Polymorphism in Uranyl Chelate Complexes. Part 2.† The Crystal and Molecular Structure of the Alpha form of Bis(1,1,1,5,5,5-Hexafluoropentane-2,4-dionato)dioxo(trimethyl phosphate)uranium(VI)

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The crystal structure of the title complex α-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$ has been determined from 1 079 three-dimensional single-crystal (*hkl*) data collected on a four-circle goniometer with Cu-K_β radiation. The crystals are monoclinic, space group $P2_1/m$, with $a = 10.349(6)$, $b = 21.590(12)$, $c = 5.560(3)$ Å, and $\beta = 92.01°$, $R = 0.075$. Two bidentate hfpd molecules and one unidentate trimethyl phosphate molecule are co-ordinated to the uranyl group, forming a pentagonal bipyramid of oxygen atoms around the U^{VI}. The pentagonal ring (four carbonyl oxygen atoms and one trimethyl phosphate oxygen atom) is planar and normal to the linear uranyl group. The hfpd molecules are planar, but tilted by 22.5° to the plane of the pentagonal ring in a boat configuration. The crystal structure is molecular, and the low melting point can be explained by the predominant intermolecular contacts between similarly charged fluorine atoms of CF_3 groups. The thermal-vibration parameters are large on the periphery of the molecules, approaching liquid-crystal values, and the CF_3 groups have two-fold positional disorder. The trimethyl phosphate group is also disordered. The structure is compared with those of other metal–hfpd complexes and of pentagonal-bipyramidal uranyl complexes.

COMPLEXES of fluorinated pentane-2,4-dione (Hpd) are extensively used for gas-chromatographic analysis of metals.[1] Mixed-ligand complexes such as $[UO_2(hfpd)_2\{PO(OBu)_3\}]$ (hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) have been used for the determination of the uranyl ion by this method.[2] The complex $[UO_2(hfpd)_2\{PO(OMe)_3\}]$ was prepared in our laboratories for similar studies. Guinier photographs and differential scanning calorimetry (d.s.c.) studies[3] showed this complex to be dimorphic, having a yellow α and an orange β form. In this paper the crystal structure of the α form is described.

EXPERIMENTAL

Morphology.—Sublimed and solution-grown crystals were regular, transparent, pale yellow needles or plates. On standing in air, they decomposed slowly to an opaque powder. A solution-grown crystal was mounted with Araldite adhesive inside a thin-walled quartz capillary of diameter 0.06 cm. Rotation and Weissenberg photographs (Cu-K_α radiation) showed that the crystals were monoclinic, space group $P2_1(C_2^2)$ or $P2_1/m(C_{2h}^2)$, with the cell dimensions given below. The crystal was mounted with c^* along the tube axis and the crystal faces were ±(010), ±(100), and ±(101), with interfacial distances of 0.009 0, 0.053 2, and 0.051 4 cm, respectively. The crystal volume was 28×10^{-6} cm³. The morphology is shown in Figure 1.

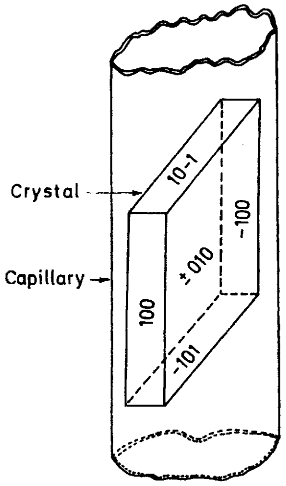

FIGURE 1 Morphology of α-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$ crystals

Data Collection and Reduction.—The *X*-ray intensity data were collected on a four-circle diffractometer (c^* along the ϕ axis), with Cu-K_β radiation (λ 1.392 3 Å); the counter was a Si(Li) solid-state detector with an energy discriminator. Least-squares analysis was carried out for the 2θ values of 35 reflections between 45 and 70°. The intensities of 1 287 reflections to 2θ 76° were measured with ω scans; the half-widths were *ca.* 0.33° in ω. A standard reflection, (230), measured every 20 reflections, varied between 96 000 and 101 000 background corrected counts over the collection period. This variation was found to be caused by changes in the *X*-ray tube temperature, rather than decomposition, and was corrected for by normalising each intensity to the previous standard. The intensities were corrected for absorption [μ(Cu-K_β) 168 cm^{-1}], and the transmission factors were between 3 and 22%. The absorption corrections and reduction to $F(hkl)$ values were carried out by the program DRACULA,[4] in which the experimental errors are computed by the formulae (1)—(3) where Q is the background-corrected intensity, A the absorption factor, I the total integrated intensity, and α and β (50 counts and 0.05) allow for constant and intensity-dependent systematic errors.

$$\sigma^2(Q) = \sigma_1^2 + \sigma_2^2 \qquad (1)$$

$$\sigma_1 = \sigma(I)A \qquad (2)$$

$$\sigma_2^2 = (\alpha + \beta I)A \qquad (3)$$

Generally $\sigma(F)$ was 5—10% of F. Averaging equivalent reflections gave a total of 1 079 independent $F(hkl)$ values for the structure analysis.

