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Structures of Tetranitratobis(tripyrrolidinophosphine oxide)uranium(IV) and Tetranitratobis(triphenylphosphine oxide)uranium(IV)

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Abstract. (1) $[U(NO_3)_4(C_{12}H_{24}N_3OP)_2]$, $M_r = 1000.7$, tetragonal, $P4_12_12$, $a = 10.607$ (11), $c = 33.497$ (4) Å, $V = 3769$ (1) Å^3, $Z = 4$, $D_x = 1.76$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 4.42$ mm^{-1}, $F(000) = 1984$, $T = 243$ (3) K, final $wR = 0.050$ ($R = 0.070$) for 1883 independent observed reflections. (2) $[U(NO_3)_4$-$(C_{18}H_{15}OP)_2]$, $M_r = 1042.7$, monoclinic, $P2_1/n$, $a = 13.996$ (1), $b = 17.461$ (3), $c = 16.438$ (2) Å, $\beta = 91.13$ (1)°, $V = 4016$ (1) Å^3, $Z = 4$, $D_x = 1.72$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 3.99$ mm^{-1}, $F(000) = 2096$, $T = 295$ K, $wR = 0.053$ ($R = 0.094$) for 5969 observed reflections. The uranium(IV) is ten-coordinated in both complexes, with the U—O distances for the phosphoryl groups [mean = 2.234 (9) Å] significantly shorter than the U—O distances for the nitrate groups [mean = 2.470 (12) Å].

Introduction. The thermal decomposition of $[U(NO_3)_4L_2]$ where L = tris(dimethylamino)phosphine oxide (tdpo), triphenylphosphine oxide (tppo) and trispyrrolidinophosphine oxide (tpyrp) has been investigated (Strydom & van Vuuren, 1986). From the observed enthalpy of the decomposition reaction an order of the stability of the complexes was proposed as:

$$[U(NO_3)_4(tppo)_2] > [U(NO_3)_4(tdpo)_2] > [U(NO_3)_4(tpyrp)_2].$$
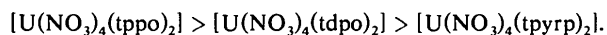
Crystal-structure determinations of uranium nitrate complexes are mainly concerned with the structures of

uranyl nitrato complexes, and no structure determinations of a uranium(IV) nitrato complex could be found in the Cambridge Structural Database (see Allen, Kennard & Taylor, 1983). This may be a result of the apparent instability of some of the uranium(IV) nitrates in X-rays: it is not yet possible to obtain X-ray-stable crystals of the $[U(NO_3)_4(tdpo)_2]$ complex, and usable diffraction data for the $[U(NO_3)_4(tpyrp)_2]$ complex had to be obtained at low temperature. It was of interest to obtain structural data for these complexes in order to gain a better understanding of the related solid-state chemistry, and in this paper we present the first crystal structures of uranium(IV) nitrato complexes, that of $[U(NO_3)_4(tpyrp)_2]$ (1) and $[U(NO_3)_4(tppo)_2]$ (2).

Experimental. Crystals obtained from the slow evaporation from methylene chloride solutions in a petroleum ether atmosphere for both (1) and (2). Crystal sizes: (1) $0.17 \times 0.20 \times 0.26$, (2) $0.30 \times 0.23 \times 0.12$ mm. Lattice parameters refined using 25 reflections in the ranges (1) $7 \leq \theta \leq 17$ and (2) $7 \leq \theta \leq 19°$, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scans in range $3 \leq \theta \leq 25°$, scan angle (1) $(0.53 + 0.34\tan\theta)$, (2) $(0.57 + 0.34\tan\theta)°$. Scan rate variable (1) $0.05°$ s^{-1}, max. time 50 s refl^{-1}, (2) $0.092°$ s^{-1}, max. time 50 s refl^{-1}. Range of hkl: (1) $0 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 40$, (2) $0 \leq h \leq 16$, $0 \leq k \leq 20$, $-19 \leq l \leq 19$. For (1) 2031 reflections measured, 1704 observed $[I > 2\sigma(I)]$, for (2) 7310 reflections measured, 4495 observed $[I > 2\sigma(I)]$. Stan-

$$[U(NO_3)_4(C_{12}H_{24}N_3OP)_2] \text{ AND } [U(NO_3)_4(C_{18}H_{15}OP)_2]$$

Table 1. Fractional coordinates ($\times 10^4$, $\times 10^5$ for U) and equivalent isotropic thermal parameters ($\times 10^3$ Å^2, $\times 10^4$ Å^2 for U)

