

Structure of Barium Tetrakis[oxalato(2-)-O¹,O²]uranium(IV) Octahydrate

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Abstract. Ba₂U(C₂O₄)₄·8H₂O, $M_r = 1008.91$, monoclinic, $C2/c$, $a = 10.388(2)$, $b = 28.703(3)$, $c = 9.261(1)$ Å, $\beta = 123.55(1)^\circ$, $V = 2301(1)$ Å³, $Z = 4$, $D_x = 2.912$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 101.366$ cm⁻¹, $F(000) = 1840$, $T = 295(1)$ K, $R = 0.029$ for 1823 observed reflections. The U atom is nine-coordinated to four oxalate groups acting as bidentate ligands and to one water molecule. The coordination geometry about the U atom is between tricapped trigonal prism and capped square antiprism. The crystal packing involves a remarkable network of Ba–O interactions and O–O hydrogen bonds.

Introduction. The present work forms part of a study on the stereochemistry of highly coordinated actinide(IV) complexes. Among oxalate derivatives, structural data only exist for K₄[Th(C₂O₄)₄]·4H₂O (Akhtar & Smith, 1975) and for the two polymorphs of the uranium analogue K₄[U(C₂O₄)₄]·4H₂O (Favas, Kepert, Patrick & White, 1983). In both complexes the actinide ion is ten-coordinate with bidentate and bridging quadridentate oxalate ligands, so that the structure consists of infinite polymeric chains parallel to a crystallographic axis. We investigate here the structure of a novel oxalato complex of uranium(IV) with barium as cation, considering the possibility of a new stoichiometry or stereochemical type.

Experimental. Single crystals of Ba₂U(C₂O₄)₄·8H₂O obtained by reaction of a solution of BaCl₂ in 3M hydrochloric acid and 1M oxalic acid with uranium(IV) oxalate hexahydrate, U(C₂O₄)₂·6H₂O. Intensity data recorded at 295(1) K on an Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Crystal size 0.25 × 0.30 × 0.35 mm. Cell parameters refined by least squares from angle data of 25 reflections ($10 < 2\theta < 19^\circ$). Systematic absences consistent with space

groups Cc and $C2/c$. 2405 reflections collected (θ – 2θ scan mode) in range $4 \leq 2\theta \leq 50^\circ$, index range $h -9/+12$, $k 0/+34$, $l 0/-10$, 2167 considered observed [$I > \sigma(I)$], averaged to 2083 unique reflections ($R_{\text{int}} = 0.01$). Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption correction (transmission factors range from 53.05 to 99.86%). Structure solved by direct methods. Position of U and Ba atoms deduced from E map. Successive difference Fourier synthesis and LS refinement revealed the position of the light atoms except H and permitted the exclusion of the alternative non-centrosymmetric space group Cc . Full-matrix least-squares refinement [minimizing $\sum w(\Delta F)^2$] on 1823 independent reflections with $F^2 \geq 3\sigma(F^2)$, $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{1/2}/Lp$, A (the ignorance factor) = 0.04. Anisotropic thermal parameters except for water O atoms. An attempt to treat the water O atoms anisotropically did not result in any significant improvements of the R factors and some of the thermal tensors did not remain positive definite. Final agreement factors: $R = 0.029$, $wR = 0.046$, $S = 1.698$, $(\Delta/\sigma)_{\text{max}} = 0.01$, $\Delta\rho$ in final difference Fourier map within $+1.8$ and -1.3 e Å⁻³. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1979) *SDP* programs.

