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## Structure of Dinitratodioxobis(triisobutyl phosphate)uranium(VI) at 139 K\*

BY JOHN H. BURNS AND GEORGE M. BROWN

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

AND ROBERT R. RYAN

*Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545, USA*

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**Abstract.**  $[\text{UO}_2(\text{NO}_3)_2(\text{C}_{12}\text{H}_{27}\text{O}_4\text{P})_2]$ ,  $M_r = 926.64$ , triclinic,  $P\bar{1}$ ,  $a = 8.54$  (1),  $b = 10.298$  (2),  $c = 11.501$  (6) Å,  $\alpha = 98.15$  (3),  $\beta = 106.38$  (7),  $\gamma = 101.86$  (4)°,  $V = 928.0$  Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.66$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha_1) = 0.70926$  Å,  $\mu = 39.2$  cm<sup>-1</sup>,  $F(000) = 462$ ,  $T = 139$  K, final  $R(F) = 0.022$  for 2419 reflections. Crystals are composed of discrete centrosymmetric molecules containing a linear uranyl ion equatorially coordinated by two bidentate nitrate ions and two monodentate triisobutyl phosphate molecules. The U=O bond length is 1.758 (3) Å and has a Zachariasen bond strength of 2. Equatorial U–O lengths are 2.371 (4) Å to phosphate and 2.508 (4) and 2.511 (4) Å to nitrate O atoms. All other bond lengths and angles are also within the normal range.

**Introduction.** Organophosphorus compounds are widely used to extract U<sup>VI</sup> from solution in strong acids (Sekine & Hasegawa, 1977), and it is of interest to know the structures of the extraction complexes formed (Burns, 1981, 1983). The most frequently employed neutral extractant, tri-*n*-butyl phosphate (tbp), forms a

complex  $\text{UO}_2(\text{tbp})_2(\text{NO}_3)_2$  that is a liquid at room temperature (Healy & McKay, 1956). However, the analog with triisobutyl phosphate (tibp) crystallizes readily; so we determined its structure because it provides essentially the same chemical information. In spite of its crystallinity at 300 K, there are very large thermal motions of the molecules and a suitably refined structure was obtained only by cooling the crystals to low temperature.

**Experimental.** Crystals prepared by reacting tibp and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at 343 K and removal of the free  $\text{H}_2\text{O}$  by vacuum desiccation. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, Mo  $K\alpha$  radiation. Isotherm  $\text{N}_2$  boil-off cold-stream device for cooling to 139 K. Unit-cell dimensions determined from least-squares refinement using setting angles of 25 reflections in range 35–45° ( $2\theta$ ). Absorption corrections were determined from data of a reflection with  $\chi$  near 90° whose absorption was measured as a function of  $\phi$  (Furnas, 1957), plus a superimposed spherical correction based on a radius of 0.15 mm; transmissions ranged from 0.286 to 0.456. Intensities of reflections with  $0 \leq h \leq 9$ ,  $-11 \leq k \leq 10$ , and  $-12 \leq l \leq 11$  were measured to  $\sin \theta/\lambda = 0.54$  Å<sup>-1</sup>; all 2419 were observable at the level  $I > 2\sigma(I)$ . Standard reflection every 2  $h$  varied less than 2%. Structure determined by heavy-

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atom method; light atoms, including H atoms, found in electron-density maps. Least-squares refinement based on  $F_o$  with weights proportional to the reciprocal of  $[\sigma^2(F_o) + 0.0002F_o^2]$ , where  $\sigma^2(F_o)$  was based on counting statistics. Total of 314 parameters varied: one scale factor, an isotropic extinction parameter (Larson, 1967; Zachariasen, 1967), positions of all atoms except U, anisotropic thermal parameters for nonhydrogen atoms, isotropic thermal parameters for H atoms. Function minimized was  $\sum w(|F_c| - |F_o|)^2$ . In last cycle  $(\Delta/\sigma)_{\max} = 0.04$ . Atomic scattering factors and anomalous-dispersion corrections were from Cromer & Waber (1965) and Cromer & Liberman (1970). Secondary-extinction parameter refined to a mosaic block size of  $6(5) \times 10^{-6}$  cm. Agreement indices were  $R(F) = 0.022$ ,  $wR(F) = 0.029$  and  $S = 3.0$ .  $R_{\text{int}}$  for 140 replicates was 0.01. A final difference map showed one peak  $1.1 \text{ \AA}$  from the U atom with a height of  $1 \text{ e \AA}^{-3}$ ; all others were  $\leq 0.5 \text{ e \AA}^{-3}$  and were in close

proximity to other non-hydrogen atoms. Computer programs used were the Los Alamos system of Larson (1977) and Cromer & Larson (1977) for Fourier, least squares, and distances and angles. The drawing was made with ORTEPII (Johnson, 1976).

