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Actinide Structural Studies. 13.* Three Pyridine–Acetylacetonate Complexes of Actinyl(VI) Ions

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Abstract. Bis(1,3-diphenyl-1,3-propanedionato)oxo(pyridine)uranium(VI) (1), $[UO_2(C_{15}H_{11}O_2)_2(C_5H_5N)]$, $M_r = 795{\cdot}6$, monoclinic, $P2_1/n$, $a = 10{\cdot}158\,(2)$, $b = 21{\cdot}937\,(8)$, $c = 13{\cdot}888\,(4)$ Å, $\beta = 103{\cdot}49\,(1)°$, $U = 3009\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}76$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 51{\cdot}48$ cm^{-1}, $F(000) = 1536$, $T = 289$ K, $R = 0{\cdot}036$ for 3269 unique observed reflections. Bis[1-(*tert*-butoxy)-1,3-butanedionato]dioxo(pyridine)uranium(IV) (2), $[UO_2(C_8H_{13}O_3)_2(C_5H_5N)]$, $M_r = 663{\cdot}5$, orthorhombic, $Cmc2_1$, $a = 15{\cdot}939\,(9)$, $b = 19{\cdot}532\,(8)$, $c = 9{\cdot}777\,(6)$ Å, $U = 3044\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}45$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 50{\cdot}81$ cm^{-1}, $F(000) = 1280$, $T = 289$ K, $R = 0{\cdot}048$ for 1178 unique observed reflections. Dioxobis(2,4-pentanedionato)(pyridine)neptunium(VI) (3), $[NpO_2(C_5H_7O_2)_2(C_5H_5N)]$, $M_r = 546{\cdot}4$, orthorhombic, $Fdd2$, $a = 29{\cdot}617\,(5)$, $b = 11{\cdot}406\,(2)$, $c = 10{\cdot}595\,(4)$ Å, $U = 3579\,(2)$ Å^3, $Z = 8$, $D_x = 2{\cdot}03$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 37{\cdot}95$ cm^{-1}, $F(000) = 2056$, $T = 173$ K, $R = 0{\cdot}046$ for 625 unique observed reflections. The bond angle of 177·9 (2)° for (1) indicates a very slightly non-linear uranyl group. The neptunyl bond in complex (3) is slightly more distorted [176·5 (19)°], whilst in complex (2) the uranyl group deviates even more from linearity [175·8 (8)°]. In (1), the phenyl groups are displaced out of the equatorial plane. Two rings are twisted inwards towards each other about this plane, whilst the other two are directed above and below, and are twisted away from each other, forming a cavity into which the pyridine ring nestles. The methyl groups of the *tert*-butoxy moiety in complex (2) and those of the 2,4-pentanedione ligand in (3) are displaced above and below the equatorial plane. The pyridine molecule of (2) is perpendicular to the equatorial plane, while those of (1) and (3) are set obliquely [dihedral angles 36·9 (2) and 49·0 (2)°].

Introduction. We have previously reported the structure of dioxobis(2,4-pentanedionato)(pyridine)uranium(VI) (4) which is notable amongst complexes involving the uranyl ion for the large deviation from linearity of the O—U—O bond angle, 173·5 (8)° (Alcock, Flanders & Brown, 1984). With this in mind, we began an investigation of complexes with related β-diketonate ligands to examine their effect on this O—U—O angle, and describe here the analagous complexes with bis phenyl and *tert*-butoxy substituted acetylacetone (acac). In addition, the synthesis and structural determination of dioxobis(2,4-pentanedionato)(pyridine)neptunium(VI) (3), which is isomorphous with (4), is reported.

