$U_6O_8(OTf)_8(py)_8$] (**1**) or [$U_6O_8I_8(py)_{10}$] (**3**). Complexes **1** and **3** were easily isolated in good yield because they were deposited as microcrystalline powders with the release of free cyclooctatetraene as a unique byproduct. A similar reaction in THF gave [$U_6O_8(OTf)_8(THF)_8$] (**2**), whose isolation was impeded by polymerization of the solvent. With complexes [U(η^8-C_8H_8)$_2$] and [$UO_2(OTf)_2$] in a molar ratio of 4:3 or in the presence of excess uranocene, only crystals of the mono(η^8-C_8H_8) aggregate [U_6O_8(η^8-C_8H_8)$(OTf)_6(py)_8$] (**4**) were obtained. The crystal structures of **1**·2py, **2**·2THF, **3**·py, and **4**·py were determined. Whereas uranocene and uranyl(VI) compounds are generally viewed as the most robust uranium compounds, they were found to fuse together into hexanuclear assemblages. These studies revealed the unusual four-electron reductive capacity of a uranium(IV) complex, in particular uranocene, which, through the loss of its two C_8H_8 ligands, induces the activation and reduction of the strong U═O bonds of the uranyl moiety.

Introduction

Uranyl(VI) salts are by far the most stable and ordinary forms of uranium in most processing and environmental conditions. The stability of the trans dioxo $\{UO_2\}^{2+}$ cation originates from the combination of metal 5f/6d and oxygen 2p orbitals to form the very strong metal−oxo bonds.[1] However, novel aspects of uranyl chemistry in anhydrous organic media were discovered during the last years, in particular the reduction of the metal center, coupled or not with the activation of the U═O bonds.[2] The discovery of uranocene [$U(COT)_2$] (COT = η^8-C_8H_8) was a milestone in the history of actinide chemistry.[3] The remarkable stability of this uranium(IV) compound was explained by the covalent stabilization originating from the overlap of 5f orbitals with a symmetry-allowed combination of the highest occupied orbitals in the dianionic ligand and by steric constraints imposed by the two rings.[4] Here, we report that uranocene easily reacts with the uranyl complexes [UO_2X_2] (X = OSO_2CF_3 = OTf and I) to give uranium(IV) oxide clusters with a $U_6(\mu_3\text{-}O)_8$ core. These striking transformations involving the reputedly most chemically robust molecular uranium compounds revealed the unprecedented four-electron reductive capacity of a tetravalent complex through the full oxidation and dissociation of its ligands, resulting in the formation of a polynuclear assemblage.

Experimental Section

All experiments were carried out under argon (< 5 ppm oxygen or water) in anhydrous solvents using Schlenk-vessel and vacuum-line techniques or in a glovebox. [$UO_2(OTf)_2$],[5] [$UO_2I_2(THF)_3$],[6] [$UO_2(py)_{2.3}K(OTf)_2$],[7] and [$U(COT)_2$][3] were prepared as previously described. Diethyl ether and tetrahydrofuran (THF) were dried over a mixture of sodium benzophenone and pyridine over potassium. The ^{1}H NMR spectra were recorded on a Bruker DPX 200 instrument at 23 °C. Elemental analyses were performed by Analytische Laboratories (Lindlar, Germany).

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*To whom correspondence should be addressed. E-mail: jean-claude.berthet@cea.fr..

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Caution! *Depleted uranium (primary isotope* ^{238}U*) is a weak* α*-emitter (4.197 MeV) with a half-life of* 4.47×10^9 *years; all of the manipulations and reactions should be carried out in monitored fume hoods or in a glovebox, in a laboratory equipped with* α*- and* β*-counting equipment.*

