Pyrazolonato Complexes of Uranium. Crystal Structures of Bis-oxobis(1-phenyl-3-methyl-4-acetylpyrazol-5-onato)aquouranium(VI) and Bis-oxobis(1-phenyl-3-methyl-4-benzoylpyrazol-5-onato(propanol)uranium(VI)

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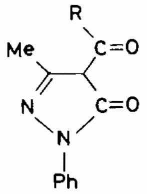
Abstract

The complexes $[UO_2L_2(H_2O)]$ (L = 1-phenyl-3-methyl-4-acylpyrazolonato, $RCOC_{10}H_8N_2O$, R = Me (**2**) or Ph (**3**) have been synthesised. X-ray diffraction studies show that **2** is monoclinic, space group $C2/c$, $a = 22.798(5)$, $b = 15.939(3)$, $c = 13.703(3)$ Å, $\beta = 97.24(2)°$, $R = 0.084$ for 1925 reflections. Complex **3** is obtained from propanol–acetone as $UO_2L_2(PrOH)$ (**4**) which is monoclinic, space group Cc, $a = 12.719(2)$, $b = 15.668(5)$, $c = 18.000(7)$ Å, $\beta = 102.27(2)°$, $R = 0.071$ for 2612 reflections. In each case, the coordination at uranium is pentagonal bipyramidal with short U–O bonds to oxygen atoms in axial positions. Four of the equatorial positions are occupied by oxygen atoms from the enolato ligands and the fifth by an oxygen atom from the solvent.

Introduction

The 1-phenyl-3-methyl-4-acylpyrazolones ((**1a**) and (**1b**)) have been investigated as extractants for metals [1], and **1b** appears to be a better extractant than the more expensive but widely used thenoyltrifluoroacetone for U(VI) in acid solution [2]. Studies in aqueous solution have indicated that the species extracted contain two ligands per UO_2^{2+}, and that extraction is enhanced by donors such as phosphate esters or phosphine oxides [2, 3]. Structures of specific compounds extracted into the organic layer have not however been fully determined. Complexes of a wide range of acylpyrazolones with a range of metal ions have recently been made with a view to gaining insight into factors determining selective extraction of uranium from natural ores [4]. We chose to examine the complex from the benzoylpyrazolone (**1b**) in detail since the structure of the free ligand was already known [5]: the structure of the acetyl compound (**2**) was also determined in order to clarify the role of the solvent in completing the coordination sphere of the uranium.



1

R = Me (HPMAP) (**1a**)
R = Ph (HPMBP) (**1b**)

$UO_2(PMAP)_2H_2O$
2

$UO_2(PMBP)_2(PrOH)$
4

Experimental

All ^1H and ^{13}C NMR data are for samples in acetone-d_8; chemical shifts are relative to $SiMe_4$. Carbon atoms are numbered as in Figs. 1 and 2.

Ligands

These were synthesised as described elsewhere [1]. HPMAP (**1a**): yield 60%. UV: λ_{max} 250.9 (ϵ 278), 286.5 nm (ϵ 4230 dm^3 mol^{-1} cm^{-1}) IR: 3300b (νOH), 1635s (νCO) cm^{-1}. NMR: δ(C), 15.5 C(20), 26.1 C(8), 105.1 C(6), 148.8 C(19), 162.3 C(2), 194.5 C(7), 121.0, 127.1, 129.9, 138.7 ppm (Ph). HPMBP (**1b**): yield 87%. UV: λ_{max} 251.3 (ϵ 765), 292.3 nm (ϵ 9510). IR: 1639s (νCO) cm^{-1}. NMR: δ(C), 15.9 C(20), 104.5 C(6), 149.0 C(19), 162.3 C(2), 191.7 C(7), 121.2, 127.3, 128.9, 129.3, 132.3, 132.7, 138.5 ppm (Ph).