Table 1. Positional and thermal parameters

$$B_{\text{eq}} = \frac{4}{3}[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + 2\beta_{12}abc\cos\gamma + 2\beta_{13}accos\beta + 2\beta_{23}bccos\alpha] \text{ (Hamilton, 1959).}$$

	x	y	z	$B_{\text{eq}}$ or $B(\text{\AA}^2)$
U	0	0	0	0.90 (1)
P	0.3875 (1)	-0.0216 (1)	0.2538 (1)	1.29 (4)
O(1)	-0.0109 (4)	0.1334 (3)	0.1086 (3)	1.56 (10)
O(2)	0.2566 (4)	-0.0104 (3)	0.1427 (3)	1.63 (10)
O(3)	0.4006 (4)	0.0710 (3)	0.3764 (3)	1.72 (11)
O(4)	0.5684 (4)	0.0168 (3)	0.2447 (3)	1.62 (10)
O(5)	0.3609 (4)	-0.1664 (3)	0.2811 (3)	1.50 (10)
O(6)	0.2648 (4)	0.1441 (3)	-0.0165 (3)	1.50 (10)
O(7)	-0.2753 (4)	-0.2863 (3)	0.1387 (3)	2.06 (11)
O(8)	-0.0340 (4)	-0.1588 (3)	0.1430 (3)	1.78 (11)
N	-0.1951 (5)	-0.2004 (4)	0.1014 (3)	1.50 (13)
C(1)	0.2567 (7)	0.0614 (5)	0.4230 (5)	1.93 (17)
C(2)	0.2737 (7)	0.1945 (6)	0.5019 (5)	2.15 (17)
C(3)	0.1317 (9)	0.1806 (8)	0.5573 (6)	3.45 (24)
C(4)	0.2757 (9)	0.3050 (6)	0.4277 (6)	3.19 (23)
C(5)	0.6179 (6)	0.1190 (5)	0.1756 (5)	1.72 (16)
C(6)	0.6239 (6)	0.2609 (5)	0.2343 (4)	1.65 (16)
C(7)	0.7453 (8)	0.3056 (6)	0.3663 (5)	2.61 (20)
C(8)	0.6724 (7)	0.3549 (6)	0.1519 (5)	2.34 (20)
C(9)	0.3227 (7)	-0.2847 (5)	0.1818 (5)	1.67 (16)
C(10)	0.2748 (6)	-0.4113 (5)	0.2291 (5)	1.77 (16)
C(11)	0.1210 (7)	-0.4140 (6)	0.2706 (6)	2.25 (19)
C(12)	0.2438 (8)	-0.5341 (6)	0.1263 (6)	2.64 (20)
H(11)	0.256 (6)	-0.009 (6)	0.467 (5)	2.2 (11)
H(12)	0.149 (6)	0.030 (5)	0.352 (4)	1.6 (10)
H(21)	0.375 (6)	0.217 (5)	0.564 (4)	1.7 (10)
H(31)	0.132 (7)	0.119 (7)	0.608 (6)	3.4 (14)
H(32)	0.142 (8)	0.271 (8)	0.611 (6)	5.4 (17)
H(33)	0.018 (9)	0.162 (7)	0.487 (6)	5.0 (16)
H(41)	0.286 (7)	0.383 (7)	0.481 (5)	3.3 (13)
H(42)	0.167 (8)	0.284 (6)	0.360 (6)	3.8 (14)
H(43)	0.380 (8)	0.320 (6)	0.401 (5)	3.4 (13)
H(51)	0.726 (6)	0.107 (5)	0.171 (4)	1.3 (9)
H(52)	0.540 (6)	0.091 (5)	0.090 (5)	1.7 (10)
H(61)	0.517 (6)	0.267 (5)	0.238 (4)	1.0 (9)
H(71)	0.854 (8)	0.306 (6)	0.363 (5)	3.6 (14)
H(72)	0.742 (7)	0.398 (7)	0.401 (5)	3.6 (13)
H(73)	0.711 (7)	0.245 (6)	0.418 (5)	3.1 (13)
H(81)	0.681 (7)	0.445 (7)	0.185 (5)	3.3 (13)
H(82)	0.782 (8)	0.353 (6)	0.143 (5)	3.0 (13)
H(83)	0.588 (7)	0.337 (6)	0.071 (5)	2.6 (12)
H(91)	0.231 (6)	-0.279 (5)	0.115 (4)	1.2 (9)
H(92)	0.427 (6)	-0.279 (5)	0.158 (4)	1.6 (10)
H(101)	0.372 (6)	-0.412 (4)	0.300 (4)	0.7 (8)
H(111)	0.029 (7)	-0.413 (6)	0.204 (5)	2.4 (12)
H(112)	0.094 (6)	-0.493 (6)	0.302 (4)	2.0 (11)
H(113)	0.143 (7)	-0.340 (6)	0.338 (5)	2.9 (13)
H(121)	0.336 (8)	-0.529 (6)	0.100 (5)	3.4 (14)
H(122)	0.215 (6)	-0.615 (6)	0.156 (4)	1.8 (10)
H(123)	0.146 (7)	-0.531 (6)	0.054 (5)	2.6 (12)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