$[\mathrm{U_6O_8(OTf)_8(py)_8}]$ (1). (a) A flask was charged with $[\mathrm{U(COT)_2}]$ (118 mg, 0.026 mmol) and $[\mathrm{UO_2(OTf)_2}]$ (300 mg, 0.53 mmol), and pyridine (5 mL) was condensed in. Immediately, the solution turned red-brown. After stirring for 12 h at 100 °C, the red-orange solution deposited a green microcrystalline powder, the quantity of which was increased upon the addition of THF (5 mL). After filtration, the powder of **1** was washed with THF (5 mL), a 1:1 mixture of pyridine/THF (10 mL), and diethyl ether (10 mL) and dried under vacuum (391 mg, 88%). Anal. Calcd for $\mathrm{C_{48}H_{40}F_{24}N_8O_{32}S_8U_6}$: C, 17.05; H, 1.19; N, 3.31; F, 13.48. Found: C, 17.24; H, 1.34; N, 3.33; F, 12.98. Crystals of **1**·2py were obtained in an NMR tube charged with $[\mathrm{U(COT)_2}]$ (6.6 mg, 0.015 mmol) and $\mathrm{UO_2(OTf)_2}$ (16.8 mg, 0.030 mmol) in pyridine-d_5 (0.5 mL). After 60 min at 110 °C, green crystals were deposited from the orange solution and X-ray diffraction confirmed the unit cell to be that of **1**·2py. The NMR spectrum of the solution showed only the presence of free $\mathrm{C_8H_8}$ (δ 5.64).

(b) An NMR tube was charged with $[\mathrm{U(COT)_2}]$ (3.7 mg, 0.0082 mmol), $[\mathrm{U(OTf)_4}]$ (6.9 mg, 0.0082 mmol), and $[\mathrm{UO_2(py)_{2.3}K(OTf)_2}]$ (26 mg, 0.033 mmol) in pyridine-d_5 (0.5 mL). After 15 h at 110 °C, green microcrystals of **1**·2py were deposited from the brown solution.

$[\mathrm{U_6O_8I_8(py)_{10}}]$ (3). A flask was charged with $[\mathrm{U(COT)_2}]$ (101 mg, 0.022 mmol) and $[\mathrm{UO_2I_2(THF)_3}]$ (336 mg, 0.45 mmol), and pyridine (5 mL) was condensed in. Immediately, the solution turned red-brown. After stirring for 6 h at 90 °C, the red solution deposited an ochre-brown microcrystalline powder, the quantity of which was increased after the volume of the solution was reduced to ca. 2 mL by evaporation and THF (ca. 5 mL) was added. The beige powder of **3** was filtered off, washed with THF (2 × 5 mL), a mixture of pyridine (3 mL) and diethyl ether (6 mL), and dried under vacuum (237 mg, 62%). Anal. Calcd for $\mathrm{C_{50}H_{50}N_{10}I_8O_8U_6}$: C, 17.86; H, 1.49; N, 4.16; I, 30.19. Found: C, 17.41; H, 1.48; N, 4.08; I, 28.48. A few crystals of **3**·py were obtained by the slow diffusion of pentane into a pyridine solution of **3**. A ^{1}H NMR experiment with $[\mathrm{U(COT)_2}]$ (5.0 mg, 0.012 mmol) and $[\mathrm{UO_2I_2(THF)_3}]$ (16.6 mg, 0.024 mmol) in pyridine-d_5 (0.5 mL) showed the formation of free $\mathrm{C_8H_8}$ (δ 5.64) and THF in a 1:3 molar ratio.

$[\mathrm{U_6O_8(COT)(OTf)_6(py)_n}]$ [n = 6 (4′) or n = 8 (4)]. (a) A flask was charged with $[\mathrm{U(COT)_2}]$ (147 mg, 0.33 mmol) and $[\mathrm{UO_2(OTf)_2}]$ (250 mg, 0.44 mmol), and pyridine (5 mL) was condensed in. Immediately, the solution turned brown. The mixture was heated at 100 °C for 12 h, affording a red-brown solution with a brown precipitate. The volume of the solution was reduced to ca. 2 mL by evaporation, and THF (6 mL) was added in order to increase the quantity of the brown powder. After filtration, the powder was washed with THF (10 mL) and diethyl ether (2 × 5 mL), and a beige powder of **4′** was obtained after drying under vacuum (313 mg, 94%). Anal. Calcd for $\mathrm{C_{44}H_{38}F_{18}N_6O_{26}S_6U_6}$: C, 17.44; H, 1.26; N, 2.77; F, 11.29. Found: C, 17.84; H, 1.47; N, 3.55; F, 11.31. Recording of the NMR spectra of **4′** was impeded by its poor solubility.