Synthesis of Uranium Complexes

A solution of $UO_2(CH_3CO_2)_22H_2O$ (2.12 g, 5.05 mmol) in water (50 cm^3) at 45 °C was added with stirring to HPMAP (2.16 g, 10.0 mmol) in

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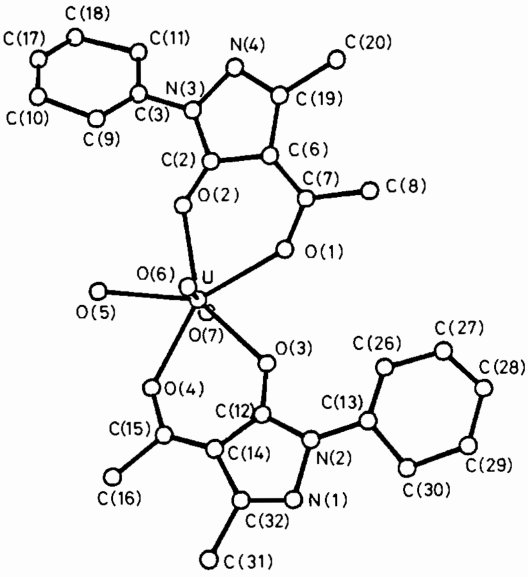

Fig. 1. Molecular structure of 2. The numbering of the atoms differs from that in the title of the paper.

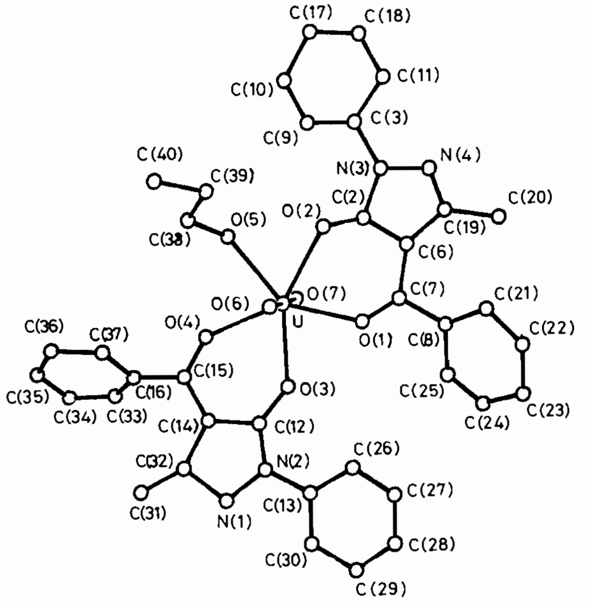

Fig. 2. Molecular structure of 4. The numbering is the same as that in 2.

ethanol (50 cm^3). The mixture was kept at 45 °C for 15 min and the orange precipitate was filtered off, washed with water, recrystallised from water–ethanol (1:2), and dried in air. Yield 3.02 g, 84%; melting point (m.p.) 214 °C. *Anal.* Found: C, 39.0; H, 3.6; N, 7.2. Calc. for $C_{24}H_{26}N_4O_8U$: C, 39.1; H, 3.6; N, 7.6%. After recrystallisation from acetone–hexane (1:1) the compound $UO_2(PMAP)_2 \cdot H_2O$ (2) had m.p. 217 °C. *Anal.* Found: C, 39.3; H, 3.7; N, 7.0. Calc. for $C_{24}H_{24}N_4O_7U$: C, 40.1; H, 3.3; N, 7.8. UV: λ_{max} 252 (ϵ 5230), 288 nm (ϵ 17 600 dm^3 mol^{-1} cm^{-1}). IR 3500b (νOH), 1600s (νCO), 925s (ν_{asym} UO_2), 260 (νUO) cm^{-1}. NMR: δ(H), 2.58 (3H, s, 3-Me), 3.18 (2H, s, H_2O), 2.92 (3H, s, 4-MeCO), 7.29–8.55 (5H, m, Ph), δ(C) 17.0 C(20), 27.4 C(8), 109.7 C(6), 150.0 C(19), 166.8 C(2), 197.8 C(7).