Experimental. Compounds (1) and (2) were prepared by adaptation of the method described by Hager (1927). This involved addition of a methanolic solution of uranyl nitrate (0·56 g; 1·42 mmol) to a methanolic solution containing two equivalents of ligand (0·25 g; 2·8 mmol). Dropwise addition of the stoichiometric amount of pyridine (0·20 cm^3: 2·4 mmol) caused turbidity of the solution, and deposited crystals on standing. These were recrystallized from methanol. The neptunyl analogue (3) was prepared by essentially the same method using 0·25 mmol of freshly prepared neptunyl(VI) nitrate, and reducing the quantities of the other reagents to the same proportions. Several crystals of (3) had to be examined to obtain a suitable single crystal as the majority were found to be twinned. The neptunium crystal was mounted in a glove box and encapsulated in a Lindemann capillary for radiation protection, and it was held at 173 K with the Syntex LT-1 device to reduce decay under irradiation. All data were collected with a Syntex $P2_1$ four-circle diffractometer. Background intensities were measured at each end of the scan for 0·25 of the scan time. Three standard reflections, monitored every 200 reflections, showed slight changes during data collection; the data were rescaled for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($25 \leq 2\theta \leq 29°$). Observed reflections $[I/\sigma(I) \geq 3{\cdot}0]$ corrected for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970). Details for each compound are given in Table 1.

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* Part 12: Alcock & Flanders (1987).

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Table 1. *Crystal data and data collection conditions*

	(1)	(2)	(3)
Crystal size (mm)	0·15 × 0·10 × 0·28	0·13 × 0·04 × 0·29	0·17 × 0·02 × 0·28
Max. transmission factor	0·57	0·74	0·74
Min. transmission factor	0·28	0·65	0·65
2θ(max.) (°)	50	50	55
Scan range about $K\alpha_1$–$K\alpha_2$ (°)	−1·05/+0·9	−0·9/+1·0	−1·0/+1·0
Reflections collected	5776	1551	907
Reflections observed [$I/\sigma(I) \geq 3{\cdot}0$]	3269	1178	625
Index range h	−12/11	0/18	0/34
k	0/25	0/23	0/13
l	0/16	0/11	0/12
Weighting constant: g	0·00016	0·00150	0·00287
R(final)	0·036	0·048	0·046
wR(final)	0·033	0·048	0·047
Max. $\Delta\rho$ on final difference Fourier map (e Å^{-3})	0·74	1·03	2·28
Min. $\Delta\rho$ on final difference Fourier map (e Å^{-3})	−0·56	−1·49	−1·44
Max. Δ/σ (final cycle)	0·142	0·058	0·675

Heavy atoms were located by Patterson methods and the remaining lighter atoms by successive Fourier syntheses. Systematic absences for (2) indicated an *A*-centred cell, with a choice of three possible space groups: *A*2$_1$*ma*, *Am*2*a* and *Amma* as non-standard settings of *Cmc*2$_1$, *Ama*2 and *Cmcm* respectively. *Cmcm* was initially selected, and the cell rotated to conform. Patterson maps were calculated and structure solution attempted in each possible space group; this was successful only in *Cmc*2$_1$. For compounds (2) and (3), refinement of an f'' multiplier showed that the correct hand had been chosen. The z coordinates of the metal ions in these structures were held fixed to define the origin. Anisotropic temperature factors were used for all atoms except hydrogens which were inserted at fixed positions and not refined ($U = 0{\cdot}07$ Å^2). For (1) and (3), methyl groups were treated as rigid CH_3 units with their initial orientation taken from the H-atom peaks on a difference Fourier synthesis but an attempt to include them for (2) was unsuccessful as the refined parameters did not converge. The large thermal parameters for the corresponding C atoms suggest that these groups are slightly disordered, though no alternative positions were detectable on the Fourier synthesis. The thermal parameters and implausible bond distance for C(4) suggest that it may also be disordered between two positions which are not far separated from each other. Final refinement on F was by cascaded least-squares methods. A weighting scheme of the form $w = 1/[\sigma^2(F) + g(F^2)]$ was applied. The relatively large residual peaks on the final Fourier synthesis for (2) and (3) were in the neighbourhood of the metal ions. Computing for complexes (1) and (2) used *SHELXTL* (Sheldrick, 1983) on a Data General DG30 apart from the absorption correction on a Burroughs B6800. Calculations for complex (3) were carried out with the *XRAY76* system (Stewart, 1976) on a Burroughs B6700 computer and with the *SHELXTL* system on a Data General NOVA 3 minicomputer. Scattering factors in the analytical form and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates are given in Tables 2–4.* Selected bond lengths and angles [with numbering scheme based on (1)] are listed in Table 5, and information on deviations from planes in Table 6. Fig. 1 shows the molecule and numbering scheme for (1). The packing diagram for (1) can be seen in Fig. 2. Fig. 3 shows the molecule and numbering scheme for (2) with the packing diagram in Fig. 4. Fig. 5 shows the molecule and numbering scheme for (3), while another view and a packing diagram for the isomorphous complex (4) are given in Alcock *et al.* (1984).