(b) An NMR tube was charged with $[\mathrm{U(COT)_2}]$ (10.0 mg, 0.022 mmol) and $[\mathrm{UO_2(OTf)_2}]$ (17.0 mg, 0.029 mmol) in pyridine-d_5 (0.5 mL). After 2 h at 100 °C, brown crystals of **4**·py suitable for X-ray diffraction analysis were formed. The NMR spectrum showed signals at δ 5.64, −34.42, and −37.10 corresponding respectively to free $\mathrm{C_8H_8}$, $[\mathrm{U(COT)(OTf)_2(py)}_n]$,[8] and residual uranocene and a broad COT resonance at δ −11.4 attributed to $[\mathrm{U(COT)(OTf)_3}]^-$. The same signal was obtained when KOTf was added to a solution of $[\mathrm{U(COT)(OTf)_2(py)}_n]$ in pyridine. The formation of $[\mathrm{U(COT)(OTf)_3}]^-$ is likely related to the presence of $\mathrm{OTf^-}$ ions from decomposition products during thermal treatment.

Table 1. Crystal Data and Structure Refinement Details

	2·2THF	**3**·py	**4**·py
chemical formula	$\mathrm{C_{48}H_{80}F_{24}}$-$\mathrm{O_{42}S_8U_6}$	$\mathrm{C_{55}H_{55}I_8}$-$\mathrm{N_{11}O_8U_6}$	$\mathrm{C_{59}H_{53}F_{18}}$-$\mathrm{N_9O_{26}S_6U_6}$
M/(g mol^{-1})	3469.78	3441.48	3266.64
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$C2/c$
a/Å	24.487(2)	13.0379(12)	14.9595(6)
b/Å	15.4290(9)	13.3827(13)	23.7905(16)
c/Å	25.622(3)	14.1952(12)	24.4040(13)
α/deg	90	114.137(6)	90
β/deg	113.497(3)	96.997(6)	103.598(4)
γ/deg	90	114.215(5)	90
V/Å^3	8877.6(14)	1932.6(4)	8441.8(8)
Z	4	1	4
D_{calcd}/(g cm^{-3})	2.596	2.957	2.570
μ(Mo Kα)/mm^{-1}	11.231	15.770	11.735
F(000)	6400	1502	5952
reflns collcd	85 837	13 143	95 958
indep reflns	8429	6685	8002
obsd reflns [$I > 2\sigma(I)$]	4922	4607	6227
R_{int}	0.082	0.084	0.034
param refined	578	453	560
R1	0.034	0.062	0.024
wR2	0.068	0.141	0.045
S	0.818	1.007	0.973
$\Delta\rho_{\mathrm{min}}$/(e Å^{-3})	−1.07	−1.92	−0.81
$\Delta\rho_{\mathrm{max}}$/(e Å^{-3})	0.95	1.66	0.72

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa CCD area detector diffractometer[9] using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The crystals were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The data were processed with HKL2000.[10] Absorption effects were corrected with *SCALEPACK*.[10] The structures were solved by direct methods with *SHELXS-97*, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix least squares on F^2 with *SHELXL-97*.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. In **3**·py, two out of the five complexed pyridine molecules are disordered over two positions (sharing the nitrogen atom in one case), which have been refined with occupancy parameters constrained to sum to unity; the solvent pyridine molecule, being very close to its image by the symmetry center, has been given a 0.5 occupancy parameter; all of the pyridine molecules but one, behaving badly on refinement, were treated as idealized hexagons with restraints on displacement parameters. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with *SHELXTL*.[11]

Results and Discussion

The reaction in pyridine of $[\mathrm{UO_2(OTf)_2}]$ and $[\mathrm{U(COT)_2}]$ in a 2:1 molar ratio, represented by eq 1, was straightforward; the solution turned immediately red-brown, and after 12 h at 110 °C, green microcrystals of **1** were deposited from the orange solution and isolated in 88% yield after the usual workup. Another experiment in an NMR tube afforded crystals of **1**·2py, identified by X-ray diffraction, and the ^{1}H NMR spectrum showed a unique singlet at δ 5.64 corresponding to free $\mathrm{C_8H_8}$. The reaction also took place in THF, at 20 °C or under reflux, but polymerization of the solvent generally occurred and the green crystals of the product were stuck in the