$[UO_2(PMBP)_2(H_2O)_2]$ (3), m.p. 230 °C, was made similarly in almost quantitative yield. *Anal.* Found: C, 47.4; H, 3.8; N, 6.7. Calc. for $C_{34}H_{28}N_4O_7U$: C, 48.4; H, 3.2; N, 6.65. Calc for $C_{34}H_{30}N_4O_8U$: C, 47.4; H, 3.5; N, 6.5%. λ_{max} ($CHCl_3$) 251 (ϵ 9290), 292 nm (26 300 dm^3 mol^{-1} cm^{-1}). IR 3400b (νOH), 1602 (νCO), 295s (ν_{asym} UO_2), 260, 250 (νUO) cm^{-1}. NMR: δ(H), 2.60 (3H, s, 3-Me), 4.33 (2H, s, H_2O), 7.7–8.75 (5H, m, Ph), δ(C) 16.6 C(20), 109.7 C(6), 149.9 C(19), 167.9 C(2), 194.8 C(7), 121.3, 126.4, 129.5, 129.8, 132.7, 139.9, 140.1 ppm (Ph).

When a sample of 3 was recrystallised from propanol–acetone (1:1), orange–red crystals of the propanol complex $UO_2(PMBP)_2(PrOH)$ (4), m.p. 223 °C, were obtained. *Anal.* Found: C, 50.1; H, 3.7; N, 6.2. Calc. for $C_{37}H_{34}N_4O_7U$: C, 50.2; H, 3.9; N, 6.3%. NMR: δ(H), 0.92 (3H, t), 1.40–1.67 (2H, m), 3.63 (2H, m), (Pr) 2.53 (6H, s, 3-Me), 7.71–8.49 (10H, m, Ph), δ(C) 10.6, 26.7, 65.0 (Pr). Other peaks were not significantly different from those in 3.

Crystal Structure Determinations

Crystal data for 2

$C_{24}H_{24}N_4O_7U$, M = 718.51, monoclinic, space group $C2/c$, a = 22.798(5), b = 15.939(3), c = 13.703(3) Å, β = 97.24(2)°, U = 4939.6 Å^3, Z = 8, D_c = 1.93 g cm^{-3}, $F(000)$ = 2752, Mo Kα radiation, λ = 0.71069 Å, μ = 62.8 cm^{-1}.

Data were measured on an Enraf-Nonius CAD 4 diffractometer, using a crystal of size 0.2 × 0.2 × 0.1 mm. Final cell dimensions were calculated from the setting angles of 25 reflections with $\theta \approx 14°$. Intensities for reflections with $2 < \theta < 25°$ and h, k, $\pm l$ were measured by a θ–2θ scan with $\Delta\theta$ = $(0.8 + 0.35 \tan\theta)°$. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz and polarisation effects and for absorption using DIFABS [6] (min. correction 0.56; max. 2.42); 1925 unique reflections with $|F^2| > \sigma(F^2)$ where $\sigma(F^2) = [\sigma^2 I + 0.04 I)]^{1/2}/$ Lp were used in the structure refinement.

The structure was solved by routine heavy atom methods and full matrix least-squares refinement of non-hydrogen atoms with only U atoms anisotropic. Hydrogen atoms were omitted. Refinement converged at $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$ = 0.084 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0.100. A final difference map had a peak of 1.7 e Å^{-3}, on the two-fold axis but was otherwise featureless. Pro-

TABLE 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for **2**[a]