The complexes exhibit pentagonal-bipyramidal geometry about the actinyl(VI) atom, involving two bidentate β-diketonate ligands and a pyridine molecule. Thus they have similar geometries to (4) and to uranyl(VI) bis(2,4-pentanedionate)hydrate (Frasson, Bombieri & Panattoni, 1966), the only other uranyl β-diketonates to have been studied structurally. In none of our complexes was the magnitude of the distortion of the actinyl bond angle as great as the 173·5 (8)° found in (4), though that in (2) approaches it [175·8 (8)°].

The packing diagram of (1) (Fig. 2) appears to be dominated by a face-to-face alignment of the phenyl rings, while for (2) the relatively low density correlates with the molecules being held apart by contacts between the methyl groups. In complex (1), the groups containing the β carbon atoms are oriented such that C(034) lies below [0·08 (5) Å] the equatorial plane. In parallel with this distortion, the C(41)–C(46) ring lies completely above this plane (though not symmetrically), with deviations in the range 0·20–0·62 (5) Å. The β carbon [C(012)] of the other ligand lies above the plane [0·15 (5) Å] and the C(11)–C(16) ring is positioned below the plane [0·11–0·51 (5) Å]. Again this displacement is not symmetrical. These rings are twisted outwards away from one another (see Fig. 1) with pairs of atoms C(15), C(16) and C(45), C(46) having maximum displacements below and above the plane respectively. The pyridine ligand slots into the cavity with a substantial out-of-plane twist [C(51), C(52), C(53) are directed below the plane, and C(54), C(55) above].

The other phenyl rings on the ligands are twisted inwards towards one another, and are displaced above and below the equatorial plane. Deviations for C(21)–C(26) lie in the range 0·23 (5) Å below [C(25)] and

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* Lists of structure factors, bond lengths and angles, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43923 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0·50 (5) Å above [C(22)]. Similarly for C(31)—C(36), deviations are in the range 0·43 (5) Å below [C(32)] and 0·76 (5) Å above [C(35)].