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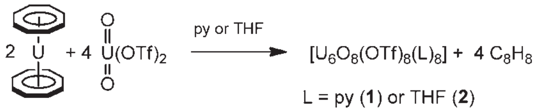
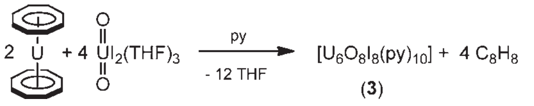
gel; in one instance, crystals of $[U_6O_8(OTf)_8(THF)_8]\cdot 2THF$ (**2**·2THF) could be collected before gel formation, and their structure was determined (vide infra). Similar treatment of $[UO_2(OTf)_2]$ with the trivalent metallocene $[U(\eta^5\text{-}C_5H_5)_3(THF)]$ or $[U(\eta^5\text{-}C_5H_4{}^tBu)_3]$ in THF also afforded crystals of **2**·2THF but with a quantity of intractable products. Replacing $[UO_2(OTf)_2]$ with $[UO_2I_2(THF)_3]$[6] in its reaction with $[U(COT)_2]$ in pyridine led to the formation of an ochre powder of **3**, according to eq 2, and red crystals of **3**·py were obtained upon the slow diffusion of pentane into a pyridine solution.

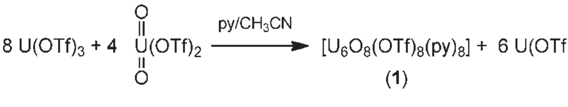


(1)



(2)

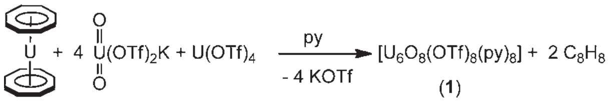
Reactions (1) and (2) are remarkable for several aspects. They run counter to the reputed chemical robustness of $[U(COT)_2]$,[3,4] whose reductive chemistry is limited to reactions with I_2 and $(Ph_2SiOH)_2O$, giving respectively $[U(COT)I_2(THF)_2]$[12] and an unexpected uranium(VI) cyclometallasiloxane,[13] while $[U(\eta^8\text{-}C_8H_7{}^nBu)_2]$ was found to reduce nitro compounds into azo derivatives with liberation of free $C_8H_7{}^nBu$.[14] Complex **1** was previously synthesized from $[U(OTf)_3]$ and $[UO_2(OTf)_2]$, according to eq 3.[15] In this reaction, the eight electrons required for the reduction of four $\{UO_2\}^{2+}$ ions into formally UO_2 groups were provided by the one-electron oxidation of $[U(OTf)_3]$.



$$8\,U(OTf)_3 + 4\,\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{U}}(OTf)_2 \xrightarrow{py/CH_3CN} \underset{(\mathbf{1})}{[U_6O_8(OTf)_8(py)_8]} + 6\,U(OTf)_4 \qquad (3)$$

However, only two of the U^{4+} ions coming from $[U(OTf)_3]$ were inserted into the framework of **1**, the synthesis of which suffered from the concomitant release of six sacrificial $[U(OTf)_4]$. In reactions (1) and (2), uranocene delivers four electrons via the sole redox activity of its two dianionic COT ligands, which are transformed into free cyclooctatetraene, without changing the 4+ oxidation state of the metal. This is unique because, in the rare examples where four electrons are released by mononuclear tris- and bis(pentamethylcyclopentadienyl)uranium(III) complexes, the metal center is eventually found in the 5+ or 6+ oxidation state.[16−18] Moreover, in the reactions of $[\{U(COT)(Cp^*)\}_2(\mu\text{-}\eta^3{:}\eta^3\text{-}C_8H_8)]$ ($Cp^* = C_5Me_5$) with organic molecules, only the bridging and nonplanar C_8H_8 ligand is redox-active, whereas the other planar $\eta^8\text{-}C_8H_8$ ligands are spectators.[18] Compared with the other few reactions in which C_5Me_5 or C_8H_8 anionic ligands behave as reductants toward organic molecules, the syntheses of **1**−**3** provide unique examples of the ligand-based reduction of another metal complex and are all the more significant given that activation of the uranyl U═O bond is not an easy task.[2,19] Comproportionation reactions (1) and (2) thus represent efficient routes to cluster formation. Finally, if $C_5Me_5{}^-$ is a much more reactive ligand than $C_8H_8{}^{2-}$, the transfer of four electrons from uranocene is much more efficient than in the aforementioned complexes with C_5Me_5 and bridging C_8H_8 groups, where each redox-active ligand delivers a single electron per metal center and where only part of the full set of ligands is involved in the reduction process.