Crystal Data.—α-$C_{13}H_{11}F_{12}O_{10}PU$, $M = 824.2$, Mono-

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† Part 1 is ref. 3.

[1] R. W. Mosher and R. E. Sievers, 'Gas Chromatography of Metal Chelates,' Pergamon, London, 1965.

[2] R. F. Sieck, J. J. Richard, Kay Iversen, and C. V. Banks, *Analyt. Chem.*, 1971, **43**, 913.

[3] J. H. Levy and A. B. Waugh, preceding paper.

[4] M. M. Elcombe, G. W. Cox, A. W. Pryor, and F. H. Moore, Report AAEC/TM 578, 1971.

clinic, $a = 10.349(6)$, $b = 21.590(12)$, $c = 5.560(3)$ Å, $\beta = 92.01(2)°$, $U = 1\,241.5$ Å^3, $Z = 2$, $D_c = 2.205$ g cm^{-3}, m.p. = 361 K, $F(000) = 768$. Space group $P2_1(C_2^2)$ or $P2_1/m(C_{2h}^2)$, the latter being confirmed by structure analysis. Cu-K_β radiation (λ 1.392 3 Å), μ(Cu-K_β) = 168 cm^{-1}; absorption corrections were applied.

Solution and Refinement of the Structure.—The uranium atoms were located in a three-dimensional Patterson synthesis. As the unit-cell volume indicated there were two formula units per cell, only $x(U)$ and $z(U)$ had to be found in the Harker section $y = 0.5$; the y co-ordinate of uranium was given the arbitrary co-ordinate $y = 0$. The uranium co-ordinates deduced from the section were (0.197, 0, 0.434).

TABLE 1

Positional ($\times 10^3$) and thermal ($\times 10^4$) vibration parameters in α-[UO$_2$(hfpd)$_2$\{PO(OMe)$_3$\}] *

Atom	N	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	1.0	802.6(1)	250	432.2(2)	55(2)	26(1)	424(9)	0	25(3)	0
P	1.0	467(1)	250	673(2)	36(12)	59(4)	447(55)	0	−10(21)	0
C(1)	2.0	949(3)	366(2)	172(5)	68(32)	51(11)	415(133)	−24(18)	139(54)	−38(30)
C(2)	2.0	774(3)	405(2)	362(7)	135(40)	39(10)	606(156)	46(17)	53(75)	34(33)
C(3)	2.0	64(4)	382(1)	986(8)	309(60)	25(8)	869(215)	−26(18)	−166(99)	23(33)
C(4)	2.0	670(4)	459(1)	415(7)	282(61)	40(9)	587(182)	−31(21)	252(82)	−2(23)
C(5)	2.0	863(3)	414(1)	196(6)	118(38)	42(8)	559(157)	15(17)	168(72)	9(28)
C(6)	1.0	246(8)	250	409(13)	11.7(16)					
C(7)	2.0	479(5)	352(2)	942(9)	11.0(12)					
O(1)	1.0	714(2)	250	159(5)	102(31)	47(7)	246(98)	0	−38(45)	0
O(2)	1.0	892(3)	250	699(5)	151(37)	36(6)	440(127)	0	−47(59)	0
O(3)	2.0	747(2)	358(1)	488(4)	97(22)	42(6)	708(113)	11(10)	140(46)	−5(22)
O(4)	2.0	959(2)	315(1)	259(4)	124(22)	17(3)	1 042(135)	3(8)	159(49)	21(19)
O(5)	1.0	609(2)	250	627(4)	86(37)	33(6)	336(107)	0	−56(49)	0
O(6)	1.0	398(3)	250	450(7)	8.9(8)					
O(7)	1.33	425(3)	325(1)	739(7)	8.5(8)					
O(7′)	0.67	421(4)	280(2)	877(8)	3.0(8)					
F(1)	1.30	555(3)	440(1)	399(6)	7.6(6)					
F(1′)	0.70	599(9)	447(3)	602(18)	12.8(21)					
F(2)	1.30	703(4)	509(2)	311(9)	9.8(8)					
F(2′)	0.70	639(7)	486(3)	199(13)	9.8(15)					
F(3)	1.30	687(4)	471(1)	657(7)	9.3(8)					
F(3′)	0.70	732(7)	510(3)	498(15)	10.5(16)					
F(4)	1.30	21(3)	418(2)	807(8)	9.5(8)					
F(4′)	0.70	75(8)	443(3)	946(17)	11.8(18)					
F(5)	1.30	141(4)	425(2)	86(7)	9.5(8)					
F(5′)	0.70	175(7)	389(4)	165(14)	11.4(17)					
F(6)	1.30	123(2)	337(1)	−86(4)	5.6(5)					
F(6′)	0.70	35(10)	383(5)	745(21)	15.0(28)					

* N is the site-occupancy factor and the temperature factors are either the isotropic Debye–Waller B factor (Å^2) or anisotropic β_i. For the latter case the temperature-factor expression is $\exp[-(\beta_{11}h^2 + \beta_{12}hk + \ldots)]$.

