Polymorphism in Uranyl Chelates. Part 3.† The Crystal and Molecular Structure of the β Form of Bis(1,1,1,5,5,5-Hexafluoropentane-2,4-dionato)dioxo(trimethyl phosphate)uranium(VI)

By **John C. Taylor** * and **A. Bruce Waugh**, Australian Atomic Energy Commission Research Establishment, Private Mail Bag, Sutherland, N.S.W. 2232, Australia

The crystal structure of the title compound β-[UO_2(hfpd)$_2${PO(OMe)$_3$}] has been determined, and is triclinic, space group $P\bar{1}$, with dimensions a = 12.352(8), b = 12.013(8), c = 11.984(8) Å and α = 105.7(2), β = 109.3(1), γ = 119.2(2)°. The structure is molecular with a packing completely different from that in the α form. The uranium atom is co-ordinated by seven oxygen atoms to form a pentagonal bipyramid. The hfpd planes are only slightly tilted with respect to the pentagonal plane, giving a nearly planar molecule, in contrast to the α form where the molecule is boat-shaped. There is no positional disorder in the CF_3 and PO(OMe)$_3$ groups in the β form, again in contrast to the α form. There are repulsive O–O, O–F, and F–F interactions between the molecules, while weak hydrogen-bonded interactions of the type H · · · O and H · · · F play a cohesive role. The different i.r. uranyl-stretching frequencies for the α and β forms are explained by the differences in their uranyl environments.

THE crystal structure of the yellow α form of the title compound [UO_2(hfpd)$_2${PO(OMe)$_3$}] was reported in Part 2. An orange β form with the same melting point (361 K) can also be crystallised. The i.r. spectrum of the β form is different from that of the α form, suggesting that the uranyl group has a different environment in the two structures.[1] A structural analysis of the β form was therefore undertaken to find the precise differences in the structures of the two polymorphs, to see if a simple transformation mechanism between the structures was possible, and to continue our series of investigations of the structures of uranium compounds. In Part 2 the extensive literature to the end of 1975 on the crystal structures of metal 1,1,1,5,5,5-hexafluoropentane-2,4-dionates was reviewed.

EXPERIMENTAL

The β form was unstable in air, so the crystal used was mounted in a glass capillary (outside diameter, 0.06 cm) with Araldite adhesive. The crystal had no dominant faces, and its irregular shape was described with 15 faces for the absorption corrections. The distances of the faces from the centre of the crystal lay between 0.0048 and 0.0080 cm, and the crystal volume was 1.5 × 10^{-6} cm^3.

Rotation and Weissenberg photographs showed the symmetry was triclinic [possible space groups $P1(C_1^1)$ or $P\bar{1}(C_i^1)$]. 2 085 Three-dimensional X-ray diffraction data were collected to 2θ 76° on a four-circle automatic diffractometer with Cu-K_β radiation (λ 1.3923 Å). The β-radiation was preferable to Cu-K_α because it gave a better UB matrix, not being a doublet, and lower absorption. It was selected with a Si(Li) detector with an energy discriminator. The 2θ values of 29 higher-angle reflections gave the dimensions of the reduced cell as a = 12.352(8), b = 12.013(8), c = 11.984(8) Å, α = 105.7(2), β = 109.3(1), and γ = 119.2(2)°

---

† Part 2 is the preceding paper.

[1] J. H. Levy and A. B. Waugh, *J.C.S. Dalton*, 1977, 1628.

A standard reflection was measured every 20 reflections. Absorption corrections were applied and $F(hkl)$ and $\sigma[F(hkl)]$ values were determined from the intensities with the computer program DRACULA.[2]

TABLE 1

Final positional parameters in β-[UO_2(hfpd)$_2${PO(OMe)$_3$}]