Table 2. *Atomic coordinates* (×10⁴) *for* (1), *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*(Å² × 10³)
U	560·7 (3)	6293·4 (1)	7937·5 (2)	45·9 (2)
O(11)	58 (5)	5568 (3)	8237 (4)	62 (2)
O(12)	1091 (6)	7021 (3)	7685 (4)	66 (2)
O(1)	2855 (5)	6020 (3)	8525 (4)	60 (2)
C(1)	3826 (7)	5824 (3)	8174 (5)	44 (3)
C(11)	5112 (7)	5686 (3)	8901 (5)	46 (3)
C(12)	5261 (9)	5850 (4)	9875 (5)	67 (4)
C(13)	6415 (9)	5696 (4)	10572 (6)	78 (4)
C(14)	7431 (8)	5376 (4)	10323 (6)	67 (4)
C(15)	7304 (9)	5223 (4)	9376 (7)	83 (4)
C(16)	6158 (8)	5378 (4)	8663 (6)	75 (4)
C(012)	3693 (7)	5736 (4)	7159 (5)	51 (3)
C(2)	2508 (8)	5781 (3)	6450 (5)	46 (3)
O(2)	1385 (5)	5910 (3)	6653 (4)	75 (3)
C(21)	2424 (7)	5631 (3)	5385 (3)	47 (3)
C(22)	3551 (8)	5556 (4)	5006 (5)	63 (3)
C(23)	3408 (9)	5378 (4)	4024 (6)	67 (4)
C(24)	2143 (9)	5297 (4)	3419 (6)	61 (3)
C(25)	1022 (8)	5385 (4)	3779 (5)	62 (3)
C(26)	1146 (7)	5559 (4)	4755 (5)	57 (3)
O(3)	−1250 (5)	6339 (3)	6571 (4)	61 (2)
C(3)	−2491 (7)	6484 (3)	6345 (5)	47 (3)
C(31)	−3168 (7)	6439 (3)	5256 (5)	43 (3)
C(32)	−2635 (8)	6033 (4)	4681 (5)	55 (3)
C(33)	−3167 (9)	6012 (4)	3667 (6)	66 (3)
C(34)	−4200 (9)	6394 (4)	3234 (6)	78 (4)
C(35)	−4724 (9)	6797 (4)	3794 (6)	75 (4)
C(36)	−4230 (8)	6818 (4)	4815 (5)	59 (3)
C(034)	−3209 (7)	6703 (3)	7016 (5)	49 (3)
C(4)	−2584 (7)	6838 (3)	8000 (5)	44 (3)
O(4)	−1341 (5)	6728 (3)	8390 (4)	60 (2)
C(41)	−3362 (8)	7154 (3)	8640 (5)	46 (3)
C(42)	−4693 (8)	7337 (4)	8306 (6)	65 (4)
C(43)	−5357 (9)	7650 (4)	8904 (7)	77 (4)
C(44)	−4694 (90)	7586 (4)	9858 (7)	82 (4)
C(45)	−3379 (9)	7599 (4)	10225 (7)	89 (5)
C(46)	−2712 (9)	7282 (4)	9618 (6)	69 (4)
N(1)	1212 (6)	6503 (3)	9809 (4)	52 (2)
C(51)	465 (8)	6284 (4)	10394 (5)	63 (3)
C(52)	773 (10)	6341 (4)	11414 (6)	83 (4)
C(53)	1953 (10)	6644 (4)	11845 (6)	72 (4)
C(54)	2749 (9)	6879 (4)	11266 (6)	67 (4)
C(55)	2352 (8)	6790 (4)	10250 (6)	62 (3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. *Atomic coordinates* (×10⁴) *for* (2), *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*(Å² × 10³)
U	0	6280·3 (4)	7500	50 (1)
O(1)	0	7149 (9)	7077 (18)	66 (7)
O(2)	0	5417 (7)	8058 (18)	63 (6)
O(3)	−1429 (9)	6447 (7)	8331 (12)	65 (4)
O(4)	−901 (9)	6004 (10)	5774 (16)	87 (6)
C(1)	−1636 (12)	5786 (9)	5699 (19)	55 (6)
C(2)	−1822 (14)	5470 (13)	4322 (25)	90 (9)
C(3)	−2257 (14)	5877 (9)	6664 (18)	58 (6)
C(4)	−2118 (13)	6213 (7)	7454 (71)	121 (16)
O(5)	−2823 (10)	6326 (7)	8573 (15)	78 (5)
C(5)	−2830 (18)	6760 (13)	9798 (25)	100 (11)
C(6)	−2559 (33)	7471 (14)	9442 (34)	149 (15)
C(7)	−3765 (24)	6735 (29)	10057 (45)	223 (24)
C(8)	−2348 (22)	6337 (14)	10966 (29)	113 (13)
N(1)	0	6571 (11)	10090 (25)	60 (8)
C(11)	0	6046 (15)	11021 (29)	59 (9)
C(12)	0	6229 (13)	12429 (124)	72 (10)
C(13)	0	6886 (15)	12850 (46)	101 (11)
C(14)	0	7387 (18)	11870 (35)	119 (19)
C(15)	0	7201 (17)	10396 (36)	103 (17)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. *Atomic coordinates* (×10⁴) *for* (3), *with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*(Å² × 10³)
Np	0	0	0	
O(1)	−421 (6)	1107 (18)	51 (28)	565 (69)
O(2)	522 (8)	1373 (18)	−731 (28)	536 (73)
O(3)	375 (6)	829 (18)	1765 (18)	505 (65)
N(1)	0	0	−2420 (24)	346 (76)
C(1)	−25 (8)	994 (23)	−3042 (28)	456 (76)
C(2)	−24 (13)	1058 (29)	−4351 (29)	672 (109)
C(3)	0	0	−4978	794 (149)
C(4)	1151 (13)	2531 (38)	−1242 (32)	768 (130)
C(5)	886 (8)	1838 (24)	−301 (22)	403 (83)
C(6)	1015 (10)	1772 (25)	992 (26)	479 (90)
C(7)	760 (8)	1270 (26)	1956 (27)	440 (85)
C(8)	924 (12)	1308 (30)	3253 (28)	64 (113)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 5. *Bond lengths* (Å) *and bond angles* (°) *around the metal atoms with e.s.d.'s in parentheses*