Structure factors were calculated for the uranium contribution alone (neutral-uranium scattering curve,[5] corrected for anomalous dispersion,[6] $\Delta f' = -5.0$ e and $\Delta f'' = 11.2$ e) with the least-squares program LINUS.[7] The x and z co-ordinates of U and an overall Debye–Waller B factor were refined to give $x(U) = 0.196\,8(4)$, $z(U) = 0.432\,3(7)$, and $B = 2.9(2)$ Å^2, the value of $R' = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ being 0.33. A three-dimensional difference synthesis gave the positions of the phosphorus atom, five oxygen atoms, and five carbon atoms, and structure factors including these 11 additional atoms gave R 0.26. In this analysis the neutral-atom scattering curves[5] for P, O, C, and F were used uncorrected for anomalous dispersion. The remaining atoms in the structure, further removed from the uranium atom, and with higher temperature factors, were located by successive difference syntheses, the maps being pursued until they showed no other features but background noise. The final structure had a mirror plane; thus the space group was $P2_1/m$ and not $P2_1$.

Positional disorder was found in the CF$_3$ and MeO groups. Occupancy factors for the disorder positions were estimated from the difference-map peak heights. The complete structure was refined finally with anisotropic temperature factors for U, P, and the undisordered C and O atoms, and isotropic temperature factors for the other atoms or partial atoms. The final residuals were R' 0.075, $R = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.108$, and $\chi^2 = \Sigma w(|F_o| - |F_c|)^2/(N_o - N_v) = 1.17$ where N_o and N_v were the number of observations and variables and w the weighting factors.

Table 1 gives the final positional and thermal parameters, Table 2 the root-mean-square (r.m.s.) amplitudes of vibration of the anisotropically refined atoms along their principal axes, and Table 3 the angles between the principal axes and the unit-cell edges. Table 4 gives the observed bond lengths and angles. The final observed and calculated structure factors are listed in Supplementary Publication No. SUP 22051 (3 pp.).*

RESULTS AND DISCUSSION

Overall Crystal Structure.—The structure is shown projected down the short c axis in Figure 2. It is a packing of [UO$_2$(hfpd)$_2$\{PO(OMe)$_3$\}] molecular units which themselves have mirror plane symmetry. The intermolecular attractions are weak because the peripheral fluorine or hydrogen atoms of the CF$_3$ or CH$_3$ groups have large thermal vibrations and there are many

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies)

[5] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3, p. 201.

[6] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891

[7] P Coppens and W. C. Hamilton, *Acta Cryst.*, 1970, **A26**, 71.

TABLE 2

R.m.s. amplitudes (Å) of vibration along principal axes R_1, R_2, and R_3 of the atomic vibration ellipsoids for atoms whose thermal parameters were refined anisotropic*ally*

	Amplitude along		
Atom	R_1	R_2	R_3
U	0.169 (4)	0.247 (2)	0.259 (4)
P	0.14(2)	0.27(2)	0.37(1)
C(1)	0.09(10)	0.26(4)	0.38(4)
C(2)	0.17(6)	0.29(5)	0.38(4)
C(3)	0.23(4)	0.31(5)	0.46(5)
C(4)	0.19(6)	0.30(4)	0.45(4)
C(5)	0.16(7)	0.31(3)	0.36(4)
O(1)	0.18(4)	0.25(4)	0.33(3)
O(2)	0.24(4)	0.29(3)	0.31(4)
O(3)	0.17(4)	0.32(3)	0.36(3)
O(4)	0.19(2)	0.22(3)	0.42(3)
O(5)	0.18(5)	0.26(4)	0.28(2)

TABLE 3

Angles (°) between principal axes R_1, R_2, R_3 of the vibration ellipsoids of atoms refined anisotropically and the unit-cell edges

		Angle with		
Atom	Principal axis	*a*	*b*	*c*
U	R_1	172(1)	90	83(1)
	R_2	90	0	90
	R_3	83(1)	90	7(1)
P	R_1	174(7)	90	96(7)
	R_2	84(7)	90	174(7)
	R_3	90	0	90
C(1)	R_1	148(10)	95(11)	58(11)
	R_2	114(13)	122(15)	138(14)
	R_3	110(10)	33(15)	114(13)
C(2)	R_1	140(14)	50(12)	93(20)
	R_2	108(22)	107(22)	25(21)
	R_3	56(11)	45(11)	65(21)
C(3)	R_1	76(16)	14(16)	90(22)
	R_2	57(15)	98(25)	34(14)
	R_3	143(13)	78(8)	56(14)
C(4)	R_1	55(9)	70(20)	138(16)
	R_2	91(16)	154(19)	116(19)
	R_3	145(9)	75(13)	121(10)
C(5)	R_1	143(11)	82(16)	55(13)
	R_2	80(22)	152(29)	64(25)
	R_3	55(11)	63(29)	47(20)
O(1)	R_1	63(25)	90	27(25)
	R_2	27(25)	90	117(25)
	R_3	90	0	90
O(2)	R_1	123(28)	90	147(28)
	R_2	90	0	90
	R_3	147(28)	90	57(28)
O(3)	R_1	153(6)	80(10)	65(7)
	R_2	97(17)	168(17)	80(28)
	R_3	64(8)	84(30)	27(13)
O(4)	R_1	83(43)	11(39)	98(15)
	R_2	21(18)	100(45)	108(8)
	R_3	70(6)	85(5)	20(6)
O(5)	R_1	139(25)	90	132(25)
	R_2	49(25)	90	139(25)
	R_3	90	0	90