The immediate color change during reactions (1) and (2), from yellow to brown, was a clear indication of the prior reduction of $[UO_2X_2]$ salts into pentavalent uranyl intermediates by the $C_8H_8{}^{2-}$ ligands of uranocene, as they were reduced by $K(C_5Me_5)$ or $K_2(C_8H_8)$.[7] Indeed, complex **1** was obtained by treatment of the uranyl(V) compound $[UO_2(py)_{2.3}K(OTf)_2]$[7] with an equimolar mixture of $[U(COT)_2]$ and $[U(OTf)_4]$ (equivalent to $[U(COT)(OTf)_2]$)[8] in pyridine, according to eq 4. Green crystals of **1**·2py were deposited from the brown solution after heating for 15 h at 110 °C (ca. 60% yield).



(4)

In view of the marked tendency of the $\{AnO_2\}^+$ species (An = U, Np, Pu) to form cation−cation interactions of the type An═O → M (M = Li, K, Tl, d transition metal or actinide),[7,20] it seems likely that such interactions are responsible for the trapping of the strong Lewis acid U^{4+} ions released in the medium, giving species intermediate in the formation of the U_6O_8 framework. The oxidation state of the tetravalent uranium atom of uranocene is not expected to change during these reactions. Indeed, mixed-valent uranium(IV)−uranyl(VI) complexes such as $[C_6N_2H_{14}]_2[\{U^{VI}O_2F_2\}_2U^{IV}F_8]$, $[N(CH_2CH_2NH_3)_3][U^{IV}{}_2F_{10}]_2[U^{VI}O_2F_3]$, and $[U^{IV}(\eta^5\text{-}C_5H_5)_3(NCMe)_2][U^{VI}O_2Cl_4]$ have been reported to be stable, and a redox transfer reaction between uranium(IV) and -(V) species is not likely.[21]

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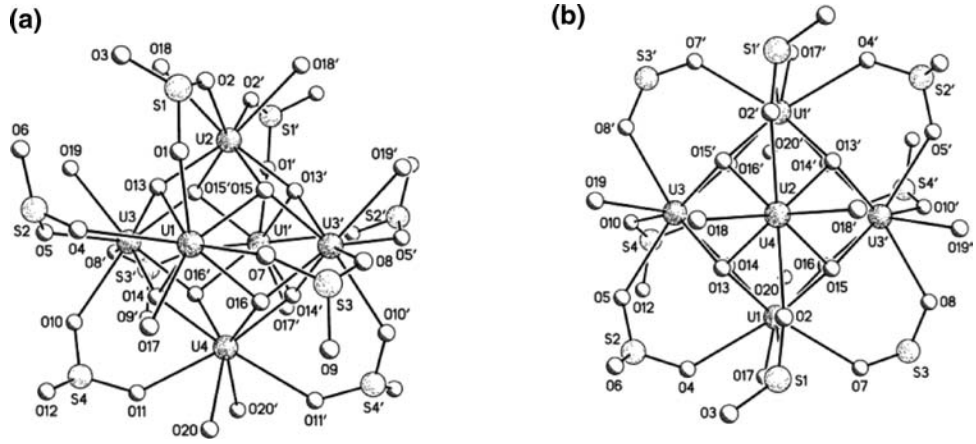