The atomic numbering refers to (1); the values for (2), (3) and (4) relate to corresponding atoms.

	(1)	(2)	(3)	(4)
M—O(11)	1·751 (5)	1·746 (18)	1·78 (2)	1·83 (1)
M—O(12)	1·747 (6)	1·771 (4)	—	—
M—O(1)	2·360 (5)	2·440 (14)	2·33 (2)	2·34 (1)
M—O(2)	2·299 (6)	2·281 (15)	2·37 (2)	2·44 (1)
M—O(3)	2·317 (4)	—	—	
M—O(4)	2·367 (5)	—	—	
M—N(1)	2·569 (6)	2·595 (24)	2·56 (3)	2·47 (1)
O(11)—*M*—O(12)	177·9 (2)	175·8 (8)	176·5 (19)	173·5 (8)
O(11)—*M*—O(1)	90·3 (2)	87·1 (4)	89·9 (9)	89·1 (5)
O(11)—*M*—O(2)	91·8 (2)	93·1 (6)	91·2 (10)	89·6 (6)
O(11)—*M*—N(1)	86·7 (2)	91·1 (7)	91·7 (10)	93·2 (5)
O(11)—*M*—O(4)	90·1 (2)	—	—	—
O(11)—*M*—O(3)	90·8 (2)	—	—	—
O(12)—*M*—N(1)	91·2 (2)	84·7 (7)	—	—
O(12)—*M*—O(1)	88·6 (2)	91·4 (4)	—	—
O(12)—*M*—O(2)	89·6 (3)	90·2 (6)	—	—
O(12)—*M*—O(4)	89·7 (2)	—	—	—
O(12)—*M*—O(3)	91·1 (2)	—	—	—
O(1)—*M*—O(2)	70·5 (2)	71·9 (5)	71·6 (7)	71·1 (4)
O(3)—*M*—O(4)	70·1 (2)	—	—	—

Table 6. *Deviations* (Å) *from mean planes* (*defined by starred atoms*); *e.s.d.'s* 0·05 Å

Complex (1)