TABLE 4

Interatomic distances (Å) and angles (°) in the complex

(*a*) Bonds

(*i*) Uranium co-ordination polyhedron

U–O(4) (×2) (carbonyl)	2.37(2)	U–O(2) (uranyl)	1.72(3)
U–O(3) (×2) (carbonyl)	2.42(2)	O(4)–O(4) (pentagonal ring)	2.79(4)
U–O(5) (phosphate)	2.31(3)	O(4)–O(3) (pentagonal ring)	2.75(3)
U–O(1) (uranyl)	1.75(3)	O(3)–O(5) (pentagonal ring)	2.85(3)

TABLE 4 (*Continued*)

(*ii*) Trimethyl phosphate group

P–O(5)	1.50(3)	C(6)–O(6)	1.58(9)
P–O(6)	1.41(4)	C(7)–O(7)	1.38(6)
P–O(7)	1.72(3)	C(7)–O(7′)	1.70(6)
P–O(7′)	1.41(5)		

(*iii*) hfpd Group

C(1)–O(4) (carbonyl)	1.21(4)	C(3)–F(6)	1.21(4)
		C(3)–F(4′)	1.34(8)
C(2)–O(3) (carbonyl)	1.28(4)	C(3)–F(5′)	1.50(8)
		C(3)–F(6′)	1.36(12)
C(1)–C(5)	1.38(4)	C(4)–F(1)	1.26(5)
C(2)–C(5)	1.35(4)	C(4)–F(2)	1.27(5)
C(1)–C(3)	1.63(5)	C(4)–F(3)	1.38(6)
C(2)–C(4)	1.61(5)	C(4)–F(1′)	1.32(9)
C(3)–F(4)	1.33(5)	C(4)–F(2′)	1.36(8)
C(3)–F(5)	1.34(5)	C(4)–F(3′)	1.35(8)

(*iv*) Intermolecular contacts

U ··· U	13.752(1)	U ··· P	11.956(5)
U ··· P	13.163(7)	P ··· P	12.151(1)

F ··· F across centre of symmetry

F(1) ··· F(3)	3.16(5)	F(3) ··· F(3)	4.37(8)
F(2) ··· F(3)	4.06(5)		

To phosphate carbon in mirror plane

C(6) ··· F(4)	5.40(7)	C(6) ··· F(5′)	3.37(9)
C(6) ··· F(4′)	5.17(10)	C(6) ··· F(6)	3.54(7)
C(6) ··· F(5)	4.30(6)		

To phosphate carbon off mirror plane

C(7) ··· F(1)	3.24(6), 3.68(6)	C(7) ··· F(2′)	3.59(9)
C(7) ··· F(1′)	4.35(12)	C(7) ··· F(3)	5.14(7), 3.73(6)
C(7) ··· F(2)	4.54(7), 5.45(6)	C(7) ··· F(3′)	5.23(9)

Uranyl contact between molecules

O(2) ··· O(1)	3.20(5)

Uranyl contact with CF_3 groups

O(2) ··· F(6)	5.39(4)	O(2) ··· F(4)	3.90(5)

Uranyl contact with phosphate oxygen and phosphate carbon

O(1) ··· O(5)	3.11(4)	O(1) ··· C(7)	3.46(5)

(*b*) Angles

(*i*) Pentagonal ring (*ca.* 72°)

O(3)–U–O(4)	69.9(7)	O(5)–U–O(3)	74.0(5)
O(4)–U–O(4)	72.1(9)		

(*ii*) Uranyl oxygen–uranium–ring oxygen (*ca.* 90°)

O(2)–U–O(4)	89.8(10)	O(2)–U–O(5)	92.5(12)
O(2)–U–O(3)	90.7(7)		

(*iii*) Uranyl (*ca.* 180°)

O(1)–U–O(2)	179.2(14)

(*iv*) Trimethyl phosphate group

O(5)–P–O(6)	108.8(19)	P–O(7)–C(7)	118.4(32)
O(5)–P–O(7)	107.0(13)	P–O(6)–C(6)	126.8(47)
O(5)–P–O(7′)	119.8(21)	P–O(7′)–C(7)	117.9(34)
P–O(5)–U	161.8(16)		

