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Structure of Tetrakis(cyclopentadienyl)uranium(IV) Acetate Dioxide*

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Abstract. $[U(C_5H_5)(CH_3CO_2)_2]_4O_2$, $M_r = 2 \times 858.43$, triclinic, $P\bar{1}$, $a = 9.354\,(4)$, $b = 12.988\,(5)$, $c = 19.613\,(7)$ Å, $\alpha = 82.74\,(3)$, $\beta = 98.24\,(3)$, $\gamma = 102.89\,(4)°$, $V = 2287.6$ Å^3, $Z = 4$, $D_x = 2.492$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 134.501$ cm^{-1}, $F(000) = 1544$, $T = 295\,(1)$ K, $R = 0.043$ for 3390 reflections $[I > 3\sigma(I)]$. In this tetrameric complex, each U^{IV} atom is seven coordinated in a distorted pentagonal-bipyramidal geometry. The bridging between U atoms occurs through acetate and oxide O atoms. The cyclopentadienyl ligands occupy the apical coordination sites of the bipyramids.

Introduction. Acetate ions can function as both monodentate and bidentate ligands but the crystallochemical factors which favour one of these two coordinations are not known. The title compound is a product obtained while attempting to synthesize tris(cyclopentadienyl)uranium acetate.

Within the large series of cyclopentadienyl complexes of uranium(IV), the title compound is the first observed where the uranium(IV) exhibits a coordination number of seven. Its characterization and structure analysis by single-crystal X-ray diffraction is reported here.

Experimental. $[U(C_5H_5)(CH_3CO_2)_2]_4O_2$ was obtained from partial hydrolysis of $[U(C_5H_5)_3(CH_3CO_2)]$ in tetrahydrofuran solution. Recrystallization in *n*-pentane yielded green prismatic single crystals. The selected specimen (0.30 × 0.30 × 0.40 mm) was sealed in a thin-walled glass capillary under an inert atmosphere. X-ray diffraction data were measured with an Enraf–Nonius CAD-4 X-ray diffractometer using graphite-monochromated Mo $K\alpha$ radiation and θ–2θ scans. The unit-cell dimensions were determined from 25 reflections in the range $4 \leq 2\theta \leq 44°$. No systematic absences were detected. Intensity data were collected in the range $4 \leq 2\theta \leq 45°$, $h\ -11 \rightarrow 0$, $k\ -15 \rightarrow 15$, $l\ -23 \rightarrow 23$; 5947 unique reflections were collected, 3390 of which were considered observed $[I \geq 3\sigma(I)]$ and used in refinement. The intensities of three standard reflections measured at 30 min intervals showed no deviations from the mean. The intensities were corrected for Lorentz–polarization effects. Empirical absorption corrections were also applied using the program *DIFABS*

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* Octa-μ-acetato-di-μ-oxo-tetrakis[(cyclopentadienyl)uranium-(IV)].

† On leave from University of Liège, Belgium.

Table 1. *Atomic positional parameters and isotropic thermal parameters* (Å^2)

E.s.d.'s are given in parentheses.