U—O(1)	1.758 (3)	C(5)—O(4)	1.471 (6)
O(2)	2.371 (4)	—C(6)	1.504 (7)
—O(6)	2.508 (4)	—H(51)	0.97 (5)
—O(8)	2.511 (4)	—H(52)	0.98 (5)
P—O(2)	1.479 (4)	C(6)—C(7)	1.520 (7)
—O(3)	1.548 (4)	—C(8)	1.523 (7)
—O(4)	1.551 (4)	—H(61)	0.94 (5)
—O(5)	1.551 (4)	C(7)—H(71)	0.94 (6)
N—O(6)	1.273 (5)	—H(72)	0.98 (7)
—O(7)	1.208 (5)	—H(73)	0.98 (6)
—O(8)	1.278 (5)	C(8)—H(81)	0.94 (7)
C(1)—O(3)	1.463 (6)	—H(82)	0.97 (6)
—C(2)	1.499 (7)	—H(83)	0.97 (6)
—H(11)	0.94 (6)	C(9)—O(5)	1.458 (6)
—H(12)	1.00 (5)	—C(10)	1.506 (7)
C(2)—C(3)	1.511 (8)	—H(91)	0.95 (5)
—C(4)	1.517 (8)	—H(92)	0.99 (5)
—H(21)	0.91 (5)	C(10)—C(11)	1.515 (8)
C(3)—H(31)	0.91 (7)	—C(12)	1.526 (7)
—H(32)	1.01 (8)	—H(101)	0.99 (4)
—H(33)	1.03 (7)	C(11)—H(111)	0.93 (5)
C(4)—H(41)	0.91 (6)	—H(12)	0.94 (6)
—H(42)	0.99 (6)	—H(113)	0.95 (6)
—H(43)	1.01 (6)	C(12)—H(121)	0.92 (6)
		—H(122)	0.96 (5)
		—H(123)	1.01 (5)
O(1)—U—O(2)	90.7 (1)	O(3)—C(1)—C(2)	108.8 (4)
O(1)—U—O(6)	90.6 (1)	C(1)—C(2)—C(3)	108.8 (5)
O(1)—U—O(8)	90.0 (1)	C(1)—C(2)—C(4)	111.1 (5)
O(7)—N—O(8)	123.2 (4)	C(3)—C(2)—C(4)	112.0 (5)
O(7)—N—O(6)	122.5 (4)	O(4)—C(5)—C(6)	113.5 (4)
O(6)—N—O(8)	114.4 (4)	C(5)—C(6)—C(7)	112.0 (5)
		C(5)—C(6)—C(8)	107.8 (4)
P—O(2)—U	164.3 (2)	C(7)—C(6)—C(8)	111.7 (5)
O(2)—P—O(3)	114.9 (2)	O(5)—C(9)—C(10)	108.9 (4)
O(2)—P—O(4)	113.0 (2)	C(9)—C(10)—C(11)	111.2 (4)
O(2)—P—O(5)	113.5 (2)	C(9)—C(10)—C(12)	108.3 (4)
O(3)—P—O(4)	104.1 (2)	C(11)—C(10)—C(12)	111.5 (5)
O(3)—P—O(5)	104.3 (2)		
O(4)—P—O(5)	106.0 (2)		