(*v*) hfpd Group

O(4)–C(1)–C(5)	134(3)	F(6′)–C(3)–C(1)	119(6)
C(2)–C(5)–C(1)	115(3)	F(1)–C(4)–F(3)	103(3)
O(3)–C(2)–C(5)	131(3)	F(1)–C(4)–F(2)	120(5)
F(6)–C(3)–F(5)	113(4)	F(3)–C(4)–F(2)	105(4)
F(6)–C(3)–F(4)	112(4)	F(1)–C(4)–C(2)	113(3)
F(5)–C(3)–F(4)	95(3)	F(3)–C(4)–C(2)	105(4)
C(1)–C(3)–F(5)	109(4)	F(2)–C(4)–C(2)	109(3)
C(1)–C(3)–F(6)	115(3)	F(2′)–C(4)–F(3′)	93(5)
C(1)–C(3)–F(4)	112(3)	F(2′)–C(4)–F(1′)	131(6)
F(4′)–C(3)–F(6′)	80(6)	F(3′)–C(4)–F(1′)	99(6)
F(4′)–C(3)–F(5′)	86(6)	F(2′)–C(4)–C(2)	106(4)
F(6′)–C(3)–F(5′)	142(7)	F(3′)–C(4)–C(2)	109(4)
F(4′)–C(3)–C(1)	112(5)	F(1′)–C(4)–C(2)	114(4)
F(5′)–C(3)–C(1)	99(4)		

approaches between similarly charged atoms, *e.g.* the $CF_3 \cdots CF_3$ contacts across the centre of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The intermolecular contacts are further illustrated in Figure 3, the view down the *b* axis. Uranyl oxygen atoms from different molecules are in proximity in the *c* direction (Figure 2) with O(1) $\cdots$ O(2) 3.20(5) Å, while the uranyl oxygen atom O(1) approaches a co-ordinated phosphate oxygen atom from an adjacent molecule [O(1) $\cdots$ O(5) 3.11(4) Å]. Presumably, the main cohesive forces are hydrogen–oxygen and –fluorine interactions; however, the hydrogen atoms were not found in this analysis.

The Uranium Co-ordination Polyhedron.—The characteristic dimensions for the uranyl group are observed in this structure (Table 4). The O(1)–U–O(2) angle [179.2(14)°] is linear, and the uranyl distances close to the usual value of *ca.* 1.71 Å [U–O(1) 1.75(3) and U–O(2) 1.72(3) Å]. The uranyl oxygens O(1) and O(2) form the apices of a pentagonal bipyramid, the five oxygen atoms in the pentagonal ring being two O(3) atoms and two

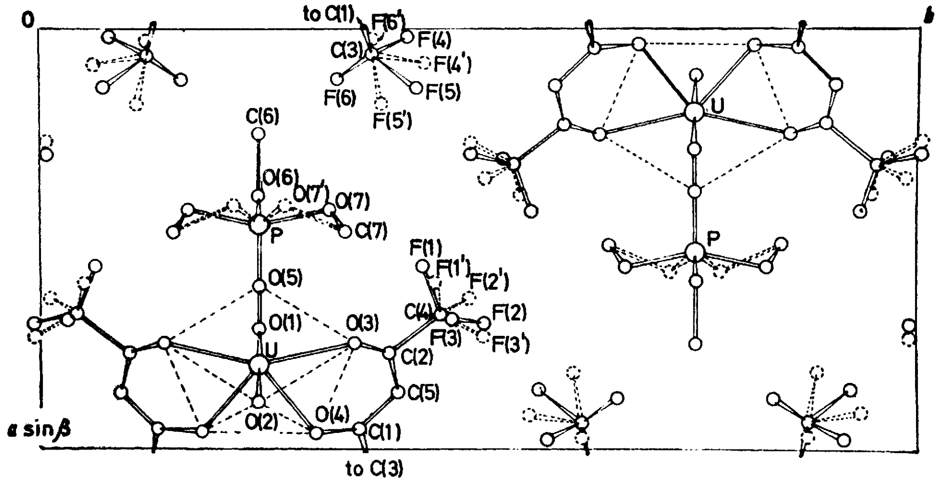

FIGURE 2 Crystal structure of α-[$UO_2(hfpd)_2\{PO(OMe)_3\}$] seen down the short *c* axis