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)].$$

	x	y	z	B_{eq}/B_{iso}
Molecule 1				
U(1)	0.19541 (8)	0.04692 (6)	0.12646 (4)	2.45 (2)
U(2)	0.07387 (8)	0.22079 (6)	−0.04189 (4)	2.59 (2)
O(1)*	0.116 (1)	0.092 (1)	0.0279 (6)	2.7 (3)
O(2)	0.377 (1)	0.204 (1)	0.1103 (6)	3.2 (3)
O(3)	0.296 (2)	0.305 (1)	0.0193 (7)	4.8 (4)
O(4)	0.066 (1)	0.170 (1)	0.1525 (7)	3.7 (4)
O(5)	−0.018 (2)	0.262 (1)	0.0564 (7)	4.2 (4)
O(6)	−0.047 (1)	−0.078 (1)	0.1255 (6)	3.7 (4)
O(7)	−0.264 (1)	−0.174 (1)	0.1034 (7)	3.8 (4)
O(8)	0.177 (1)	−0.122 (1)	0.0671 (6)	3.2 (3)
O(9)	0.388 (1)	−0.012 (1)	0.0741 (7)	4.1 (4)
C(1)	0.203 (2)	−0.093 (2)	0.247 (1)	4.2 (5)†
C(2)	0.352 (3)	0.073 (2)	0.228 (1)	4.7 (5)†
C(3)	0.405 (3)	0.031 (2)	0.239 (1)	4.8 (6)†
C(4)	0.302 (3)	0.076 (2)	0.265 (1)	5.1 (6)†
C(5)	0.184 (2)	0.000 (2)	0.268 (1)	4.4 (5)†
C(6)	0.064 (2)	0.346 (2)	−0.167 (1)	3.8 (5)†
C(7)	0.173 (3)	0.409 (2)	−0.121 (1)	4.9 (6)†
C(8)	0.094 (2)	0.432 (2)	−0.072 (1)	4.2 (5)†
C(9)	−0.056 (3)	0.394 (2)	−0.090 (1)	5.5 (6)†
C(10)	−0.078 (2)	0.337 (2)	−0.147 (1)	3.8 (5)†
C(11)	0.391 (2)	0.283 (2)	0.0667 (9)	2.8 (5)
C(12)	0.538 (2)	0.367 (2)	0.075 (1)	4.3 (6)
C(13)	−0.000 (3)	0.2542 (2)	0.121 (1)	4.3 (6)
C(14)	−0.074 (3)	0.307 (2)	0.162 (1)	5.8 (6)
C(15)	−0.186 (2)	−0.096 (2)	0.130 (1)	3.2 (5)
C(16)	−0.242 (3)	−0.019 (2)	0.166 (1)	5.1 (7)
C(17)	0.315 (2)	−0.098 (2)	0.0556 (9)	3.5 (5)
C(18)	0.378 (2)	−0.172 (2)	0.020 (1)	4.7 (6)
Molecule 2				
U(3)	0.31246 (8)	0.30173 (6)	0.54065 (4)	2.74 (2)
U(4)	0.41542 (9)	0.44506 (7)	0.35981 (4)	3.04 (2)
O(10)*	0.383 (1)	0.415 (1)	0.4621 (6)	2.7 (3)
O(11)	0.444 (2)	0.203 (1)	0.4878 (7)	5.2 (4)
O(12)	0.511 (2)	0.288 (1)	0.3872 (7)	4.4 (4)
O(13)	0.136 (2)	0.237 (1)	0.4512 (7)	4.9 (4)
O(14)	0.197 (2)	0.314 (1)	0.3478 (7)	5.7 (5)
O(15)	0.552 (1)	0.364 (1)	0.6058 (6)	3.4 (4)
O(16)	0.773 (2)	0.446 (1)	0.6442 (7)	5.2 (4)
O(17)	0.331 (1)	0.470 (1)	0.5993 (6)	3.5 (4)
O(18)	0.116 (1)	0.402 (1)	0.5465 (7)	3.5 (3)
C(19)	0.307 (3)	0.196 (2)	0.672 (1)	4.8 (6)†
C(20)	0.338 (3)	0.122 (2)	0.633 (1)	6.7 (7)†
C(21)	0.207 (3)	0.095 (2)	0.588 (1)	5.9 (6)†
C(22)	0.097 (3)	0.151 (2)	0.601 (1)	4.7 (5)†
C(23)	0.163 (2)	0.215 (2)	0.657 (1)	4.2 (5)†
C(24)	0.318 (3)	0.477 (2)	0.221 (1)	5.6 (6)†
C(25)	0.430 (3)	0.569 (2)	0.233 (1)	4.4 (5)†
C(26)	0.569 (3)	0.532 (2)	0.246 (1)	6.0 (6)†
C(27)	0.538 (3)	0.425 (2)	0.242 (1)	6.2 (7)†
C(28)	0.377 (3)	0.388 (2)	0.227 (1)	6.1 (7)†
C(29)	0.509 (2)	0.216 (2)	0.434 (1)	3.7 (6)
C(30)	0.574 (3)	0.121 (2)	0.422 (1)	7.2 (8)
C(31)	0.116 (2)	0.251 (2)	0.386 (1)	4.4 (6)
C(32)	−0.023 (3)	0.183 (2)	0.350 (1)	6.4 (7)
C(33)	0.693 (2)	0.370 (2)	0.615 (1)	4.6 (6)
C(34)	0.758 (3)	0.284 (2)	0.596 (1)	5.6 (7)
C(35)	0.192 (2)	0.476 (2)	0.580 (1)	3.5 (5)
C(36)	0.127 (3)	0.560 (2)	0.598 (1)	5.8 (7)

