

Structure of $[(\text{UO}_2)_4\text{O}_2\text{Cl}_4(\text{C}_4\text{H}_8\text{O})_2(\text{H}_2\text{O})_4]$, a Tetranuclear Uranyl(VI) Complex

BY G. VAN DEN BOSSCHE

Institut de Physique B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

M. R. SPIRLET

Physique Expérimentale B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

J. REBIZANT

Commission of the European Communities, JRC Karlsruhe, Postfach 2266, D-7500 Karlsruhe, Federal Republic of Germany

AND J. GOFFART*

Institut de Radiochimie B16, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

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Abstract. *abst*-Tetraqua-*efop*-tetra- μ -chloro-*gn*-di- μ_3 -oxo-*cdijlmqr*-octa-oxo-*hf*-bis(tetrahydrofuran)tetra-uranium, $M_r = 1470.20$, orthorhombic, *Cmca*, $a = 16.865$ (5), $b = 11.017$ (3), $c = 21.747$ (4) Å, $V = 4040$ (3) Å³, $Z = 4$, $D_x = 2.417$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 15.4643$ mm⁻¹, $F(000) = 2544$, $T = 295$ (1) K, $R = 0.051$ for 811 observed reflections. The crystal structure consists of discrete uncharged tetrameric molecules separated by van der Waals contacts. The molecular structure is quite unusual with four uranyl groups linked through double bridges of two types: one double O bridge and four O/Cl bridges. The coordination polyhedron about each U atom is a pentagonal bipyramid with the uranyl O atoms in apical positions while the bridging Cl and O atoms lie in the equatorial plane. The remaining equatorial positions are occupied by tetrahydrofuran or water molecules.

Introduction. In the sphere of our investigation on the bonding and coordination geometry in organoactinide complexes, the title compound has been obtained. We report here its characterization and structure analysis by X-ray diffraction.

Experimental. Treatment by air of a solution of (1,4,7-trimethylindenyl)uranium(IV) trichloride bis(tetrahydrofuran), synthesized as described elsewhere (Beeckman, Goffart, Rebizant & Spirlet, 1986), yielded by oxidation and hydration dark yellow prismatic crystals of the title complex. The chemical formula established by X-ray diffraction was confirmed by elemental analysis. Single crystal (0.3 × 0.2 × 0.2 mm), suitable for X-ray analysis, sealed in a

thin-walled glass capillary under an inert atmosphere. Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell parameters refined by least squares from angle data of 25 reflections with $13 \leq 2\theta \leq 35^\circ$. Space group established from systematic absences and successful refinement. 1935 unique reflections collected (θ – 2θ scan mode) in range $4 \leq 2\theta \leq 50^\circ$ (hkl , $h+k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h \neq 2n$); index range h 0/+24, k 0/+20, l 0/+28.

Three reflections monitored periodically showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects: empirical absorption corrections (transmission factors range from 65.64 to 92.07%). Structure solved by direct methods and Fourier techniques; full-matrix least-squares refinement {minimizing $\sum w(\Delta F)^2$; $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/L_p$ where A , the ignorance factor, is 0.04} on 811 independent reflections with $F^2 \geq 3\sigma(F^2)$. Anisotropic thermal parameters except for the water oxygen atom. Earlier attempts to treat O(w) anisotropically did not result in any improvement of the R factors and its thermal tensor did not remain positive definite. H atoms of THF molecules in calculated positions, included in final structure-factor calculation with an isotropic $B = 5.0$ Å². $R = 0.051$, $wR = 0.073$, $S = 1.75$, $(\Delta/\sigma)_{\text{max}} = 0.01$, $\Delta\rho$ in final difference Fourier map within 1.958 and -0.987 e Å⁻³. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1981) *SDP* programs.

Discussion. The structure may be regarded as being built up from discrete uncharged tetrameric molecules, one of which is drawn separately in Fig. 1; the

* Chercheur qualifié FNRS.

molecular packing is illustrated by Fig. 2. Table 1* contains final atomic positional parameters for the non-H atoms. Some important distances and angles within a tetrameric molecule are given in Table 2. The symmetry code used in the discussion is described in Table 2. The tetrameric molecule has C_{2h} symmetry.

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43648 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

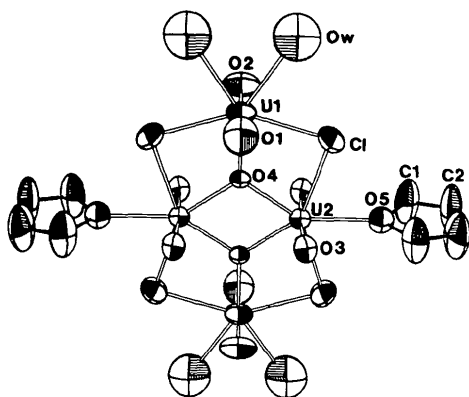


Fig. 1. A view of one tetrameric complex as viewed parallel to the normal of the plane of the four U atoms. The numbering of the atoms is shown. The thermal ellipsoids are scaled to include 50% probability. (H atoms are omitted for clarity.)