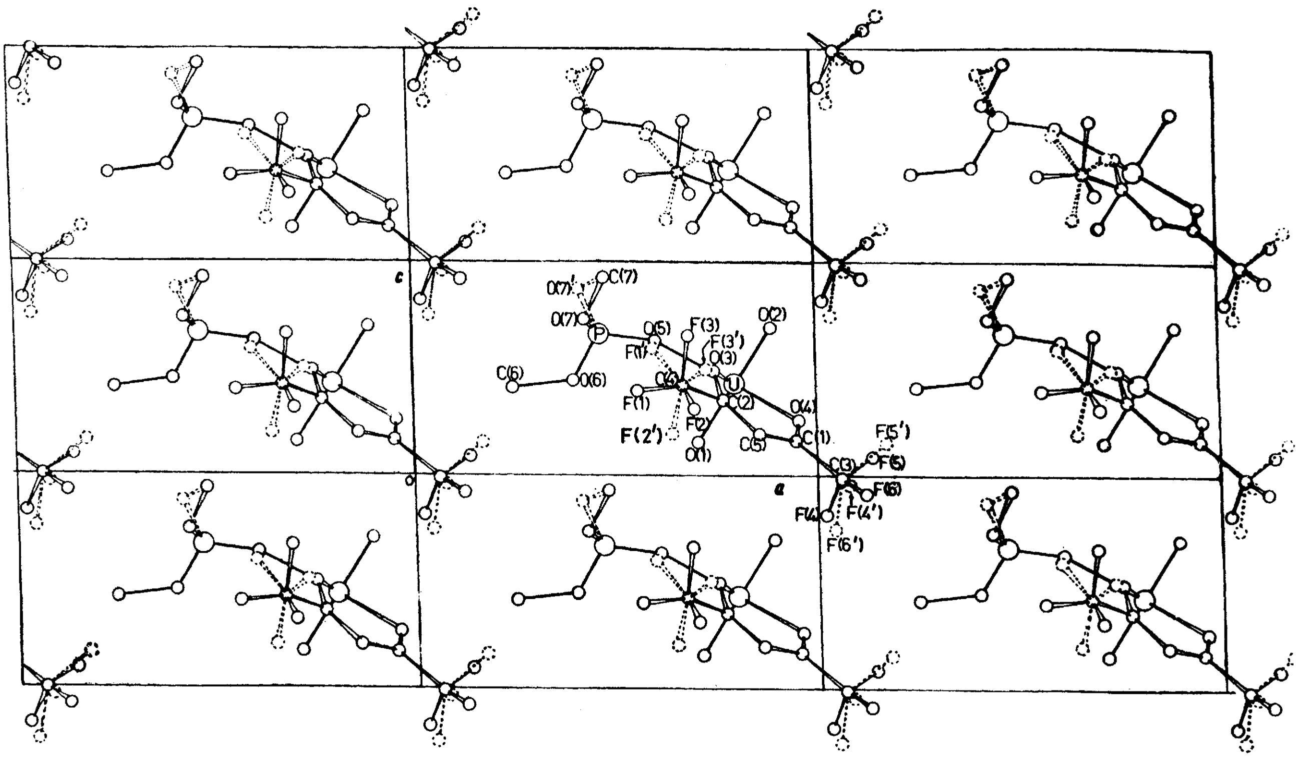

FIGURE 3 Crystal structure of α-[$UO_2(hfpd)_2\{PO(OMe)_3\}$] seen down the *b* axis

O(4) atoms from the bidentate hfpd molecule and one phosphate oxygen atom O(5). The uranium–carbonyl oxygen distances [2.37(2) (×2) and 2.42(2) (×2) Å] are slightly longer than the ionic radius sums [8] (0.87 + 1.40 = 2.27 Å) indicating weak bonding of the hfpd molecules. The uranium–phosphate oxygen bond is also weak. The equatorial pentagon is nearly regular, the O–U–O angles in the ring (Table 4) being close to the pentagonal angle of 72°. The two hfpd ligands have an ideal bite for the formation of a pentagonal bipyramid with a further unidentate ligand. In uranyl pentane-2,4-dionate for example, such a bipyramid is formed by two deprotonated pd molecules and a water oxygen atom.[9] The pentagonal-bipyramid arrangement is the most common polyhedron in uranyl complexes, and many examples with oxygen atoms at all of the seven positions can now be cited.[9-19] The dimensions of the polyhedron in $[UO_2(hfpd)_2\{PO(OMe)_3\}]$ agree with those in the other structures.

The uranyl group is normal to the ring plane, with the O(uranyl)–U–O (ring) angles in Table 5 *ca.* 90°. Least-squares planes were calculated for the uranium atom and the five ring atoms (Table 5). The ring system is approximately planar as no atom deviates more than 0.03 Å from the plane of the system (pentagonal ring + uranium atom).

TABLE 5

Planarity of pentagonal ring system

Equation of U,O(3),O(3′),O(4),O(4′),O(5) plane: $0.4893x + 0.8544z = 6.0923$

Atom	Deviation (Å) from plane
U	0.024
O(3), O(3′)	0.008
O(4), O(4′)	−0.006
O(5)	−0.030

The hfpd Ligand Molecule.—The parent molecule Hhfpd exists as a keto–enol tautomer with a planar molecule and an internal hydrogen bond. The parent has been studied by electron diffraction [20] [C=O 1.259(6), C–C(ring) 1.407(10), C–C(CF_3) 1.546(3), and C–F 1.337(2) Å]. The dimensions of the hfpd ligand in the present structure (Table 4) agree with these values within the errors.