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
(1)				
U	13114 (6)	13114 (6)	0	288 (1)
O(1)	−492 (11)	2285 (12)	−166 (3)	44 (3)
P(1)	−1764 (5)	2738 (6)	−273 (2)	45 (1)
N(1)	−1656 (19)	4021 (19)	−534 (6)	74 (6)
C(1)	−2647 (33)	4733 (38)	−670 (13)	196 (18)
C(2)	−2189 (34)	5822 (31)	−801 (13)	157 (15)
C(3)	−853 (35)	5963 (34)	−815 (11)	177 (16)
C(4)	−469 (25)	4684 (35)	−652 (11)	192 (16)
N(2)	−2670 (17)	1841 (19)	−524 (5)	59 (5)
C(5)	−3104 (23)	597 (24)	−337 (7)	71 (8)
C(6)	−3241 (44)	−241 (43)	−682 (17)	232 (25)
C(7)	−2959 (59)	468 (52)	−973 (14)	251 (37)†
C(8)	−2545 (26)	1754 (29)	−981 (7)	124 (12)
N(3)	−2473 (14)	2945 (12)	140 (4)	39 (4)
C(9)	−1901 (20)	3401 (31)	502 (6)	93 (9)
C(10)	−2940 (24)	3915 (29)	737 (6)	103 (10)
C(11)	−4069 (21)	3885 (34)	516 (7)	107 (10)
C(12)	−3900 (24)	3128 (27)	196 (6)	105 (10)
N(4)	605 (18)	−73 (18)	−708 (6)	55 (6)†
O(2)	195 (13)	−468 (14)	−379 (5)	74 (5)
O(3)	1170 (19)	913 (20)	−739 (4)	115 (7)
O(4)	284 (20)	−613 (26)	−1000 (5)	188 (11)
N(5)	2344 (22)	3400 (17)	499 (6)	68 (6)
O(5)	1209 (13)	3426 (12)	337 (4)	57 (4)
O(6)	2933 (12)	2362 (13)	429 (4)	50 (4)
O(7)	2743 (16)	4189 (14)	718 (5)	75 (5)
(2)				
U	51980 (4)	34560 (3)	69814 (3)	463 (1)
O(2)	3699 (6)	3763 (5)	7275 (4)	64 (3)
P(3)	2707 (3)	3977 (2)	7616 (3)	64 (1)
C(4)	2857 (10)	4543 (8)	8508 (9)	65 (4)
C(5)	3526 (11)	4317 (9)	9083 (9)	83 (5)
C(6)	3628 (13)	4742 (12)	9823 (12)	132 (7)
C(7)	3038 (16)	5341 (13)	9930 (13)	134 (9)
C(8)	2359 (15)	5580 (13)	9404 (12)	132 (8)
C(9)	2312 (12)	5172 (9)	8654 (9)	91 (6)
C(10)	2058 (9)	3130 (8)	7909 (8)	61 (4)
C(11)	2128 (10)	2488 (9)	7378 (10)	88 (5)
C(12)	1585 (10)	1847 (10)	7598 (11)	99 (6)
C(13)	1098 (10)	1818 (11)	8229 (12)	97 (6)
C(14)	979 (13)	2409 (11)	8819 (11)	109 (7)
C(15)	1515 (11)	3080 (11)	8540 (10)	89 (5)
C(16)	2031 (12)	4501 (9)	6865 (9)	74 (5)
C(17)	1059 (12)	4502 (10)	6818 (11)	105 (6)
C(18)	547 (11)	4922 (13)	6213 (11)	123 (7)
C(19)	1054 (14)	5356 (11)	5745 (12)	112 (7)
C(20)	2040 (13)	5379 (9)	5731 (11)	100 (6)
C(21)	2493 (11)	4939 (9)	6332 (9)	73 (5)
O(22)	6769 (5)	3310 (5)	7183 (5)	63 (3)
P(23)	7797 (3)	3145 (2)	7456 (2)	58 (1)
C(24)	8317 (9)	4008 (8)	7883 (10)	70 (4)
C(25)	8121 (11)	4683 (10)	7492 (11)	112 (6)
C(26)	8522 (14)	5342 (10)	7781 (15)	153 (9)
C(27)	9108 (15)	5334 (11)	8503 (14)	127 (8)
C(28)	9354 (12)	4653 (11)	8811 (10)	95 (6)
C(29)	8977 (10)	3978 (9)	8551 (8)	70 (5)
C(30)	8447 (10)	2861 (8)	6637 (8)	63 (4)
C(31)	8042 (12)	2704 (9)	5892 (14)	124 (7)
C(32)	8568 (16)	2539 (15)	5219 (11)	155 (9)
C(33)	9464 (17)	2430 (12)	5249 (12)	114 (7)
C(34)	9916 (13)	2559 (12)	5932 (13)	138 (8)
C(35)	9459 (11)	2771 (10)	6664 (9)	101 (6)
C(36)	7831 (9)	2424 (8)	8249 (8)	56 (4)
C(37)	7340 (12)	2561 (10)	8899 (11)	100 (6)
C(38)	7321 (13)	2031 (13)	9573 (11)	118 (7)
C(39)	7859 (12)	1370 (10)	9514 (13)	109 (7)
C(40)	8358 (12)	1232 (9)	8782 (10)	90 (6)
C(41)	8348 (11)	1768 (9)	8197 (9)	80 (5)
O(42)	5124 (9)	4870 (6)	7173 (7)	109 (4)
O(43)	5606 (8)	4267 (7)	8164 (6)	88 (4)
N(44)	5443 (11)	4900 (9)	7878 (9)	84 (5)
O(45)	5494 (9)	5515 (7)	8204 (7)	126 (4)
O(46)	4103 (6)	2526 (6)	6257 (6)	83 (3)
O(47)	5533 (7)	2544 (6)	5891 (6)	88 (3)
N(48)	4723 (10)	2248 (7)	5788 (7)	69 (4)
O(49)	4522 (7)	1749 (6)	5345 (7)	103 (4)
O(50)	4655 (8)	3973 (7)	5714 (6)	106 (4)
O(51)	6143 (8)	4078 (6)	5936 (6)	93 (4)