Discussion. Final atomic parameters are given in Table 1 and selected bond distances and angles in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43302 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

$$B_{eq} = \frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\alpha B(1,2) + acc\cos\beta B(1,3) + bcc\cos\gamma B(2,3)].$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
U	0.500	0.10745 (1)	0.250	1.518 (7)
Ba(1)	0.000	0.22776 (2)	0.250	2.07 (1)
Ba(2)	0.500	0.46579 (2)	0.250	1.84 (1)
C(1)	0.4064 (6)	0.1893 (2)	0.4164 (7)	2.2 (1)
O(1)	0.3582 (5)	0.1679 (2)	0.2747 (5)	2.8 (1)
O(1')	0.3354 (5)	0.2175 (2)	0.4447 (5)	2.7 (1)
C(2)	0.5738 (7)	0.1759 (3)	0.5614 (7)	2.4 (1)
O(2)	0.6387 (4)	0.1458 (2)	0.5224 (5)	2.1 (1)
O(2')	0.6332 (6)	0.1945 (2)	0.7068 (6)	4.6 (1)
C(3)	0.3051 (6)	0.0529 (2)	0.3752 (6)	1.7 (1)
O(3)	0.4277 (5)	0.0754 (2)	0.4388 (5)	2.4 (1)
O(3')	0.2654 (5)	0.0272 (2)	0.4529 (5)	2.6 (1)
C(4)	0.1928 (6)	0.0570 (2)	0.1754 (6)	1.8 (1)
O(4)	0.2449 (4)	0.0772 (2)	0.0961 (5)	2.2 (1)
O(4')	0.0622 (5)	0.0410 (2)	0.1050 (5)	3.1 (1)
O(W1)	0.500	0.0179 (3)	0.250	2.8 (1)*
O(W2)	0.500	0.3675 (5)	0.250	7.0 (3)*
O(W3)	0.7534 (6)	0.0639 (3)	0.7697 (7)	4.5 (1)*
O(W4)	0.118 (1)	0.1503 (5)	0.474 (1)	12.6 (4)*
O(W5)	0.106 (2)	0.2163 (5)	-0.003 (2)	16.8 (6)*

Table 2. Uranium-ligand distances and shape characteristics of the coordination polyhedron about the U atom

Superscript (i) refers to the twofold symmetry operation: $-x, y, \frac{1}{2}-z$.

(a) U—O bond distances (Å)

U—O(1)	2.366 (4)	U—O(3)	2.433 (4)
U—O(2)	2.374 (3)	U—O(W1)	2.569 (6)
U—O(4)	2.374 (4)		

(b) Lengths of the polyhedron edges (Å)

O(2)—O(1)	2.601 (5)	O(2)—O(1')	2.841 (5)
O(3)—O(4)	2.649 (5)	O(1)—O(3)	2.944 (6)
O(2)—O(3)	2.760 (5)	O(1)—O(4)	2.958 (6)
O(W1)—O(4)	2.788 (5)	O(1)—O(1')	3.222 (6)
O(W1)—O(3)	2.791 (5)	O(3)—O(4)	3.590 (5)
O(2)—O(3')	2.831 (5)		

(c) δ angles ($^\circ$): Selected dihedral angles between adjacent polytopal faces compared with ideal values taken from Drew (1977)

Values observed	Ideal values in		
	TCTP	CSAP [capped with O(2)]	CSAP [capped with O(W1)]
O(W1)O(3)—O(4)O(2)	17.1	25.8 (29.1)	0.0
O(2)O(3)—O(4)O(W1)	17.1	25.8 (29.1)	37.4
O(2)O(1)—O(1')O(2)	33.7	25.8 (29.1)	0.0
O(2)O(3)—O(1)O(4)	44.9	47.5 (47.2)	37.4
O(2)O(1')—O(4)O(3)	45.3	47.5 (47.2)	51.6
O(W1)O(3)—O(4)O(1)	51.0	47.5 (47.2)	51.6
O(W1)O(4')—O(3)O(1')	51.0	47.5 (47.2)	51.6
O(2)O(1')—O(3)O(4)	44.9	47.5 (47.2)	51.6
O(2)O(1)—O(4)O(3)	45.3	47.5 (47.2)	51.6

(d) Dihedral angles between LS planes ($^\circ$)

Maximum deviation from LS plane (Å)