Atom	10^3x	10^3y	10^3z
U	82.4(1)	322.9(1)	23.8(1)
P	174(1)	367(1)	−235(1)
C(1)	425(5)	431(6)	−217(6)
C(2)	−43(6)	176(9)	−459(9)
C(3)	202(5)	613(5)	−180(4)
C(4)	335(3)	701(4)	245(5)
C(5)	326(4)	709(4)	359(4)
C(6)	233(4)	583(5)	354(3)
C(7)	433(5)	838(5)	251(5)
C(8)	231(5)	594(4)	480(4)
C(9)	−185(4)	−50(4)	−211(3)
C(10)	−258(3)	−86(3)	−152(4)
C(11)	−204(4)	1(5)	−25(6)
C(12)	−254(5)	−167(4)	−357(5)
C(13)	−267(7)	−12(7)	84(9)
O(1)	219(2)	317(2)	102(2)
O(2)	−57(2)	328(2)	−51(2)
O(3)	136(3)	352(2)	−134(2)
O(4)	83(5)	228(4)	−367(4)
O(5)	180(5)	480(5)	−268(4)
O(6)	331(5)	406(6)	−182(6)
O(7)	270(2)	587(2)	129(2)
O(8)	143(3)	453(2)	252(2)
O(9)	−66(3)	75(2)	−165(2)
O(10)	−83(3)	143(2)	63(2)
F(1)	398(3)	859(3)	153(3)
F(2)	559(3)	903(6)	318(7)
F(3)	446(6)	952(4)	326(5)
F(4)	291(6)	718(4)	569(4)
F(5)	298(5)	552(5)	539(4)
F(6)	107(3)	502(5)	460(3)
F(7)	−290(5)	−142(3)	−451(3)
F(8)	−166(4)	−189(4)	−363(3)
F(9)	−367(4)	−301(3)	−403(3)
F(10)	−395(3)	−169(3)	−16(3)
F(11)	−301(7)	56(5)	106(7)
F(12)	−213(4)	−60(5)	139(4)

TABLE 2

Interatomic distances (Å) and angles (°) in β-[UO_2(hfpd)$_2${PO(OMe)$_3$}]

(*a*) Intramolecular bond lengths

U Co-ordination polyhedrou		Phosphate group	
U–O(1) (uranyl)	1.68(2)	P–O(3)	1.46(2)
U–O(2) (uranyl)	1.70(2)	P–O(4)	1.47(4)
U–O(7) (carbonyl)	2.41(2)	P–O(5)	1.48(3)
U–O(8) (carbonyl)	2.37(2)	P–O(6)	1.58(4)
U–O(3) (phosphate)	2.26(2)	O(4)–C(2)	1.27(5)
U–O(9) (carbonyl)	2.38(2)	O(5)–C(3)	1.50(5)
U–O(10) (carbonyl)	2.44(2)	O(6)–C(1)	1.29(6)
hfpd Unit I		hfpd Unit II	
C(4)–O(7)	1.29(4)	C(9)–O(9)	1.25(3)
C(6)–O(8)	1.23(4)	C(11)–O(10)	1.33(4)
C(4)–C(5)	1.38(5) (in ring)	C(9)–C(10)	1.32(4) (in ring)
C(5)–C(6)	1.37(4) (in ring)	C(10)–C(11)	1.29(5) (in ring)
C(6)–C(8)	1.49(4) (to CF_3)	C(11)–C(13)	1.74(7) (to CF_3)
C(4)–C(7)	1.57(7) (to CF_3)	C(9)–C(12)	1.51(5) (to CF_3)
C(7)–F(1)	1.22(4)	C(12)–F(7)	1.24(4)
C(7)–F(2)	1.13(4)	C(12)–F(8)	1.26(4)
C(7)–F(3)	1.52(9)	C(12)–F(9)	1.28(4)
C(8)–F(4)	1.21(4)	C(13)–F(10)	1.46(6)
C(8)–F(5)	1.28(4)	C(13)–F(11)	1.07(6)
C(8)–F(6)	1.27(4)	C(13)–F(12)	1.22(5)

TABLE 2 (*Continued*)

O–O Distances round pentagonal ring

O(7)–O(8) (bite of hfpd I)	2.75(2)
O(8)–O(10)	2.81(3)
O(10)–O(9) (bite of hfpd II)	2.74(3)
O(9)–O(3)	2.85(3)
O(3)–O(7)	2.80(3)

Uranyl oxygen–ring oxygen contacts

O(1)–O(3)	2.89(3)	O(2)–O(3)	2.80(3)
O(1)–O(7)	2.88(3)	O(2)–O(7)	3.02(3)
O(1)–O(8)	2.78(3)	O(2)–O(8)	3.00(3)
O(1)–O(9)	2.95(3)	O(2)–O(9)	2.90(3)
O(1)–O(10)	3.04(3)	O(2)–O(10)	2.86(3)

(*b*) Intramolecular bond angles

Uranyl (*ca.* 180°)

O(1)–U–O(2)	178.0(9)

O(Uranyl)–U–O (ring) (*ca.* 90°)