Figure 1. Views of complex **2** in **2**·2THF along the equatorial plane (a) and down the C_2 axis (b). The carbon, fluorine, and hydrogen atoms are omitted. Atoms are represented as spheres for clarity. Selected bond lengths (Å): U1−O13 2.281(5); U1−O14 2.211(5); U1−O15 2.273(6); U1−O16 2.257(5); U1−O1 2.488(5); U1−O4 2.566(6); U1−O17 2.512(5); U1−O7 2.518(5); U2−O13 2.220(6); U2−O15 2.246(5); U2−O18 2.543(6); U2−O2 2.598(5); U3−O15′ 2.220(6); U3−O13 2.284(5); U3−O14 2.283(5); U3−O16′ 2.290(5); U3−O10 2.489(5); U3−O5 2.501(5); U3−O8′ 2.542(5); U3−O19 2.589(6); U4−O16 2.214(5); U4−O14 2.273(6); U4−O11 2.542(6); U4−O20 2.530(5); ⟨U−O(THF)⟩ 2.54(2); ⟨U−O(OTf)⟩ 2.53(4); ⟨U−O(oxo)⟩ 2.25(3). Symmetry code: ′ = $-x, y, {}^1/_2 - z$.

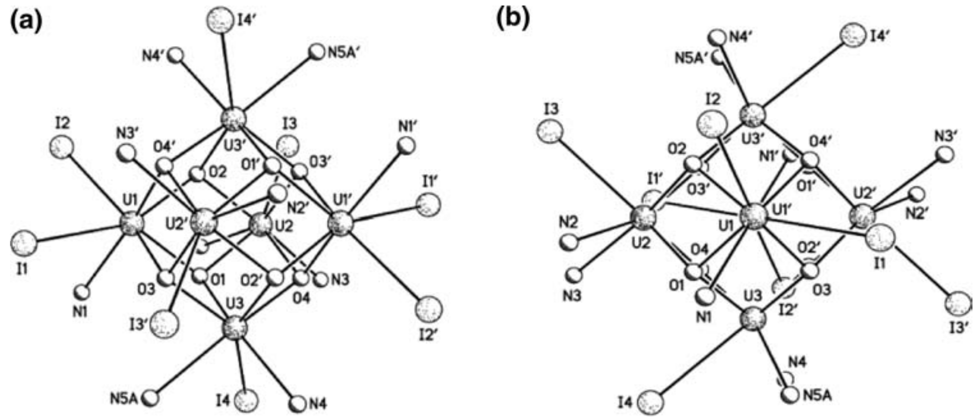
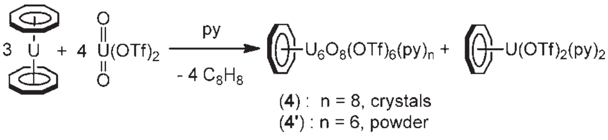


Figure 2. Views of complex **3** in **3**·py along the equatorial plane (a) and down the U1−U1′ axis (b). The carbon and hydrogen atoms are omitted. Only one position of the disordered atom N5 is represented. Atoms are represented as spheres for clarity. Selected bond lengths (Å): U1−I1 3.1498(18); U1−I2 3.0873(16); U2−I3 3.1228(14); U3−I4 3.1736(16); U1−O1 2.329(14); U1−O2 2.257(13); U1−O3 2.228(10); U1−O4′ 2.239(12); U2−O1 2.205(13); U2−O2 2.225(13); U2−O3′ 2.272(11); U2−O4 2.305(11); U3−O1 2.231(11); U3−O2′ 2.298(12); U3−O3 2.235(12); U1−N1 2.668(13); U2−N2 2.609(10); U2−N3 2.614(16); U3−N4 2.573(16); U3−N5A 2.657(12); ⟨U−I⟩ 3.13(3); ⟨U−O⟩ 2.25(4); ⟨U−*N*⟩ 2.63(3). Symmetry code: ′ = $-x, 1 - y, 1 - z$.