Table 1 (cont.)

	x	y	z	U_{eq}
N(52)	5386 (12)	4179 (7)	5429 (10)	95 (5)
O(53)	5590 (9)	4389 (7)	4648 (7)	148 (5)
O(54)	4963 (10)	2888 (8)	8190 (8)	142 (5)†
O(55)	5506 (9)	2079 (7)	7421 (8)	144 (5)†
N(56)	5089 (15)	2197 (13)	8093 (14)	170 (8)†
O(57)	5253 (10)	1625 (10)	8604 (9)	190 (7)†

† Isotropic temperature factors refined.

Table 2. Selected bond distances (Å) and bond angles (°) for (1) and (2)

(1)

U−O(1)	2·244 (12)	U−O(2)	2·565 (14)
U−O(3)	2·517 (13)	U−O(5)	2·514 (12)
U−O(6)	2·503 (13)		
O(2)−N(4)−O(3)	122 (2)	U−O(1)−P(1)	171·5 (8)
O(5)−N(5)−O(6)	113 (2)		

(2)

U−O(2)	2·227 (8)	U−O(22)	2·232 (8)
U−O(42)	2·491 (10)	U−O(43)	2·463 (11)
U−O(46)	2·516 (9)	U−O(47)	2·450 (10)
U−O(5)	2·381 (11)	U−O(55)	2·444 (11)
U−O(54)	2·251 (14)	U−O(55)	2·545 (13)
O(42)−N(44)−O(43)	112·5 (14)	O(54)−N(56)−O(55)	110 (2)
O(46)−N(48)−O(47)	112·7 (11)	U−O(22)−P(23)	170·2 (5)
O(50)−N(52)−O(51)	112·9 (14)	U−O(2)−P(3)	171·3 (5)

dard reflections: (1) 249, 4,0,24 and 318, (2) 145, 235 and 454, measured every 60 min, decay (1) −1·9% (not corrected), (2) −14·3% (corrected). Lorentz and polarization corrections and empirical absorption based on ψ scans of nine reflections were applied for both data sets (North, Phillips & Mathews, 1968): transmission factors (1) 0·907–1·000, av. 0·962, (2) 0·935–1·000, av. 0·976.