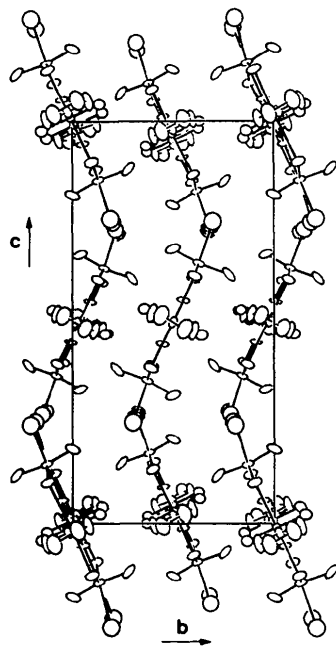


Fig. 2. View of the crystal packing along the *a* axis.

The U atoms of the four uranyl groups form a planar rhomb; they are linked through double bridges of two types. Between U(2) and U(2ⁱ) there is a double O bridge with a U—U distance of 3.682 (3) Å; U(1) and U(2) are joined through an O—Cl bridge with a U—U distance of 3.944 (1) Å. The coordination polyhedron about each uranium is a pentagonal bipyramid with the uranyl oxygens in apical positions. The four pentagonal bipyramids are linked together by sharing edges. The U(1) bipyramid shares the two edges Cl—O(4) and Clⁱⁱ—O(4) of 3.00 (1) Å with the two bipyramids about U(2) and U(2ⁱ) respectively; the U(2) bipyramid shares three edges with the neighbouring bipyramids: Cl—O(4) and Clⁱⁱⁱ—O(4ⁱ) of 3.00 (1) Å with U(1) and U(1ⁱ) respectively and O(4)—O(4ⁱ) of 2.63 (4) Å with U(2ⁱ). Each O(4) oxygen belongs to three uranyl groups and the three O(4)—uranium bonds have an almost trigonal arrangement. One of the three U—O bridge bonds, U(1)—O(4), is very much shorter than the two others, perhaps owing to repulsion between the O(4) and O(4ⁱ) atoms of the double bridge joining U(2) and U(2ⁱ). This could explain the significant discrepancies between the U(1)—X and U(2)—X [X = Cl, O(4)] bonds as well as the short intramolecular contact Cl...O(4) of 3.00 (1) Å. Values of 2.18 (2) and 2.205 (2) Å have

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
U(1)	0.0	0.1288 (2)	0.14650 (8)	5.31 (4)
U(2)	0.10915 (9)	0.0	0.0	3.26 (3)
Cl	0.1579 (5)	0.1064 (9)	0.1122 (4)	6.4 (2)
O(1)	0.0	-0.018 (3)	0.182 (1)	8 (1)
O(2)	0.0	0.278 (3)	0.119 (2)	8 (1)
O(3)	0.114 (1)	0.141 (2)	-0.032 (1)	5.1 (5)
O(4)	0.0	0.051 (3)	0.055 (1)	4.5 (7)
O(5)	0.256 (2)	0.0	0.0	4.4 (6)
O(w)	0.093 (2)	0.196 (3)	0.247 (2)	15 (1)
C(1)	0.310 (2)	-0.098 (3)	0.021 (2)	8 (1)
C(2)	0.387 (2)	-0.054 (4)	0.016 (3)	11 (2)

Table 2. Some important distances (Å) and angles (°) with *e.s.d.*'s in parentheses

U(1)—O(1)	1.79 (3)	U(2)—O(3)	1.71 (2)
U(1)—O(2)	1.75 (3)	U(2)—Cl	2.829 (7)
U(1)—Cl	2.777 (7)	U(2)—O(4)	2.26 (1)
U(1)—O(4)	2.17 (2)	U(2)—O(5)	2.48 (2)
U(1)—O(w)	2.78 (3)	O(5)—C(1)	1.48 (3)
		C(1)—C(2)	1.40 (4)
		C(2)—C(2 ⁱⁱⁱ)	1.38 (6)
O(1)—U(1)—O(2)	174.2 (12)	O(3)—U(2)—O(3 ⁱⁱⁱ)	174.0 (10)
Cl—U(1)—O(4)	73.6 (1)	Cl—U(2)—O(4)	71.3 (4)
Cl—U(1)—O(w)	72.2 (6)	Cl—U(2)—O(5)	73.1 (2)
O(w)—U(1)—O(w ⁱⁱ)	68.5 (13)	O(4)—U(2)—O(4 ⁱ)	71.2 (8)
		U(2)—O(5)—C(1)	128 (1)
		C(1)—O(5)—C(1 ⁱⁱⁱ)	105 (2)
		O(5)—C(1)—C(2)	107 (2)
		C(1)—C(2)—C(2 ⁱⁱⁱ)	110 (2)

Symmetry code: (i) $-x, -y, -z$; (ii) $-x, y, z$; (iii) $x, -y, -z$.

been observed for the shortest U—O bridge bond in similar tetranuclear uranyl complexes (Åberg, 1976; Perrin & Le Marouille, 1977).