Plane 1: O(1), O(3), O(4)	
Plane 2: O(1'), O(3'), O(4')	
Plane 3: O(W1), O(4), O(2), O(3')	0.16 (3)
Plane 4: O(4), O(1'), O(1), O(2)	0.04 (2)
Plane 5: O(3), O(4), O(3'), O(4')	0.03 (2)
Plane 6: O(1), O(2), O(2'), O(1')	0.32 (2)

Dihedral angles

1/2	8.1 (2)
3/4	3.1 (2)
5/6	0.0 (2)

The crystal structure is made up of independent monomeric $[\text{U}(\text{C}_2\text{O}_4)_4\cdot\text{H}_2\text{O}]^{4-}$ anions (Fig. 1). Ba cations and water molecules occupy the spaces between the anions and support the crystal packing through Ba—O and O—O (probable hydrogen bonding) interactions (see Fig. 3).

In the $[\text{U}(\text{C}_2\text{O}_4)_4\cdot\text{H}_2\text{O}]^{4-}$ anion, as illustrated in Fig. 1, the oxalate groups are coordinated as bidentate ligands to the U atom which is also linked to one water O atom, having therefore a coordination number of nine.

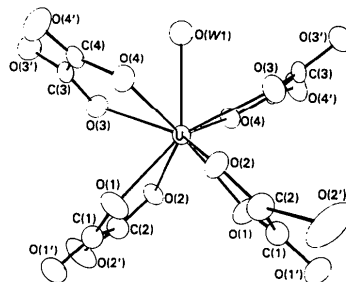


Fig. 1. The $[\text{U}(\text{C}_2\text{O}_4)_4\cdot\text{H}_2\text{O}]^{4-}$ anion.

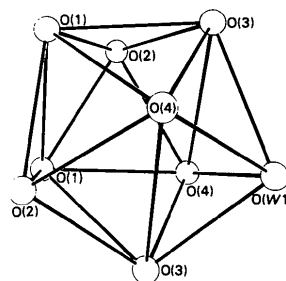


Fig. 2. The coordination polyhedron about the U atom.

Table 3. Ba—O bond distances and O—O close contacts (Å) (< 3.10 Å)

Ba(1)—O(2 ⁱⁱ)	2.769 (5)	Ba(2)—O(3 ^{iv})	2.917 (4)
Ba(1)—O(1 ⁱⁱ)	2.837 (4)	Ba(2)—O(4 ^{iv})	2.986 (4)
Ba(1)—O(1')	2.921 (4)	Ba(2)—O(4 ^{iv})	3.042 (4)
Ba(1)—O(W4)	2.82 (1)	Ba(2)—O(W3)	2.800 (5)
Ba(1)—O(W5)	3.11 (1)	Ba(2)—O(W2)	2.82 (1)
Ba(2)—O(4 ⁱⁱⁱ)	2.799 (4)		
O(1)—O(W5)	2.82 (1)	O(3')—O(W1 ^{iv})	2.788 (5)
O(1')—O(W4)	3.09 (1)	O(3')—O(W3 ⁱⁱⁱ)	2.881 (6)
O(2)—O(W3)	3.028 (7)	O(4)—O(W1)	2.788 (5)
O(2')—O(W4 ^{iv})	2.93 (1)	O(4')—O(W3 ^{iv})	3.059 (6)
O(3)—O(W1)	2.791 (5)	O(W2)—O(W5)	3.07 (2)
O(3)—O(W3)	3.080 (8)		

Symmetry code: (ii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (v) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (vi) $1-x, y, \frac{1}{2}-z$; (vii) $x, -y, \frac{1}{2}+z$; (viii) $1-x, y, 1-z$; (ix) $-1+x, y, -1+z$.