	x	y	z	U_{iso}/U_{eq} (Å^2)
U	3832.1(5)	2308.9(7)	3186.8(7)	62
O(1)	3410(10)	2404(15)	4692(17)	103
O(2)	3866(8)	981(11)	3900(12)	61
O(3)	3510(9)	3667(12)	3364(14)	79
O(4)	4149(8)	3110(13)	1859(13)	75
O(5)	4342(7)	1402(11)	2115(11)	55
O(6)	4491(9)	2574(14)	3860(15)	93
O(7)	3152(8)	2024(13)	2469(14)	80
N(1)	3782(10)	5790(15)	2781(17)	73
N(2)	3538(9)	5118(14)	3365(15)	63
N(3)	3924(8)	−46(13)	5071(14)	50
N(4)	3756(8)	−182(12)	6007(14)	49
C(2)	3803(10)	719(14)	4749(16)	41
C(3)	4177(12)	−729(18)	4577(20)	66
C(6)	3526(10)	1146(14)	5499(16)	41
C(7)	3307(11)	1945(17)	5442(18)	54
C(8)	3050(14)	2402(22)	6293(25)	91
C(9)	4631(14)	−528(22)	4103(24)	94
C(10)	4927(16)	−1291(26)	3629(29)	115
C(11)	3920(14)	−1514(22)	4697(23)	90
C(12)	3683(11)	4375(17)	2959(19)	59
C(13)	3206(11)	5295(17)	4132(19)	58
C(14)	4043(11)	4505(15)	2227(17)	49
C(15)	4225(12)	3900(17)	1701(19)	59
C(16)	4553(12)	4047(18)	801(20)	67
C(17)	4739(14)	−1958(22)	3773(24)	94
C(18)	4264(15)	−2233(24)	4102(27)	109
C(19)	3541(10)	539(14)	6254(15)	38
C(20)	3285(12)	596(17)	7264(20)	64
C(26)	3086(12)	4741(18)	4818(20)	67
C(27)	2754(12)	4963(19)	5593(20)	72
C(28)	2585(15)	5740(23)	5690(26)	100
C(29)	2758(22)	6365(37)	5042(39)	178
C(30)	2972(20)	6115(32)	4075(35)	156
C(31)	4365(13)	5974(20)	1462(23)	83
C(32)	4042(12)	5407(17)	2187(19)	62

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

grams from the Enraf-Nonius SDP-Plus package were used. Final atomic coordinates, bond lengths and angles are given in Tables 1 and 2, and the structure is shown in Fig. 1.

Crystal data for 4

$C_{37}H_{34}N_4O_7U$, M = 884.7, monoclinic, space group Cc, a = 12.719(2), b = 15.668(5), c = 18.000(7) Å, β = 102.27(2)° U = 3504.8 Å^3, Z = 4, D_c = 1.68 g cm^{-3}, $F(000)$ = 1728, Mo Kα radiation, λ = 0.71069 Å, μ = 44.4 cm^{-1}.

Data from a crystal 0.2 × 0.2 × 0.2 mm were collected as for **2**. Intensities for reflections with $2 < \theta < 25°$ and h, k, $\pm l$ [2612 reflections with $|F^2| > \sigma(F^2)$] were used in the structure refinement and a correction was made for absorption [min. 0.57; max. 1.45]. The structure was solved by heavy atom methods with full matrix least-squares refinement of non-hydrogen atoms and only U anisotropic. Hydrogen atoms were omitted. Refinement converged at R = 0.071; R' = 0.164. (R = 0.080, R' = 0.172 for the opposite absolute structure).

Fractional atomic coordinates are given in Table 3 and bond lengths and angles in Table 4. The structure is shown in Fig. 2.

Results and Discussion

The reactions between uranyl acetate and the acylpyrazolones **1a** and **1b** yield complexes $[UO_2L_2(H_2O)_n]$ (L = PMAP (**5**) or PMBP (**3**)). There is some doubt about the value of n. The observed microanalysis values for C, H and N from samples of **5** or **3** recrystallised from aqueous ethanol agreed better with the calculated values if n was assumed to be 2 rather than 1. However, the compound obtained when the acetyl compound **5** was recrystallised from hexane–acetone was the monoaquo complex **2**: since the m.p., IR and NMR spectra of **5** and **2** were almost identical we cannot on

TABLE 2. Intramolecular distances (Å) and angles (°) for **2** with e.s.d.s in parentheses