Structure solutions: Patterson and difference Fourier analysis using SHELX76 (Sheldrick, 1976), H atoms in calculated positions (C−H = 1·08 Å, H−C−H = 109·4°). The non-H atoms in both structures were refined anisotropically, except for N(4) and C(7) in (1) and O(54), O(55), N(56) and O(57) in (2) which were refined isotropically due to nonpositive-definite coefficients; H atoms were assigned a common U_{iso} for (1) = 0·21 (3) and for (2) = 0·08 (2) Å^2, using all reflections ($F_o > 0$) and $\sigma^{-2}(F)$ weights (Sheldrick, 1976), $\sum w |\Delta F|^2$ minimized: (1) $wR = 0·050$ and $R = 0·070$ with 1883 reflections for 222 parameters, (2) $wR = 0·053$ and $R = 0·094$ with 5969 reflections for 517 parameters. Scattering factors for the neutral atoms were taken from International Tables for X-ray Crystallography (1974), and the anomalous-dispersion terms for uranium were taken from Cromer & Liberman (1970). $(\Delta/\sigma)_{max}$ (1) 0·56, (2) 1·02, max. residual electron density: (1) 2·31 (less than 1 Å from U), (2) 3·4 e Å^{-3} (less than 1 Å from U).

Discussion. Final fractional coordinates with equivalent isotropic thermal parameters are given in Table
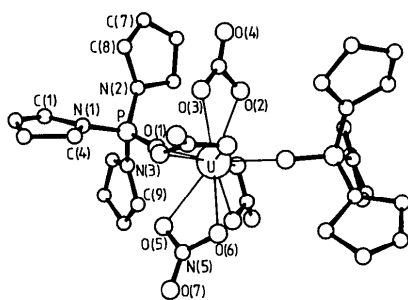
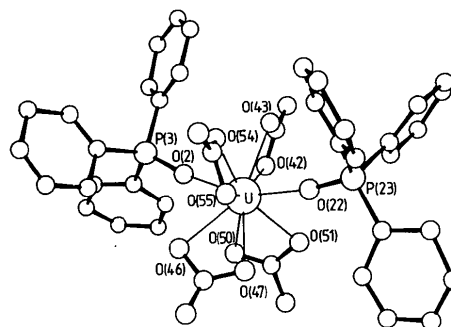Fig. 1. Perspective view of [U(NO₃)₄(tpyrp)₂] (1) showing the numbering scheme.

Fig. 2. Perspective view of [U(NO₃)₄(tppo)₂] (2) showing the numbering scheme.

1;* Table 2 contains selected bond distances and bond angles. The molecules, with numbering schemes used, are depicted in Figs. 1 and 2.

The uranium(IV) is ten-coordinated in both complexes, two O atoms from each nitrate group being bonded to the U atom together with two O atoms from the neutral donor ligands. The U—O distances are 2·503 (13) to 2·565 (14) Å for the nitrate-group O atoms in (1), and 2·251 (14) to 2·545 (13) Å in (2). The shorter U—O(phosphoryl) distances (1) 2·244 (12) and (2) 2·227 (8) and 2·232 (8) Å are similar to the distances observed in the [Ce(NO₃)₄(tppo)₂] complex (Caughlan, Hart & van Nice, 1971). The nitrate angles in (1) show a greater variation [113 (2)–122 (2)°] than those of (2) [110 (2)–113 (1)°]. The crystal structures

of [U(NO₃)₄(tpyrp)₂] (1) and [U(NO₃)₄(tppo)₂] (2) do not differ to such an extent as to allow an explanation for the observed stability order (Strydom & van Vuuren, 1986), and further attempts to obtain usable data for the [U(NO₃)₄(tdpo)₂] complex are in progress.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44871 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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