The planarity of the hfpd group is preserved in this complex. Table 6 gives the least-squares plane and atomic deviations from it, for the hfpd atoms. As the errors in these deviations are 0.02—0.04 Å, the hfpd molecule is planar to within the experimental errors. The planes of the hfpd molecules are tilted by 22.5° to the plane of the pentagonal ring in a boat configuration (Figure 4). This tilting could be caused by the intermolecular forces, or by preference for these bonding angles at the carbonyl oxygen atoms. Tilting of the ligand planes with respect to the co-ordination plane of the uranyl group is also seen in other pentagonal-bipyramidal complexes such as dioxo(pyridine)bis-(tropolonato)uranium(VI),[21] $[UO_2(saldien)]$ [saldien = *NN′*-3-azapentane-1,5-diylbis(salicylideneiminate)],[22] (ethanol)dioxobis(tropolonato)uranium(VI),[23] and [*NN′*-ethylenebis(salicylideneiminato)](methanol)dioxouranium(VI).[24] (The dihedral angles are 3.5—5.4, 31, 22.5(boat), and 21—42° respectively in these structures.)

TABLE 6

Planarity of hfpd molecule

Equation of plane (crystal axes): $0.5693x + 0.3524y + 0.7223z = 9.0827$

Atom	Deviation (Å)
O(3)	0.002
O(4)	0.004
C(1)	−0.016
C(2)	0.012
C(3)	0.036
C(4)	0.024
C(5)	−0.061

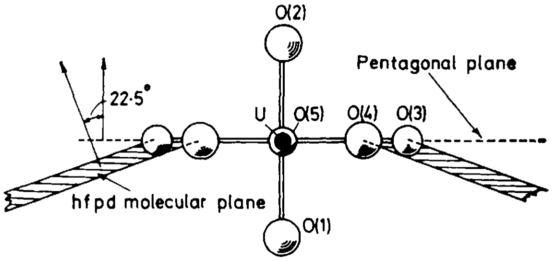

FIGURE 4 Tilt of 22.5° between the planes of the hfpd ligand molecules and the plane of the pentagonal ring system, to give a boat configuration

The crystal structures of 16 metal–hfpd complexes

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have been determined.[25-35] In all of these the diketone ring is planar with delocalisation, and the dihedral angles between the ring and the co-ordination planes lie between 0 and 17°. The C–O distances are about the same as in Hhfpd, and i.r. studies show a correlation between ν(C–O) and the C–O distance. In one of the complexes,[31] the hfpd molecule is unidentate but its planarity and delocalisation are still maintained. The hfpd molecules are evidently weakly bound in these complexes. The data for the hfpd structures are summarised in Table 7. Although detailed structure analyses have not been carried out, $[Re(hfpd)_3]$ and $[Re(pd)_3]$ have been studied [36] by spectroscopy, mass spectroscopy, magnetic susceptibility, and *X*-ray diffraction techniques. In both cases the metal is octahedrally co-ordinated, with $[Re(hfpd)_3]$ having a hexagonal unit cell and $[Re(pd)_3]$ the monoclinic $[Mn(pd)_3]$ type.

TABLE 7

Some structural data for metal–hfpd complexes

Compound	ν(CO) cm⁻¹	C=O Distance Å	Diketone dihedral angle (°)	Ref.
$[Mg(hfpd)_3(C_{14}H_{19}N_2)]$		1.24(1)—1.28(1)		25
$[Ni_6(tfpd)_{10}(OH)_2(OH_2)_2]$		1.273 (av.)		26
[Cu(hfpd)(bipy)]	1 655	1.22(1), 1.26(1)		28
$[Cu(hfpd)_2(py)_2]$	1 655	1.24(1), 1.26(1)	5	29
$[Cu(hfpd)_3(C_{14}H_{19}N_2)]$		1.21(1)—1.28(1)		25
$[Cu(hfpd)_2(pyz)]$	1 639, 1 526	1.27(1), 1.25(1)	*ca.* 0	30
$[\{Cu(hfpd)_2\}_2pyz]$	1 638, 1 528		9, 17	30
$[Cu(hfpd)_2(Me_2en)_2]$	1 675, 1 615 1 540	1.235 (4), 1.233(4)	14	27, 31
$[Cu(hfpd)_2(ted)]$	1 640, 1 530	1.262(7), 1.247(8)	0	32
$[Zn(hfpd)_2(py)_2]$	1 660, 1 645	1.25(1), 1.29(1)		29
$Rb_2[Na(hfpd)_3]$	1 670, 1 650	1.26(5), 1.22(6)		33
$[Zr(\eta\text{-}C_5H_5)(hfpd)_3]$		1.23(1)—1.27(1)	0, 4.5, 8.4	34
$Cs[Y(hfpd)_4]$		1.23(2)—1.28(2)	8	35
$Cs[Eu(hfpd)_4]$		1.23(2)—1.27(2)	8	35
$Cs[Am(hfpd)_4]$		1.19(3)—1.28(3)	8	35
Hhfpd		1.259(6)		20
$[UO_2(hfpd)_2\{PO(OMe)_3\}]$		1.21(4), 1.28(4)	22.5	This work

bipy = 2,2′-Bipyridyl, py = pyridine, pyz = pyrazine, Me_2en = *NN*-dimethylethylenediamine, and ted = 1,4-diazabicyclo[2.2.2]-octane