* Oxide O atoms.

† Atoms refined isotropically (cyclopentadienyl C atoms).

Table 2. *Selected distances* (Å) *and angles* (°)

E.s.d.'s are given in parentheses. Cp denotes centroid of ring

Molecule 1		Molecule 2	
U(1)—C(1)	2.80 (2)	U(3)—C(19)	2.77 (2)
U(1)—C(2)	2.82 (2)	U(3)—C(20)	2.80 (3)
U(1)—C(3)	2.76 (2)	U(3)—C(21)	2.74 (2)
U(1)—C(4)	2.79 (2)	U(3)—C(22)	2.76 (2)
U(1)—C(5)	2.77 (2)	U(3)—C(23)	2.82 (2)
U(1)—Cp(I)	2.53 (2)	U(3)—Cp(III)	2.50 (2)
U(1)—O(1)*	2.03 (1)	U(3)—O(10)*	2.06 (1)
U(1)—O(2)	2.37 (1)	U(3)—O(11)	2.37 (1)
U(1)—O(4)	2.36 (1)	U(3)—O(13)	2.33 (1)
U(1)—O(6)	2.47 (1)	U(3)—O(15)	2.44 (1)
U(1)—O(8)	2.58 (1)	U(3)—O(17)	2.56 (1)
U(1)—O(9)	2.50 (1)	U(3)—O(18)	2.49 (1)
U(2)—C(6)	2.77 (2)	U(4)—C(24)	2.76 (2)
U(2)—C(7)	2.77 (2)	U(4)—C(25)	2.79 (2)
U(2)—C(8)	2.70 (2)	U(4)—C(26)	2.81 (2)
U(2)—C(9)	2.79 (2)	U(4)—C(27)	2.78 (2)
U(2)—C(10)	2.81 (2)	U(4)—C(28)	2.76 (2)
U(2)—Cp(II)	2.50 (2)	U(4)—Cp(IV)	2.50 (2)
U(2)—O(1)*	2.10 (1)	U(4)—O(10)*	2.05 (1)
U(2)—O(3)	2.35 (1)	U(4)—O(12)	2.38 (1)
U(2)—O(5)	2.38 (1)	U(4)—O(14)	2.35 (1)
U(2)—O(6^{i})	2.57 (1)	U(4)—O(15^{i})	2.59 (1)
U(2)—O(7^{i})	2.50 (1)	U(4)—O(16^{i})	2.48 (1)
U(2)—O(8^{i})	2.42 (1)	U(4)—O(17^{i})	2.45 (1)
Cp(I)—U(1)—O(1)*	178.4 (4)	Cp(III)—U(3)—O(10)*	176.3 (4)
Cp(I)—U(1)—O(2)	98.0 (4)	Cp(III)—U(3)—O(11)	96.1 (4)
Cp(I)—U(1)—O(4)	97.6 (4)	Cp(III)—U(3)—O(13)	95.1 (4)
Cp(I)—U(1)—O(6)	95.2 (6)	Cp(III)—U(3)—O(15)	95.8 (4)
Cp(I)—U(1)—O(8)	100.0 (4)	Cp(III)—U(3)—O(17)	103.4 (4)
Cp(I)—U(1)—O(9)	94.4 (4)	Cp(III)—U(3)—O(18)	94.6 (4)
O(1)*—U(1)—O(2)	83.1 (4)	O(10)*—U(3)—O(11)	81.3 (4)
O(1)*—U(1)—O(4)	82.4 (4)	O(10)*—U(3)—O(13)	81.8 (4)
O(1)*—U(1)—O(6)	83.6 (4)	O(10)*—U(3)—O(15)	86.6 (4)
O(1)*—U(1)—O(8)	78.6 (4)	O(10)*—U(3)—O(17)	80.2 (4)
O(1)*—U(1)—O(9)	86.1 (4)	O(10)*—U(3)—O(18)	86.8 (4)
O(2)—U(1)—O(4)	80.9 (4)	O(11)—U(3)—O(13)	78.6 (6)
O(2)—U(1)—O(9)	76.4 (4)	O(11)—U(3)—O(15)	83.9 (5)
O(4)—U(1)—O(6)	84.6 (4)	O(13)—U(3)—O(18)	78.9 (5)
O(6)—U(1)—O(8)	65.1 (4)	O(15)—U(3)—O(17)	65.6 (4)
O(8)—U(1)—O(9)	50.5 (4)	O(17)—U(3)—O(18)	51.0 (4)