O(1)* −0·03, C(1)* 0·01, C(2)* 0·10, O(2)* −0·07, U(1)* −0·02, O(3)* −0·03, C(3)* −0·06, O(4)* 0·09, C(4)* 0·04, N(1)* −0·04, C(012) 0·15, C(034) −0·08, C(11) −0·11, C(12) −0·07, C(13) −0·26, C(14) −0·49, C(15) −0·51, C(16) −0·31, C(21) 0·15, C(22) 0·50, C(23) 0·45, C(24) 0·08, C(25) −0·23, C(26) −0·18, C(31) 0·02, C(32) −0·43, C(33) −0·28, C(34) 0·31, C(35) 0·76, C(36) 0·60, C(41) 0·20, C(42) 0·26, C(43) 0·47, C(44) 0·62, C(45) 0·54, C(46) 0·33

Complex (2)

O(3)* 0·13, C(4)* −0·01, C(1)* −0·20, O(4)* 0·16, U(1)* 0·01, O(3′)* 0·13, C(4′)* −0·01, C(1′)* −0·22, O(4′)* 0·16, N(1)* −0·22, C(2) −0·35, C(3) −0·37, C(5) 0·23, C(6) 1·65, C(7) 0·09, C(8) −0·93, O(5) −0·17

Complex (3)

O(2)* −0·26, C(7)* 0·26, C(5)* −0·01, O(3)* −0·05, Np* 0·00, O(3′)* 0·05, C(5′)* 0·01, C(7′)* −0·26, O(2′)* 0·26, C(6) 0·28, C(4) 0·15, C(8) 0·53, C(6′) −0·28, C(4′) 0·15, C(8′) −0·53

In complex (2), primed atoms are related to unprimed ones by a mirror plane. The *β* carbon [C(3)] in this complex lies below the equatorial plane by 0·37 (5) Å. C(2) and O(5) are both displaced below the plane [deviations 0·35 and 0·17 (5) Å respectively]. C(5) is above the plane [0·23 (5) Å], and the orientation of the *tert*-butyl group with respect to the plane is such that C(6) is above [1·65 (5) Å], C(7) is virtually coplanar [0·09 (5) Å], and C(8) is directed below the plane [0·93 (5) Å].

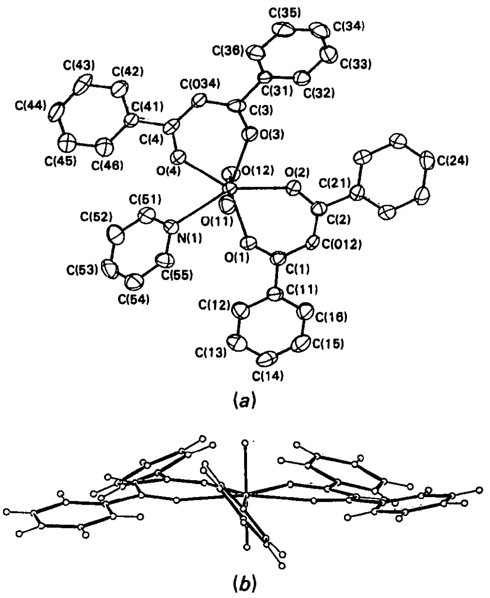

Fig. 1. (*a*) The molecule of (1) showing the atomic numbering scheme (50% probability ellipsoids). (*b*) Side-on view showing deviations out of plane.