The U—O distances in the uranyl groups are in the range of observed values for equatorial coordination when the uranyl oxygens are not further coordinated [mean value: 1.764 Å (*Gmelin Handbook of Inorganic Chemistry*, 1983)]; nevertheless the uranyl groups deviate slightly from linearity with O—U—O angles of 174.2 (12) and 174.0 (10)°, being bent towards the exterior of the molecular unit. The three negatively polarized ligands around U(1) seem to push the O(1) and O(2) uranyl oxygens towards the other two ligands, the two neutral water molecules O(*w*). The bisectrix of the O(1)—U(1)—O(2) angle is effectively directed towards the line joining these two water molecules. Likewise the four negatively polarized ligands around the U(2) atom must push the O(3) uranyl oxygens towards the fifth ligand, the neutral THF oxygen; the bisectrix of the O(3)—U(2)—O(3ⁱⁱⁱ) angle is effectively directed towards the O(5) atom.

Least-squares planes have been calculated through (a) all four uranium atoms U(1), U(1ⁱ), U(2) and U(2ⁱ), (b) the U(1) pentagon, (c) the U(2) pentagon and (d) the uranyl groups of U(1) and U(2). The angles between these planes are respectively (a,b) = 4 (1), (a,c) = 2 (1), (b,c) = 6 (1), (a,d) = 89 (1), (b,d) = 85 (1) and (c,d) = 91 (1)°. The largest deviations from the expected values of 0 and 90° occur for the angles with the plane through the U(1) pentagon; this could be explained by the fact that the bridging Cl and O atoms as well as the THF oxygens lie in the plane of the four U atoms while the water oxygens are 0.21 (4) Å out of

this plane. The THF's form dihedral angles of 89 (2)° with the plane of the four U atoms. The bond distances in the THF molecules are foreshortened compared with the values expected for a single conformation, the thermal vibrations principally of the terminal C atoms being large (Table 1). Such disorder in THF with the outermost carbon atoms elongated perpendicular to the ring has been observed in many other crystals Reynold, Zalkin & Templeton, 1977; Rietz, Edelstein, Ruben, Templeton & Zalkin, 1978; Smith & Raymond, 1979).

There are no short intermolecular interactions that could correspond to hydrogen bonds so that the stacking in the crystal is assumed to be mainly a result of van der Waals interactions.

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Structure of *trans*-Dibromotetrakis(pyridine)rhodium(III) Bromide Hexahydrate

BY MARIEL M. MUIR, GRISELL M. GOMEZ, JAMES A. MUIR AND SERGIO SANCHEZ

Departments of Chemistry and Physics, University of Puerto Rico, Rio Piedras, PR 00931, USA

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Abstract. $[\text{RhBr}_2(\text{C}_5\text{H}_5\text{N})_4]\text{Br}\cdot 6\text{H}_2\text{O}$, $M_r = 767.2$, monoclinic, $P2_1/c$, $a = 12.663$ (3), $b = 10.703$ (3), $c = 21.585$ (7) Å, $\beta = 98.19$ (2)°, $V = 2895.6$ Å³, $Z = 4$, $D_x = 1.76$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 46.20$ cm⁻¹, $F(000) = 1512$, $T = 296$ K, final $R = 0.047$ for 2438 observed reflections. The crystal structure is composed of *trans*- $[\text{Rh}(\text{py})_4\text{Br}_2]^+$ cations packed in layers separated by Br⁻ anions and H₂O molecules. The Rh atom has a nearly regular octahedral geometry with an average Rh—N bond length of

2.069 (2) Å and an average Rh—Br bond length of 2.478 (1) Å.

Introduction. The study of photoaquation reactions of Rh^{III} complexes has increased in the past few years (Muir & Huang, 1973; Ford & Petersen, 1975; Clark & Petersen, 1981; Muir, Zinner, Paguaga & Torres, 1982). For complexes of the type *trans*- $[\text{Rh}(A)_4X_2]^+$, where *A* is a heterocyclic amine and *X* is Cl or Br, both photoaquation of halide and amine have been obtained