Cp(II)—U(2)—O(1)	175.5 (4)	Cp(IV)—U(4)—O(10)	178.0 (4)
Cp(II)—U(2)—O(3)	94.6 (4)	Cp(IV)—U(4)—O(12)	99.1 (4)
Cp(II)—U(2)—O(5)	97.4 (4)	Cp(IV)—U(4)—O(14)	96.2 (4)
Cp(II)—U(2)—O(6^{i})	104.0 (4)	Cp(IV)—U(4)—O(15^{i})	102.1 (4)
Cp(II)—U(2)—O(7^{i})	97.0 (4)	Cp(IV)—U(4)—O(16^{i})	96.4 (4)
Cp(II)—U(2)—O(8^{i})	100.9 (4)	Cp(IV)—U(4)—O(17^{i})	95.7 (4)
O(1)*—U(2)—O(3)	81.0 (4)	O(10)*—U(4)—O(12)	80.9 (5)
O(1)*—U(2)—O(5)	81.1 (4)	O(10)*—U(4)—O(14)	81.8 (4)
O(1)*—U(2)—O(6)*	79.4 (4)	O(10)*—U(4)—O(15^{i})	78.9 (4)
O(1)*—U(2)—O(7)*	82.9 (4)	O(10)*—U(4)—O(16^{i})	82.9 (4)
O(1)*—U(2)—O(8)*	88.3 (4)	O(10)*—U(4)—O(17^{i})	86.3 (4)
O(3)—U(2)—O(5)	79.7 (5)	O(12)—U(4)—O(14)	79.3 (5)
O(3)—U(2)—O(7^{i})	78.0 (5)	O(12)—U(4)—O(17^{i})	82.4 (5)
O(5)—U(2)—O(8^{i})	83.6 (4)	O(14)—U(4)—O(16^{i})	79.2 (5)
O(6^{i})—U(2)—O(7^{i})	50.2 (4)	O(15^{i})—U(4)—O(16^{i})	50.7 (4)
O(6^{i})—U(2)—O(8^{i})	65.9 (4)	O(15^{i})—U(4)—O(17^{i})	65.1 (4)

Symmetry code: (i) atoms obtained by inversion through the centre of symmetry of the tetrameric units.

* Oxide O atoms.

(Walker & Stuart, 1983); the minimum and maximum transmission coefficients were 0.7986 and 1.2916. The structure was solved by direct methods and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$: $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I) + (AI)^2]^{1/2}/\mathrm{Lp}$, where the ignorance factor $A = 0.06$. Anisotropic thermal parameters were used for U, O and acetate atoms. The cyclopentadienyl C atoms were refined isotropically. H atoms were not included. A secondary-extinction coefficient refined to a value of $g = 8.4 \times 10^{-8}$ $\{F_c = F_c/[1 + g(F_c^2\mathrm{Lp})]\}$. The refinement converged to $R = 0.043$, $wR = 0.054$, $S = 1.45$, $(\Delta/\sigma)_{\max} = 0.02$. Maximum and minimum $\Delta\rho$ values in final difference Fourier map were 1.96 and -1.46 e Å^{-3}, the highest peaks being close to the U atoms. Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The programs used were from the Enraf–Nonius (1986) *SDP* system.