O(1)–U–O(7)	87.6(8)	O(2)–U–O(7)	92.8(8)
O(1)–U–O(8)	84.6(9)	O(2)–U–O(8)	93.6(8)
O(1)–U–O(9)	91.5(9)	O(2)–U–O(9)	89.2(8)
O(1)–U–O(10)	93.2(9)	O(2)–U–O(10)	85.3(9)
O(1)–U–O(3)	93.3(9)	O(2)–U–O(3)	88.8(9)

Pentagonal ring (*ca.* 72°)

O(8)–U–O(10)	71.5(7)	O(3)–U–O(7)	73.7(7)
O(10)–U–O(9)	69.3(7)	O(7)–U–O(8)	70.2(6)
O(9)–U–O(3)	75.7(7)		

hfpd Unit I		hfpd Unit II	
U–O(8)–C(6)	140(2)	U–O(10)–C(11)	131(2)
O(8)–C(6)–C(5)	126(2)	O(10)–C(11)–C(10)	129(3)
C(6)–C(5)–C(4)	120(3)	C(11)–C(10)–C(9)	123(3)
C(5)–C(4)–O(7)	129(3)	C(10)–C(9)–O(9)	127(3)
C(4)–O(7)–U	133(2)	C(9)–O(9)–U	137(2)
O(8)–C(6)–C(8)	115(3)	O(10)–C(11)–C(13)	96(4)
C(5)–C(6)–C(8)	118(3)	C(10)–C(11)–C(13)	134(3)
C(6)–C(8)–F(4)	116(3)	C(11)–C(13)–F(10)	93(4)
C(6)–C(8)–F(5)	112(3)	C(11)–C(13)–F(11)	114(4)
C(6)–C(8)–F(6)	116(3)	C(11)–C(13)–F(12)	99(4)
F(4)–C(8)–F(5)	105(4)	F(10)–C(13)–F(11)	112(6)
F(5)–C(8)–F(6)	97(3)	F(11)–C(13)–F(12)	142(8)
F(6)–C(8)–F(4)	110(4)	F(12)–C(13)–F(10)	84(3)
O(7)–C(4)–C(7)	104(3)	C(10)–C(9)–C(12)	118(3)
C(5)–C(4)–C(7)	125(4)	O(9)–C(9)–C(12)	115(3)
C(4)–C(7)–F(1)	116(5)	C(9)–C(12)–F(7)	118(3)
C(4)–C(7)–F(2)	115(4)	C(9)–C(12)–F(8)	110(4)
C(4)–C(7)–F(3)	97(6)	C(9)–C(12)–F(9)	116(3)
F(1)–C(7)–F(2)	127(4)	F(7)–C(12)–F(8)	105(4)
F(2)–C(7)–F(3)	80(5)	F(8)–C(12)–F(9)	100(3)
F(3)–C(7)–F(1)	78(5)	F(9)–C(12)–F(7)	106(4)

Phosphate group

U–O(3)–P	177(2)	O(5)–P–O(6)	108(3)
O(3)–P–O(4)	115(2)	O(6)–P–O(4)	100(3)
O(3)–P–O(5)	117(2)	P–O(4)–C(2)	121(6)
O(3)–P–O(6)	108(2)	P–O(5)–C(3)	127(3)
O(4)–P–O(5)	107(2)	P–O(6)–C(1)	142(5)

Crystal Data.—$C_{13}H_{11}F_{12}O_{10}PU$, M = 824.2, Triclinic, a = 12.352(8), b = 12.013(8), c = 11.984(8) Å, α = 105.7(2), β = 109.3(1), γ = 119.2(2)°, U = 1 250 Å^3, Z = 2, D_c = 2.190 g cm^{-3}, $F(000)$ = 768. Space group $P1(C_1^1)$ or $P\bar{1}(C_i^1)$; the latter was confirmed by structure analysis. Cu-K_β (λ 1.392 3 Å), μ(Cu-K_β) = 168 cm^{-1}.

A three-dimensional Patterson synthesis gave the uranium position. The uranium positional parameters and temperature factors (first isotropic, then anisotropic) were refined with the least-squares program LINUS[3] [neutral-uranium scattering curve,[4] anomalous dispersion terms

---

[2] M. M. Elcombe, G. W. Cox, A. W. Pryor, and F. H. Moore, Australian Atomic Energy Commission, Report AAEC/TM578, 1971.