Bonds			
U–O(1)	2.39(2)	U–O(2)	2.33(2)
U–O(3)	2.31(2)	U–O(4)	2.41(2)
U–O(5)	2.46(2)	U–O(6)	1.71(2)
U–O(7)	1.79(2)	O(1)–C(7)	1.31(3)
O(2)–C(2)	1.26(3)	O(3)–C(12)	1.34(3)
O(4)–C(15)	1.29(3)	N(1)–N(2)	1.49(3)
N(1)–C(32)	1.23(4)	N(2)–C(12)	1.37(4)
N(2)–C(13)	1.40(3)	N(3)–N(4)	1.40(3)
N(3)–C(2)	1.31(3)	N(3)–C(3)	1.44(4)
N(4)–C(19)	1.31(3)	C(2)–C(6)	1.44(3)
C(6)–C(7)	1.37(3)	C(6)–C(19)	1.41(3)
C(7)–C(8)	1.55(4)	C(14)–C(15)	1.30(4)

(continued)

TABLE 2. *(continued)*

C(12)–C(14)	1.39(4)	C(15)–C(16)	1.54(4)
C(14)–C(32)	1.44(4)	C(19)–C(20)	1.57(4)
C(31)–C(32)	1.59(4)		

Mean C–C in Ph rings: 1.40(5)

Angles

O(1)–U–O(2)	72.0(7)	O(1)–U–O(3)	71.4(7)
O(1)–U–O(4)	144.2(7)	O(1)–U–O(5)	145.8(7)
O(1)–U–O(6)	86.6(9)	O(1)–U–O(7)	94.3(8)
O(2)–U–O(3)	143.3(7)	O(2)–U–O(4)	143.4(6)
O(2)–U–O(5)	73.9(6)	O(2)–U–O(6)	91.0(8)
O(2)–U–O(7)	88.9(8)	O(3)–U–O(4)	73.2(7)
O(3)–U–O(5)	142.7(6)	O(3)–U–O(6)	88.9(9)
O(3)–U–O(7)	91.8(8)	O(4)–U–O(5)	69.5(6)
O(4)–U–O(6)	87.1(8)	O(4)–U–O(7)	92.4(8)
O(5)–U–O(6)	91.0(8)	O(5)–U–O(7)	88.0(7)
O(6)–U–O(7)	179.0(9)	U–O(1)–C(7)	141(2)
U–O(2)–C(2)	133(2)	U–O(3)–C(12)	129(2)
U–O(4)–C(15)	135(2)	N(2)–N(1)–C(32)	104(2)
N(1)–N(2)–C(12)	106(2)	N(1)–N(2)–C(13)	122(2)
C(12)–N(2)–C(13)	131(2)	N(4)–N(3)–C(2)	112(2)
N(4)–N(3)–C(3)	119(2)	C(2)–N(3)–C(3)	129(2)
N(3)–N(4)–C(19)	105(2)	O(2)–C(2)–N(3)	125(2)
O(2)–C(2)–C(6)	128(2)	N(3)–C(2)–C(6)	107(2)
N(3)–C(3)–C(9)	115(3)	N(3)–C(3)–C(11)	115(3)
C(2)–C(6)–C(19)	103(2)	C(2)–C(6)–C(7)	126(2)
O(1)–C(7)–C(6)	118(2)	C(7)–C(6)–C(19)	131(2)
C(6)–C(7)–C(8)	124(2)	O(1)–C(7)–C(8)	117(2)
O(3)–C(12)–N(2)	118(2)	O(3)–C(12)–C(14)	131(2)
N(2)–C(12)–C(14)	111(2)	N(2)–C(13)–C(26)	125(2)
N(2)–C(13)–C(30)	112(3)	C(12)–C(14)–C(32)	100(2)
C(12)–C(14)–C(15)	123(2)	O(4)–C(15)–C(14)	125(3)
C(15)–C(14)–C(32)	136(3)	C(14)–C(15)–C(16)	123(2)
O(4)–C(15)–C(16)	112(2)	N(4)–C(19)–C(20)	118(2)
N(4)–C(19)–C(6)	113(2)	N(1)–C(32)–C(31)	116(3)
C(6)–C(19)–C(20)	129(2)		
N(1)–C(32)–C(14)	118(3)		
C(14)–C(32)–C(31)	126(2)		

Mean C–C–C in Ph rings: 120(3)

present evidence be certain that the bisaquo complex **5** is a distinct species. When the benzoyl derivative **3** was recrystallised from propanol–acetone, propanol was incorporated into the coordination sphere of the uranium as shown by the X-ray study of complex **4**.