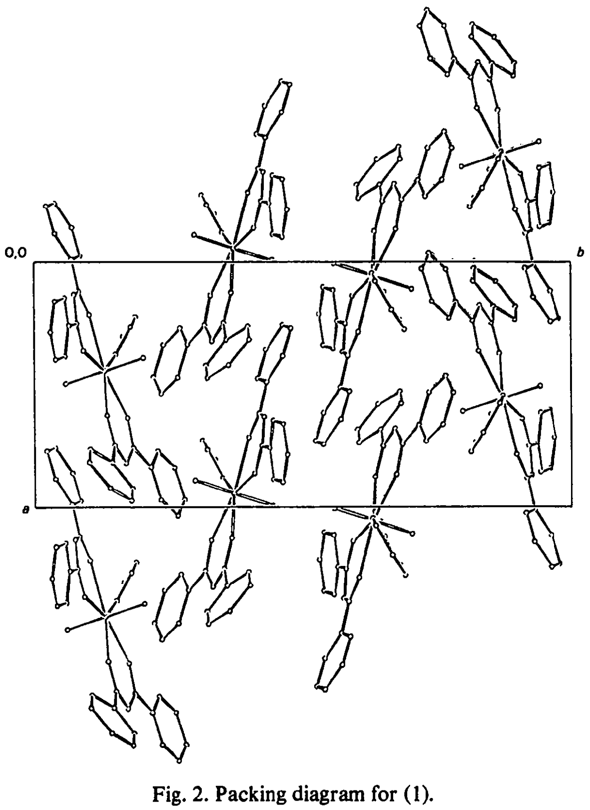

Fig. 2. Packing diagram for (1).

In complex (3), primed atoms are related to unprimed atoms by a twofold axis which passes through the Np and N(1), C(3) of the pyridine molecule. The *β* carbon [C(6)] of the dionato ligand lies above [0·28 (5) Å] the equatorial plane with its symmetry-related counterpart below the plane. The α carbon atoms, C(5) and C(7), lie below [0·01 (5) Å] and above [0·26 (5) Å] this plane, with the methyl carbon atoms C(4) and C(8) on the opposite sides [by 0·15 (5) and 0·53 (5) Å].

The ligand dimensions in each complex are as expected [apart from the possible disorder in (2)], as are the U—O distances to the chelating ligands. The U—N

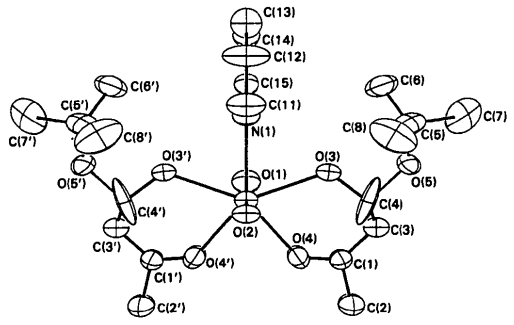

Fig. 3. A side view of molecule (2), showing the numbering scheme and the coplanarity of the pyridine ring and uranyl group (50% probability ellipsoids).

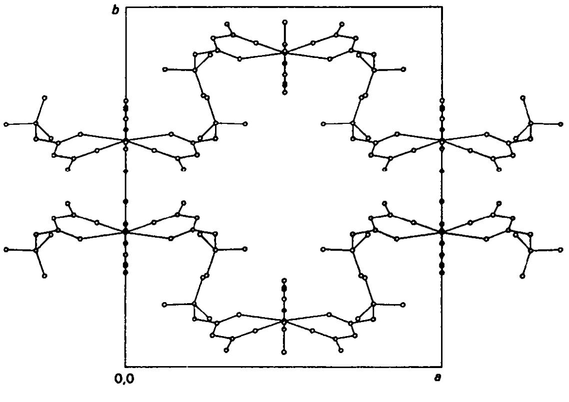

Fig. 4. Packing diagram for (2).

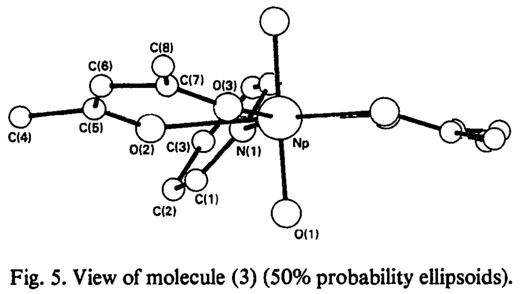

Fig. 5. View of molecule (3) (50% probability ellipsoids).

distances are longer than U—O(eq.) as predicted from the covalent radii; they are significantly longer than that found in complex (4). As expected, the Np—O(axial) and Np—O(eq.) distances in (3) are shorter by about 0·05 (1) Å than those in (4) (Alcock, Roberts & Brown, 1982), though *M*—N is greater in (3) than (4). The pyridine ring in complex (1) is twisted out of the equatorial plane, forming an angle with this plane of 36·9 (2)°, whilst in complex (2) it lies parallel to the uranyl group (90·0° twist). In complex (3) the corresponding twist is 49·0 (2)°, whilst in (4) the out-of-plane twist is 48·7 (10)°. These twists presumably reduce interference with the diketonate groups, but must have the effect of increasing repulsions between the *o*-hydrogen atoms on the pyridine and the actinyl oxygen atoms.