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

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

$\Delta f' = -4.9$ e and $\Delta f'' = 11.3$ e (ref. 5)] to give a discrepancy factor $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ of 0.28. The remaining atoms were located in difference syntheses. Final cycles with anisotropic temperature factors for all the atoms (a total of 334 variables) gave the residuals R 0.075, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.090$, and $\chi^2 = \Sigma w(|F_o| - |F_c|)^2/(N_O - N_V) = 0.95$ where N_O and N_V were the number of observations (2 085) and variables (334) and w the least-squares weighting factors $\{\sigma[F(hkl)]\}^{-2}$. A final difference synthesis indicated that the atomic centres were correctly located. No disorder of any groups was observed as distinct from the disorder that was observed in the α form (Part 2). The final positional parameters are given in Table 1. The thermal parameters and observed and calculated structure factors are available as Supplementary Publication SUP No. 22066 (8 pp.).* The interatomic distances and angles are given in Table 2.

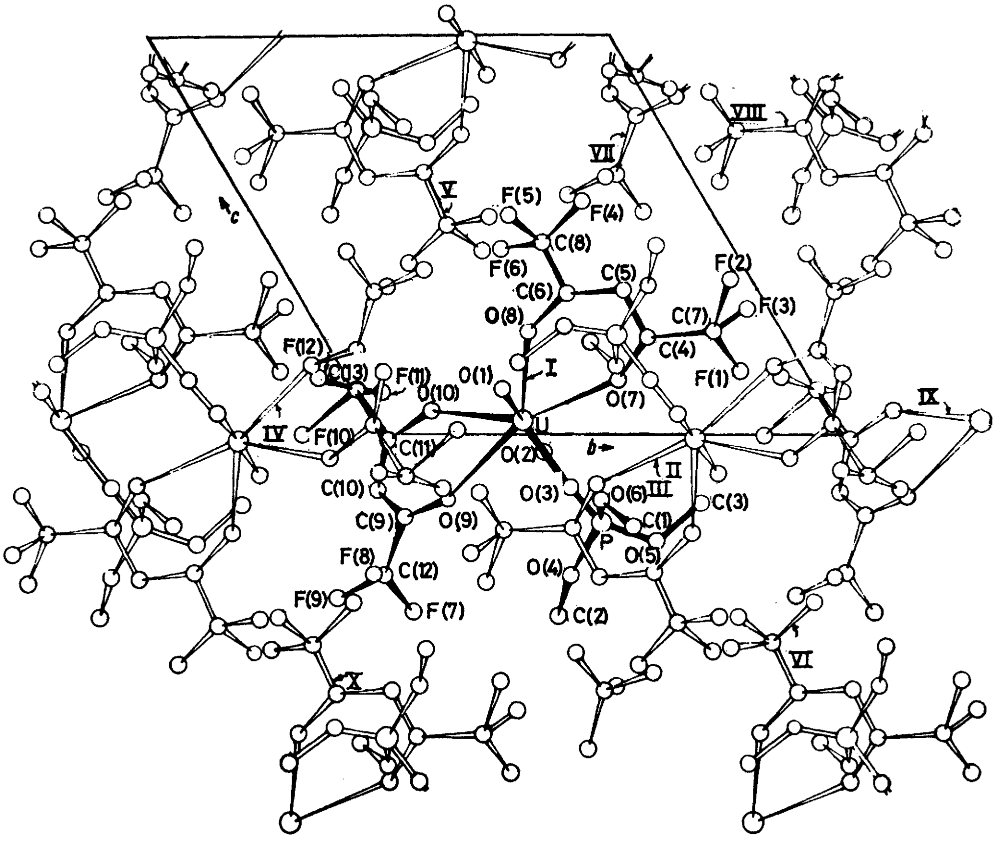

FIGURE 1 Structure of β-[UO_2(hfpd)$_2${PO(OMe)$_3$}] viewed down the a axis

DISCUSSION

The Structure of β-[UO_2(hfpd)$_2${PO(OMe)$_3$}].—The β form has a molecular structure like the α form. Despite the almost identical melting points, the packing of the molecules in the two forms is completely different. Thus, there is no simple shear or displacement transformation mechanism between α and β forms. The β form is depicted in Figure 1. The molecules are approximately planar, and the environment of the molecule in $P\bar{1}$ is quite asymmetric. The molecules tend to stack along a. A stereopair plotted by ORTEP [6] is given in Figure 2; the diagram of the α form is in Figure 3.