The broad band centred at 3300 cm^{-1} in the IR spectrum of HPMAP (**1a**) [7] disappears in the spectrum of the uranium complex, and the bands assigned to ν(CO) in the free ligands are shifted to slightly lower frequencies. These observations suggest that in **2** and **4** the uranium has reacted with the enol form of the diketone. This is confirmed by the X-ray study. In both **2** and **4** the metal is surrounded by 7 oxygen atoms at the corners of a pentagonal bipyramid as observed in a number of other uranyl bis(diketone) [8–12] and oxalate complexes [13]. The presence of the uranium atom and the uncertainties in absorption corrections result in large estimated standard deviations (e.s.d.s) in bond lengths and angles both in the compounds described in the present paper and those in the literature, but the U=O (*c.* 1.77 Å) and U–O (*c.* 2.40 Å) bond lengths in both **2** and **4** fall in the expected range. The O=U=O angle is close to 180° and the equatorial O–U–O angles close to 72°. The uncertainties in the bond lengths and angles make it difficult to see the changes which result from the conversion of the N-protonated tautomer of the free ligand [5] to the complexed O-protonated

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for 4

	x	y	z	U_{iso}/U_{eq}[a] ($Å^2$)		x	y	z	U_{iso}/U_{eq}[a] ($Å^2$)
U	0	996.9(6)	2500	43	C(17)	2172(41)	1187(36)	6560(32)	67
O(1)	291(19)	2419(17)	2211(14)	60	C(18)	2315(30)	2059(26)	6528(23)	86
O(2)	1034(19)	1619(18)	3610(14)	60	C(19)	874(36)	3830(32)	3963(29)	99
O(3)	−719(25)	1171(20)	1251(19)	68	C(20)	759(45)	4836(45)	3884(37)	95
O(4)	−780(20)	−344(18)	2019(15)	54	C(21)	1388(43)	4522(39)	2325(33)	60
O(5)	251(17)	−55(15)	3521(13)	42	C(22)	1497(32)	5152(30)	1766(24)	62
O(6)	1246(27)	697(25)	2295(21)	58	C(23)	659(40)	5278(38)	1091(32)	61
O(7)	−1221(23)	1312(22)	2735(18)	60	C(24)	−151(30)	4661(28)	999(23)	71
N(1)	−1227(24)	164(23)	−537(18)	44	C(25)	−246(32)	4027(22)	1454(26)	56
N(2)	−1085(31)	831(23)	−47(24)	50	C(26)	−527(41)	2359(40)	−29(33)	94
N(3)	1164(26)	2627(24)	4568(20)	60	C(27)	−546(41)	3118(39)	−433(34)	91
N(4)	1096(26)	3518(25)	4602(20)	61	C(28)	−1020(41)	3187(37)	−1162(31)	89
C(2)	901(34)	2355(31)	3786(26)	35	C(29)	−1579(37)	2554(33)	−1549(27)	84
C(3)	1529(23)	2092(20)	5243(17)	42	C(30)	−1542(28)	1733(25)	−1167(21)	61
C(6)	755(34)	3157(31)	3406(27)	67	C(31)	−1562(28)	−1367(26)	−413(21)	86
C(7)	420(36)	3067(33)	2579(31)	73	C(32)	−1339(32)	−621(29)	−40(24)	59
C(8)	509(29)	3895(21)	2170(24)	33	C(33)	−2389(25)	−1922(22)	1180(19)	58
C(9)	1326(30)	1254(29)	5242(23)	51	C(34)	−2666(41)	−2764(39)	1157(32)	84
C(10)	1592(29)	788(27)	5870(22)	71	C(35)	−1907(48)	−3360(49)	1455(37)	82
C(11)	1989(26)	2544(23)	5896(20)	49	C(36)	−843(42)	−3115(36)	1741(33)	91
C(12)	−942(27)	688(25)	666(21)	55	C(37)	−551(32)	−2197(31)	1703(26)	77
C(13)	−1011(21)	1646(19)	−400(16)	43	C(38)	1029(46)	−810(42)	3657(37)	147
C(14)	−1155(30)	−226(27)	708(23)	47	C(39)	2043(94)	−535(120)	3974(85)	238
C(15)	−1027(42)	−697(39)	1393(32)	20	C(40)	2724(90)	−1463(81)	4007(68)	186
C(16)	−1449(21)	−1604(20)	1402(16)	43					