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are reported in Table 2. The molecular structure is presented in Fig. 1 (Johnson, 1976). The crystal structure consists of two symmetrically independent tetrameric modules in the unit cell, each of symmetry C_i^1 {the inversion centres are at (000) and ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) respectively for molecule 1 [U(1), U(2)] and molecule 2 [U(3), U(4)]}. In the tetrameric molecules, each U atom is seven coordinated in a distorted pentagonal-bipyramidal geometry. The pentagonal base of the bipyramid is defined by five O atoms which belong to four distinct acetate ligands assuming bridging between neighbouring U atoms (Fig. 1). Two of the bridging acetate groups are monodentate simultaneously towards two neighbouring U atoms. The other two acetate groups bridge by sharing one O between two U atoms, being monodentate with respect to one U and bidentate with respect to its neighbour. The bridging between the U atoms also occurs through one oxide O atom occupying the common apex of two adjacent bipyramids. The cyclopentadienyl ligands, one for each U, lie on the non-bridged apical coordination sites of the bipyramids. As expected, the cyclopentadienyl ligands are pentahapto bonded to the U atoms. The averaged U—C distance is 2.78 (2) Å. Corresponding U—O bond distances, in two tetrameric molecules, are in quite good agreement with an average value of 2.36 (1) Å for O atoms bonded to only one U in a monodentate mode (eight such), of 2.49 (1) Å for O atoms bonded to only one U in a bidentate mode (four such) and of 2.45 (1) and 2.581 (1) Å for bridging O atoms (four such) bonded simultaneously to two neighbouring U atoms in a monodentate mode and in a bidentate mode of bonding, respectively. There are no intermolecular distances shorter than normal van der Waals contacts.

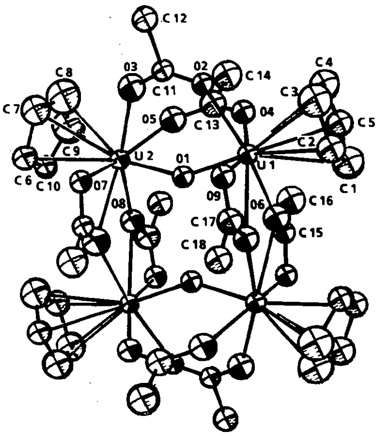

Fig. 1. The molecular structure. Thermal ellipsoids are at the 50% probability level.

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* Lists of structure amplitudes, anisotropic thermal parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54592 (35 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Zinc(II) with Tetradentate N_2S_2 Ligation

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Abstract. *trans*-3,3′-(1,2-Cyclohexanediyldinitrilo)bis(2-methylpropane-2-thiolato)]zinc(II), $[Zn(C_{14}H_{28}N_2S_2)]$, Zn(2), $M_r = 353.89$, monoclinic, $C2/c$, $a = 17.914$ (4), $b = 9.440$ (1), $c = 10.877$ (2) Å, $\beta = 110.19$ (2)°, $V = 1726$ (1) Å^3, $Z = 4$, $D_m = 1.35$ (1), $D_x = 1.360$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0.71073$ Å) = 0.17 mm^{-1}, $F(000) = 752$, $T = 298$ (1) K, $R_F = 0.026$, $wR_F = 0.037$ for 1290 reflections. 3,3′-(1,2-Cyclohexa-1,4-dienediyldinitrilo)bis(2-methylpropane-2-thiolato)]zinc(II), $[Zn(C_{14}H_{24}N_2S_2)]$, Zn(3), $M_r = 349.86$, monoclinic, $P2_1/c$, $a = 9.760$ (2), $b = 17.326$ (3), $c = 10.530$ (2) Å, $\beta = 91.49$ (2)°, $V =$

0108-2701/92/030454-04$03.00