The coordination polyhedron, illustrated in Fig. 2, has imposed C_2 symmetry, the U and the water O [O(W1)] atoms lying on a crystallographic twofold axis. Its geometry (Table 2) may be described as intermediate between the tricapped trigonal prism (TCTP) of symmetry D_{3h} and the capped square antiprism (CSAP) of symmetry C_{4v} . The distortion from TCTP towards CSAP is shown by the δ angles (Drew, 1977) reported in Table 2, and especially by the three δ angles over the v edges. Two possible CSAP's can be derived from the TCTP depending on which of the capping atoms [O(W1) or O(2)] in the TCTP polyhedron is chosen as capping atom in the CSAP. One would expect the CSAP with O(W1) as capping atom to be the most appropriate choice, but geometrical features (Table 3) indicate that the distortion is towards the CSAP, capped with the oxalate O(2) atom [c111 isomer among the seven isomers proposed for the form $M(\text{unidentate})(\text{bidentate})_4$ by Drew (1977)]. This observation is in agreement with the results of calculations in the hard-sphere model (Burgi, 1973), which predict that s_1 edges are unsuitable for a bidentate ligand.

The crystal packing is illustrated in Fig. 3. Ba—O and O—O (probable hydrogen bonds) contacts are reported in Table 3. There are two symmetrically non-equivalent Ba atoms per asymmetric unit. They interact with the oxalate O atoms which are not coordinated to the U atom. The oxalate groups thus behave as quadridentate

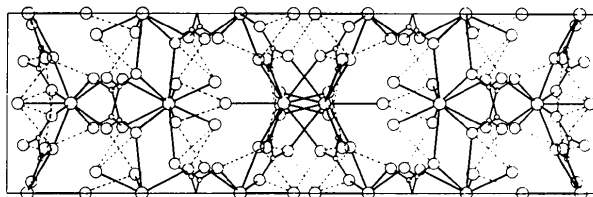


Fig. 3. View of the unit cell along the c axis.

ligands, acting as bridges between the U and Ba atoms. The two Ba atoms are also coordinated to the nearest-neighbour water O atoms and reach coordination number ten [Ba(1)] or eleven [Ba(2)]. The high temperature factors of the water O atoms O(W4) and O(W5) indicate some disorder in the relatively large holes of the packing.

References

- AKHTAR, M. N. & SMITH, A. J. (1975). *Acta Cryst.* B31, 1361–1366.
 BURGI, H. B. (1973). *Inorg. Chem.* 12, 2321–2325.
 DREW, M. G. B. (1977). *Coord. Chem. Rev.* 24, 179–275.
 Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft.
 FAVAS, M. C., KEPERT, D. L., PATRICK, J. M. & WHITE, A. H. (1983). *J. Chem. Soc. Dalton Trans.* pp. 571–581.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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Structure of *trans*-Diiodobis(triphenylstibine)palladium(II) and Observations on the Pd—I Bond Length

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Abstract. $[\text{PdI}_2\{(\text{C}_6\text{H}_5)_3\text{Sb}\}_2]$, $M_r = 1066.34$, triclinic, $P\bar{1}$, $a = 10.005$ (1), $b = 10.121$ (1), $c = 10.208$ (1) Å, $\alpha = 105.70$ (1), $\beta = 93.53$ (1), $\gamma = 116.96$ (1)°, $V = 866.3$ (2) Å³, $Z = 1$, $F(000) = 500$, $D_x = 2.044$, $D_m = 2.0$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 38.5$ cm⁻¹. Final $R = 0.054$, $wR = 0.050$ for 2134 reflections with $I \geq 2\sigma(I)$. Room temperature. The title compound is a centrosymmetric four-coordinate complex with no

unusually short intermolecular contacts. The Pd—I distance of 2.590 (1) Å is in agreement with the average of 2.596 (12) Å from 19 reported Pd—I distances when I, N or S is the *trans* atom. The Pd—I distance increases to 2.653 (11) Å when P, As or C is the *trans* atom. A *trans* effect causes the Pd—Sb distance of 2.578 (1) Å to be significantly longer than in the only other known Pd—Sb complex [2.506 (1) and 2.527 (1) Å].