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 4. Intramolecular distances (Å) and angles (°) for 4 with e.s.d.s in parentheses

Bonds			
U–O(1)	2.34(3)	U–O(2)	2.36(2)
U–O(3)	2.26(3)	U–O(4)	2.40(3)
U–O(5)	2.44(2)	U–O(6)	1.77(4)
U–O(7)	1.77(3)	O(1)–C(7)	1.20(6)
O(2)–C(2)	1.22(6)	O(3)–C(12)	1.28(5)
O(4)–C(15)	1.23(6)	O(5)–C(38)	1.53(7)
N(1)–N(2)	1.35(5)	N(1)–C(32)	1.55(6)
N(2)–C(12)	1.28(6)	N(2)–C(13)	1.44(5)
N(3)–N(4)	1.40(5)	N(3)–C(2)	1.44(6)
N(3)–C(3)	1.47(5)	N(4)–C(19)	1.23(6)
C(2)–C(6)	1.42(7)	C(6)–C(7)	1.47(7)
C(6)–C(19)	1.44(7)	C(7)–C(8)	1.51(6)
C(14)–C(15)	1.42(7)	C(12)–C(14)	1.46(6)
C(15)–C(16)	1.52(7)	C(14)–C(32)	1.46(6)
C(19)–C(20)	1.59(9)	C(31)–C(32)	1.35(6)
C(38)–C(39)	1.36(14)	C(39)–C(40)	1.69(21)
Mean C–C in Ph rings: 1.39(3)			
Angles			
O(1)–U–O(2)	73.0(9)	O(1)–U–O(3)	73(1)
O(1)–U–O(4)	145.7(9)	O(1)–U–O(5)	144.2(8)
O(1)–U–O(6)	91(1)	O(1)–U–O(7)	89(1)
O(2)–U–O(3)	146(1)	O(2)–U–O(4)	141.2(9)

(continued)