With the aim of decorating the $U_6(\mu_3\text{-}O)_8$ core of the cluster with COT ligands, reactions of $[UO_2(OTf)_2]$ with 1 mol equiv or an excess of $[U(COT)_2]$ in pyridine were carried out and, whatever the stoichiometry, afforded brown crystals of the mono-COT compound $[U_6O_8(COT)(OTf)_6(py)_8]\cdot py$ (**4**·py) together with emerald-green crystals of unreacted $[U(COT)_2]$. Complex **4** was obtained by using a 4:3 molar ratio of reactants, according to eq 5, and the concomitant formation of free C_8H_8, $[U(COT)(OTf)_2]$, and its anionic derivative $[U(COT)(OTf)_3]^-$ was indicated by ^1H NMR spectroscopy. The beige powder of $[U_6O_8(COT)(OTf)_6(py)_6]$ (**4′**) was isolated in 94% yield after the usual workup and drying, and its crystallization from pyridine gave crystals of **4**·py. The synthesis of **4** differs markedly from that of the few other organometallic clusters with a $M_6(\mu_3\text{-}O)_8$ core, of the general formula $[\{M(Cp)\}_6(\mu_3\text{-}O)_8]$ (Cp = cyclopentadienyl ligand), which were prepared either by hydrolysis of monomeric precursors or by oxidation of very reactive metal complexes.[22]



(5)

Views of complexes **2**−**4** are shown in Figures 1−3, respectively, together with selected bond lengths. The U_6O_8 core of these compounds is a tetrakis-hexahedron, e.g., a cube of oxygen atoms, each face of which is capped with a uranium atom. The uranium atoms form an octahedron and are held together with triply bridging oxygen atoms located above each face of the octahedron.

Whereas the U═O bond distances of uranyl are in the typical range (1.74−1.78 Å), the U−O(oxo) distances vary from 2.205(13) to 2.332(3) Å with an average value of 2.26(3) Å, equal to those in **1**[15] or the mixed-valent uranium(IV/V)

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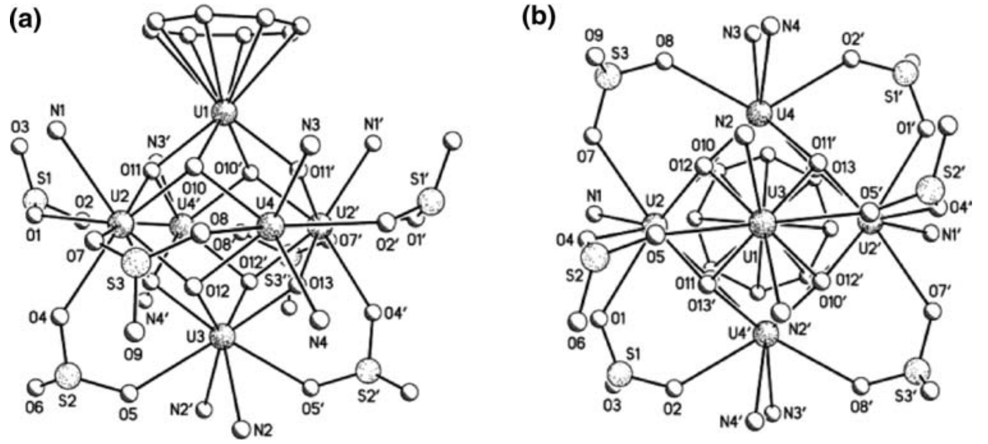

Figure 3. Views of complex **4** in **4**·py along the equatorial plane (a) and down the C_2 axis (b). The carbon atoms (except those of the COT ligand) and the fluorine and hydrogen atoms are omitted. Atoms are represented as spheres for clarity. Selected bond lengths (Å): U1−O10 2.332(3); U1−O11 2.292(3); U2−O10 2.244(3); U2−O11 2.208(3); U2−O12 2.287(3); U2−O13′ 2.281(3); U2−O1 2.554(3); U2−O4 2.508(3); U2−O7 2.560(3); U2−N1 2.673(4); U3−O12 2.232(3); U3−O13 2.241(3); U3−O5 2.602(3); U3−N2 2.667(4); U4−O10 2.226(3); U4−O11′ 2.262(3); U4−O12 2.252(3); U4−O13 2.249(3); U4−O2′ 2.542(3); U4−O8 2.555(3); U4−N3 2.670(4); U4−N4 2.646(4); ⟨U−*N*⟩ 2.665(10); ⟨U−O(OTf)⟩ 2.55(3); ⟨U−O(oxo)⟩ 2.26(3); ⟨U−C⟩ 2.724(16); U1−COT(centroid) 2.017. Symmetry code $' = -x, y, {}^3/_2 - z$.