We have therefore been surprised to find that none of the O—*M*—O groups in these complexes show substantial non-linearity compared with that found in (4). The pyridine–uranyl repulsions were believed to be responsible for the non-linear O—U—O group in this complex; however, study of the pyridine-H to actinyl-O distances shows that this steric influence is less in (4) than in the other complexes, yet the distortion of the actinyl bond is greatest (Table 7). Furthermore, there is no apparent correlation between O—*M*—O bond angles and *M*—O(axial) bond lengths which could account for this. The one parameter which does show a correlation with the distortion is the U—N distance. It may therefore be that direct O—N repulsion in the actinyl coordination sphere is responsible for the bent O—U—O group in (4). In their turn, the *M*—N distances show an inverse correlation with the *M*—O(eq.) distances, implying that the acac groups in (1)–(3) are rather more strongly held than in (4), leading to steric pressure and slight weakening of the *M*—N bond.

Table 7. *Comparison of M*—N *bond lengths* (Å), O—*M*—O *bond angles* (°), *interplane angles* (°) *and proximity of* (*pyridine*)H—O(*uranyl*) *atoms* (Å)

Atomic numbering as for Table 5.

	(1)	(2)	(3)	(4)
M—N	2·569 (6)	2·595 (2)	2·56 (3)	2·47 (1)
O(11)—*M*—O(12)	177·9 (2)	175·8 (8)	176·5 (19)	173·5 (8)
Equatorial/pyridine angle	36·9 (2)	90·0	49·0 (2)	48·7 (10)
O(11)···H(51)	2·914	2·677	3·074	3·179
O(12)···H(55)	3·145	2·634	—	—

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Actinide Structural Studies. 14.* Two Uranyl(VI) Complexes Containing 2,4-Pentanedione

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Abstract. (1) Aquadioxobis(2,4-pentanedionato)uranium(VI), $[U(C_5H_7O_2)_2(H_2O)O_2]$, $M_r = 486{\cdot}27$, monoclinic, $P2_1/c$, $a = 12{\cdot}895\ (3)$, $b = 7{\cdot}042\ (2)$, $c = 16{\cdot}633\ (3)$ Å, $\beta = 109{\cdot}46\ (2)°$, $U = 1424{\cdot}2\ (6)$ Å^3, $Z = 4$, $D_x = 2{\cdot}27$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 108{\cdot}27$ cm^{-1}, $F(000) = 896$, $T = 290$ K, $R = 0{\cdot}043$ for 1821 unique observed reflections. (2) 2,4,6-Trimethylpyridinium dinitratodioxo(2,4-pentanedionato)uranate(VI), $[C_8H_{12}N][U(C_5H_7O_2)(NO_3)_2O_2]$, $M_r = 615{\cdot}34$, orthorhombic, $P2_12_12$, $a = 6{\cdot}879\ (2)$, $b = 15{\cdot}241\ (4)$, $c = 9{\cdot}613\ (2)$ Å, $U = 1007{\cdot}9\ (4)$ Å^3, $Z = 2$, $D_x = 2{\cdot}03$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 78{\cdot}86$ cm^{-1}, $F(000) = 580$, $T = 290$ K, $R = 0{\cdot}039$ for 1936 unique observed reflections. (1) has pentagonal

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* Part 13: Alcock, Flanders, Pennington & Brown (1987).

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