The CF_3 *Groups*.—In common with other structural analyses of metal-hfpd complexes, we find that the CF_3 groups on the periphery of the molecules have very high thermal motions, with Debye–Waller factors of up to 15 Å^2 (Table 1), corresponding to r.m.s. vibration amplitudes of up to 0.5 Å. The high thermal motions give rise to systematic errors and a large spread in the measured C–F distances [1.21(4)—1.50(8) Å], although the average C–F distance (1.34 Å) agrees with distances in the other structures. Because correction of the C–F distances for these vibration effects is impracticable, the errors quoted for these distances are too low. The F–C–F angles in Table 4 also show a scatter over the range 80—142° (expected values *ca.* 109°). Some very high *B* factors of 10—30 Å^2 are also found [26] in $[Ni_6(tfpd)_{10}(OH)_2(OH_2)_2]$ (tfpd = 1,1,1-trifluoropentane-2,4-dionate); the C–F distances in this compound are 1.18—1.34 Å.

In all the Hhfpd or tfpd structures in Table 7, the CF_3 groups are disordered or approaching that state. In $[UO_2(hfpd)_2\{PO(OMe)_3\}]$ the two different CF_3 groups are disordered over two alternative positions related by a 60° rotation about the C(ring)–C(CF_3) bond. Thus, six fluorine-density locations are seen for every CF_3 group instead of three, and the relative occupancies of the two sets of positions are $\frac{2}{3}$ and $\frac{1}{3}$. The two positions are indicated for each CF_3 group in Figures 2 and 3, by solid and broken circles for the fluorine atoms. Elder [34] observed a similar two-fold disorder in a CF_3 group in $[Zr(\eta\text{-}C_5H_5)(hfpd)_3]$.

The Trimethyl Phosphate Group.—The trimethyl phosphate group in $[UO_2(hfpd)_2\{PO(OMe)_3\}]$ is also disordered, in two positions about its molecular mirror plane; the methoxy-oxygen atom not in the mirror plane is divided between the alternative positions O(7) and O(7′) (Figure 2) also in the ratio of $\frac{2}{3}$ to $\frac{1}{3}$. The other non-hydrogen atoms of the methoxy-group were found to be ordered. A similar disorder about a mirror plane is found [23] in the ethoxy-group in (ethanol)dioxobis(tropolonato)uranium(VI). The bond lengths and angles found in the $PO(OMe)_3$ molecule in the present study are similar to the dimensions found [37] in $PO(OR)_3$

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complexes with benzotrifurazan (R = Me, Et, or Pr^i), in triphenyl phosphate,[38] and dibenzylphosphoric acid.[39] In the analysis of the benzotrifurazan phosphate complexes, the crystals had to be cooled to 153 K in order to observe the non-hydrogen atoms of the phosphate molecule. With R = Me, the alkoxy-groups were so disordered that the compound was a liquid crystal. The structures of several uranyl triphenylphosphine oxides have been reported,[10,40,41] and give the same O(phosphine)–U distances as found here. The structures of phosphate compounds were reviewed by Cruickshank.[42]

Intermolecular Contacts.—The molecules stack on top of one another in the direction of the short *c* axis and contacts between molecules in the stacks are of the type O(uranyl) $\cdots$ O(uranyl), O(uranyl) $\cdots$ O(phosphate), O(uranyl) $\cdots$ CF_3, O(uranyl) $\cdots$ CH, C(methyl) $\cdots$ CF_3, and C(methyl) $\cdots$ O(uranyl). The molecules are weakly associated in the *a,b* plane also, the contacts in this direction being of the $CF_3 \cdots CF_3$ type. The approaches are illustrated in Figures 2 and 3 and some of the more important approach distances are given in Table 4.

Thermal Motion.—The intermolecular contacts are mainly between similarly charged atoms, especially the fluorine atoms of the CF_3 groups, which induce high thermal motions, weak intermolecular attractions, and a low m.p. (361 K). The thermal-vibration amplitudes up to 0.5 Å at the CF_3 groups are as large as those found in liquid crystals. The vibration amplitudes in Table 1 increase with increasing distance of the atom from the uranyl group. For the anisotropic atoms, the r.m.s. amplitudes of vibration along the principal axes of the vibration ellipsoids are given in Table 2, and vary between 0.1 and 0.4 Å. The angles which the principal axes make with the unit-cell edges are given in Table 3; the minimum vibrations are mainly along the bonds and the maximum motions normal to them.

We thank Mr. L. Szego for supplying the crystals.

[6/2021 *Received*, *29th October*, 1976]

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