complex $[U_6O_8(OTf)_{12}(H_2O)_3]\cdot 23H_2O$[23] and in line with that of 2.24(7) Å for the μ_3-oxo bridges reported in the Cambridge Structural Database (version 5.31).[24] The structure of **2** is very similar to that of **1**, with THF replacing the pyridine ligands. Four triflate ligands bridge the adjacent metal atoms in the equatorial plane (U1, U3, and the symmetry-related atoms), while four others connect the apical U2 and U4 atoms, which lie on the C_2 axis, to U1 and U1′ for the former and U3 and U3′ for the latter. The eight-coordinate uranium atoms are in an approximate square-antiprismatic environment, with the μ_3-oxygen atoms forming one square face. In the centrosymmetric structure of **3**, all of the uranium atoms are seven-coordinate, bound to one (U2 and U3) or two (U1) iodide ions and one (U1) or two (U2 and U3) pyridine molecules. The I1, I3, and I4 atoms cap a square face of the distorted trigonal prism defined respectively by the triangular faces (N1, O1, O3) and (I2, O2, O4′) for U1, (N2, O1, O2) and (N3, O3′, O4) for U2, and (N4, O2′, O4) and (N5A or N5B, O1, O3) for U3 (with the pyridine ligand containing N5 being disordered over two positions); these triangles form dihedral angles of 20.0(8), 13.0(8), and 18.2(8) or 8.9(8)°, respectively. The U−I bond lengths, which are lying from 3.0873(16) to 3.1736(16) Å and average 3.13(3) Å, are at the upper limit of the range of U−I distances in uranium(IV) complexes, which vary from 2.9558(4) Å in $[UI_4(py)_3]$[25] to 3.093(4) Å in $[U(S^iPr)_2I_2(py)_3]$.[26]

The structure of **4** is derived from that of **1** (or **2** by changing THF with pyridine ligands) by replacing two bridging OTf ligands between a single apical and two opposite equatorial uranium atoms of the U_6O_8 core with one COT ligand on the apical position and one pyridine molecule on each equatorial site. Except U1, which has the classical four-legged piano-stool configuration of the $[U(COT)X_2L_2]$ compounds, all of the other uranium atoms are in an approximate square-antiprismatic environment, with one of the square faces involving the four μ_3-oxygen atoms. The average U−C distance of 2.724(16) Å can be compared with those of 2.715(17) Å in $[U_6S_8(COT)_4(THF)_3]$,[27] 2.71(4) Å in $[U(COT)(NEt_2)(THF)_3][BPh_4]$, and 2.72(3) Å in $[U(COT)(mdt)(hmpa)_2]$ (mdt = 1,3-dithiole-4,5-dithiolate).[28] The U−O(OTf) and U−N distances in **2**−**4** are unexceptional.

Conclusion

In conclusion, uranocene, a reputedly chemically inert organouranium(IV) compound, was found to react with very robust uranyl(VI) salts to give inorganic and organometallic hexanuclear uranium(IV) oxide clusters with a rare $M_6(\mu_3\text{-}O)_8$ core. These novel reactions are based on the unique redox behavior of the two $(\eta^8\text{-}C_8H_8)^{2-}$ ligands of $[U(COT)_2]$, which deliver four electrons, favoring reduction without deoxygenation of the uranyl(VI) species and further activation of the strong U═O bonds with trapping of the released U^{4+} ions. These results indicate that other oxophilic f and d metal complexes with redox-active ligands could react with a variety of actinyl(V) or -(VI) compounds to provide new efficient routes to homo- and heteropolynuclear oxides, which are of major interest in various fields, from the environment to material sciences and catalysis.

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Supporting Information Available: Table of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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