TABLE 4. *(continued)*

O(2)-U-O(5)	71.4(8)	O(2)-U-O(6)	86(1)
O(2)-U-O(7)	92(1)	O(3)-U-O(4)	72(1)
O(3)-U-O(5)	142(1)	O(3)-U-O(6)	91(1)
O(3)-U-O(7)	91(1)	O(4)-U-O(5)	70.0(8)
O(4)-U-O(6)	91(1)	O(4)-U-O(7)	91(1)
O(5)-U-O(6)	90(1)	O(5)-U-O(7)	89(1)
O(6)-U-O(7)	178(2)	U-O(1)-C(7)	134(3)
U-O(2)-C(2)	122(2)	U-O(3)-C(12)	136(3)
U-O(4)-C(15)	137(3)	U-O(5)-C(38)	128(3)
N(2)-N(1)-C(32)	105(3)	N(1)-N(2)-C(12)	119(4)
N(1)-N(2)-C(13)	114(3)	C(12)-N(2)-C(13)	126(4)
N(4)-N(3)-C(2)	110(3)	N(4)-N(3)-C(3)	123(3)
C(2)-N(3)-C(3)	127(4)	N(3)-N(4)-C(19)	111(4)
O(2)-C(2)-N(3)	121(4)	O(2)-C(2)-C(6)	136(5)
N(3)-C(2)-C(6)	101(4)	N(3)-C(3)-C(9)	122(3)
N(3)-C(3)-C(11)	114(3)	C(2)-C(6)-C(19)	109(4)
C(2)-C(6)-C(7)	113(4)	O(1)-C(7)-C(6)	128(5)
C(7)-C(6)-C(19)	138(4)	C(6)-C(7)-C(8)	112(4)
O(1)-C(7)-C(8)	118(5)	C(7)-C(8)-C(25)	117(3)
C(7)-C(8)-C(21)	128(4)	O(3)-C(12)-C(14)	123(4)
O(3)-C(12)-N(2)	133(4)	N(2)-C(13)-C(26)	125(3)
N(2)-C(12)-C(14)	104(3)	C(12)-C(14)-C(32)	111(4)
N(2)-C(13)-C(30)	117(3)	O(4)-C(15)-C(14)	121(5)
C(12)-C(14)-C(15)	124(4)	C(14)-C(15)-C(16)	121(4)
C(15)-C(14)-C(32)	123(4)	C(15)-C(16)-C(37)	110(3)
O(4)-C(15)-C(16)	116(5)	N(4)-C(19)-C(6)	109(4)
C(15)-C(16)-C(33)	132(3)	C(6)-C(19)-C(20)	132(5)
N(4)-C(19)-C(20)	119(5)	N(1)-C(32)-C(31)	116(4)
N(1)-C(32)-C(14)	100(3)	C(38)-C(39)-C(40)	100(11)
C(14)-C(32)-C(31)	144(4)		
O(5)-C(38)-C(39)	110(8)		

Mean C-C-C in Ph rings: 120(4)

TABLE 5. Dihedral angles (°) between least-squares planes for compounds 2 and 4

Planes[a]	Compound 2	Compound 4
1-2	9	23
1-3	15	19
4-2	42	18
5-2		52
6-3	15	21
7-3		90

[a] 1, O(1) O(2) O(3) O(4) O(5); 2, O(1) O(2) C(7) C(8) C(6) C(2) C(19) C(20) N(4) N(3) C(3); 3, O(3) O(4) C(12) C(14) C(15) C(16) C(32) C(31) N(1) N(2) C(13); 4, C(3)-C(11); 5, C(8)-C(25); 6, C(13)-C(30); 7, C(16)-C(37).

tautomer. The most dramatic change in the molecular skeleton is the shortening of the N(4)–C(19) bond length from 1.342(8) to 1.23(6) Å, but the e.s.d.s indicate that even this is not completely convincing. The wavelengths of the absorption maxima in the UV spectra of the dioxouranium complexes are similar to those of the free ligand suggesting that the peaks arise from intraligand $\pi \rightarrow \pi^*$ transitions which are almost unchanged by complex formation.

In both **2** and **4** the equatorial oxygen atoms of the uranium coordination sphere are less than 0.1 Å from the least-squares plane. Table 5 shows that the ligand planes (2 and 3) are inclined at small angles (<23°) to the equatorial oxygen plane (1), and that the rings of the N-phenyl and benzoyl groups are also twisted by various angles with respect to the ligand planes. These observations suggest that the conformations of the molecules in the solid may be determined mainly by steric effects and packing forces. The pyrazolone ligands are probably too unwieldy to give oligomeric structures such as those formed by oxalate complexes, but in bis-complexes a small unidentate ligand such as water is sufficient to complete the coordination at uranium. With the more compact oxydiacetato ligand the uranium becomes eight coordinate as in $[UO_2L_2]^{2-}$ (L = $O(CH_2CO_2)_2$ [14]. The water may be displaced when the uranyl pyrazolonato complexes are recrystallised from a large excess of alcohol, but it is retained during crystallisation from acetone–hexane.

Phosphates or phosphine oxides which facilitate extraction of U(VI) by acylpyrazolones probably also give seven-coordinate uranium complexes.

Supplementary Material

Tables of observed and calculated structure factors for both structures are available from the authors on request.

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