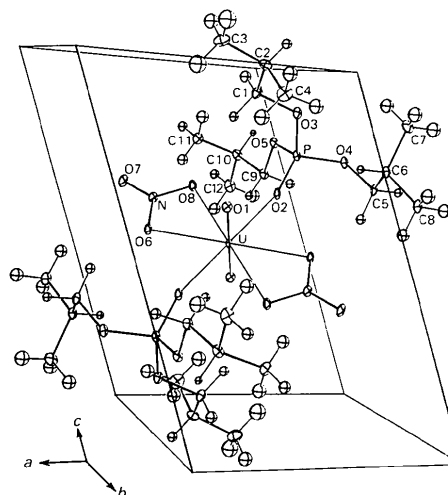


Fig. 1. The  $\text{UO}_2(\text{tibp})_2(\text{NO}_3)_2$  molecule shown in relation to the unit cell with its origin displaced by  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . Atoms are represented by their thermal ellipsoids at the 20% probability level. All nonhydrogen atoms are labelled as in Table 1.

**Discussion.** Final parameters for all atoms are given in Table 1,\* and relevant bond lengths and angles are in Table 2. Numbering of atoms is shown in Fig. 1, except for the H atoms, which are numbered according to the C atoms to which they are attached.

There are discrete centrosymmetric molecules of  $\text{UO}_2(\text{tibp})_2(\text{NO}_3)_2$  in the crystal with the configuration shown in Fig. 1 and the dimensions listed in Table 2. Each molecule contains a uranyl ion surrounded at its equator by six nearly coplanar O atoms provided by two bidentate nitrate ions and two monodentate tibp ligands; the phosphate O atoms are  $\pm 0.057$  (6) Å out of the plane of the four nitrate O atoms. The same molecular arrangement exists also in uranyl bis(nitrate) complexes in which the organic ligand is trimethyl phosphate, tmp (Agostini, Giacometti, Clemente & Vicentini, 1982), triethyl phosphate, tep (Fleming & Lynton, 1960), tri-*n*-butylphosphine oxide, tbpo (Burns, 1981), triphenylphosphine oxide, tppo (Alcock, Roberts & Brown, 1982), and triphenylarsine oxide, tpao (Panattoni, Graziani, Croatto, Zarli & Bombieri, 1968). Water molecules occupy these coordination sites in  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Dalley, Mueller & Simonsen, 1971) and  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Taylor & Mueller, 1965).

Because of the wide range of extracting abilities of these ligands (Burger, 1958; Nomura & Hara, 1961), it is relevant to compare the strengths of their bonds to U in these complexes. There are, in fact, scarcely any significant differences among them, based on the following U—O bond lengths: tmp 2.35 (1), tep 2.44 Å (unknown accuracy), tibp 2.371 (4), tbpo 2.347 (6), tppo 2.359 (7) and tpao 2.36 (3) Å. These bonds are, however, significantly shorter than bonds to water molecules when they occupy that site: 2.397 (3), 2.457 (4), 2.446 (4) Å. Thus, although all these extractants bind the uranyl ion more strongly than does water, the observed variation among their extraction coefficients must be attributed to factors other than the U—O bond strengths (e.g. entropy, lipophilicity).

The bond length of 1.758 (3) Å in the linear uranyl ion of  $\text{UO}_2(\text{tibp})_2(\text{NO}_3)_2$  is in close agreement with other accurately determined values among this class of compounds and corresponds to a U=O bond strength of 2 according to the scheme of Zachariassen (1978).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42333 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

X-ray and neutron diffraction studies on  $\text{UO}_2(\text{tibp})_2(\text{NO}_3)_2$  were performed originally at 300 K. The structure derived from these measurements had the same molecular features reported above, but a satisfactory refinement was not achieved. The thermal parameters on the C atoms were as much as ten times those at 139 K, and the H-atom thermal parameters (neutron diffraction) were even larger. This structure, containing molecules with many internal degrees of freedom with only van der Waals forces between molecules, is very flexible at 300 K; it melts at about 340 K. The unit-cell dimensions of  $\text{UO}_2(\text{tibp})_2(\text{NO}_3)_2$  at 300 K are  $a = 9.258$  (6),  $b = 9.927$  (8),  $c = 11.656$  (9) Å,  $\alpha = 100.06$ ,  $\beta = 98.55$  (5),  $\gamma = 101.55$  (6)° and  $V = 1014.5$  Å<sup>3</sup>, 8% greater than at 139 K.

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