The uranium co-ordination polyhedron is a pentagonal bipyramid of oxygen atoms, four from two bidentate hfpd molecules, one from PO(OMe)$_3$, and the remaining two being uranyl oxygens. The dimensions of the polyhedron (Table 2) are normal. Least-squares plane calculations show that the two independent hfpd molecules are strictly planar. Their dimensions agree with those in the parent Hhfpd.[7]

The pentagonal ring system is not quite planar, the result of a slight mutual twisting of the hfpd molecules; the deviations of the atoms in this plane are up to 0.1 Å from the mean plane. Relative to the pentagonal plane, hfpd unit I is tilted by 3.7° and unit II by −13.9°, a slight boat shape. This is radically different from the molecular configuration in the α form, which is markedly boat-shaped having the normals to the hfpd unit at 45° to each other. A least-squares plane calculated for the complete β-[UO_2(hfpd)$_2${PO(OMe)$_3$}] molecule (ex-

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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

[6] C. K. Johnson, Oak Ridge National Laboratory, Report ORNL-3794, 1965.

[7] A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Amer. Chem. Soc.*, 1972, **93**, 1148.

cluding fluorines) showed the deviations of the atoms from the plane to be $\leqslant 0.35$ Å, much more planar than in the α form. The CF_3 groups appear normal, each showing only three fluorine-density maxima; the $PO(OMe)_3$ group also shows no disorder. This is in contrast to the α form where both these groups are disordered.

The intermolecular contacts are in SUP No. 22066. These may be divided into: (*i*) repulsive interactions between atoms of like charge (O–O, O–F, and F–F) of which there are many ($\geqslant 3.1$ Å); and (*ii*) interactions possibly involving hydrogen atoms which would be attractive (C–H···O and C–H···F). Hamilton and Ibers[8] consider that a C···O or C···F distance of 3.2 Å in such a system is a hydrogen bond, being 0.4 Å less than the van der Waals sum (3.6 Å). In the β structure there is a C(10)–O(1) separation of 3.22 Å, and other possible attractions are C(3)–F(6) (3.28), C(3)–F(11) (3.41), and C(1)–O(1) (3.35 Å). Possibly the compound would not be crystalline but for these attractive interactions. There is thus possibly an interaction of the hydrogen atoms with uranyl oxygen atom O(1). In the α form, there is less possible interaction of hydrogen atoms with the uranyl oxygen atoms. The molecules stack along the short 5.56-Å axis. The uranyl oxygen atoms are in contact with uranyl and phosphate oxygen atoms from neighbouring molecules, and the CH_3 groups interact with CF_3 groups, except for C(7)–O(1) (3.46 Å).

Comparison of the α *and* β *Structures.*—Structural analysis reveals completely different molecular-packing schemes in the two forms. Also, the compound has a marked boat shape in the α form, whereas it approaches planarity in the β form. Disorder is found in the CF_3 and $PO(OMe)_3$ groups in the α but not in the β form; it is surprising that the melting points and densities for the two forms are nearly the same [361 K and 2.205 g cm^{-3} (α) and 361 K and 2.190 g cm^{-3} (β)].

In the β form one of the methyl groups bends down towards the centre of a hfpd molecule below it in a stack. This does not occur in the α form, where all the methyl groups are well separated from the hfpd rings. In the β form the hfpd II units of different molecules tend to be associated across the inversion centre with a ring–ring distance of 4 Å. In the α form the rings are prevented from approaching each other by the interposition of

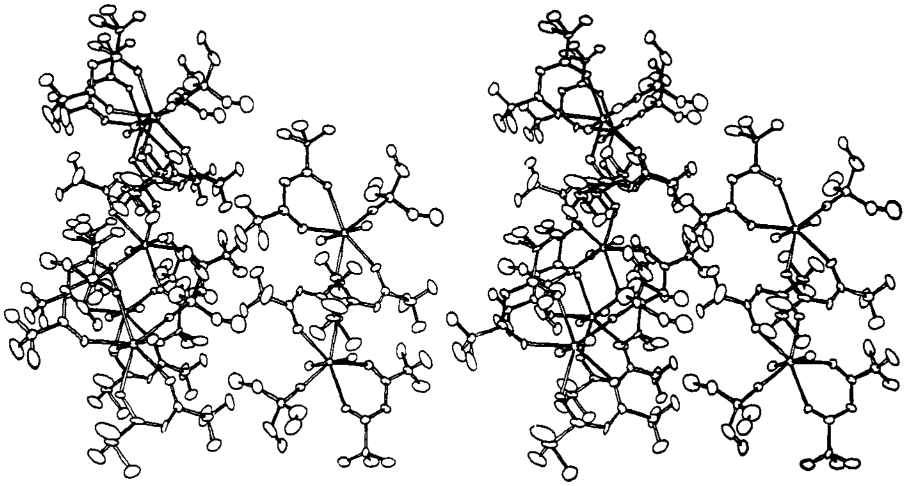

FIGURE 2 Stereoview of β-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$

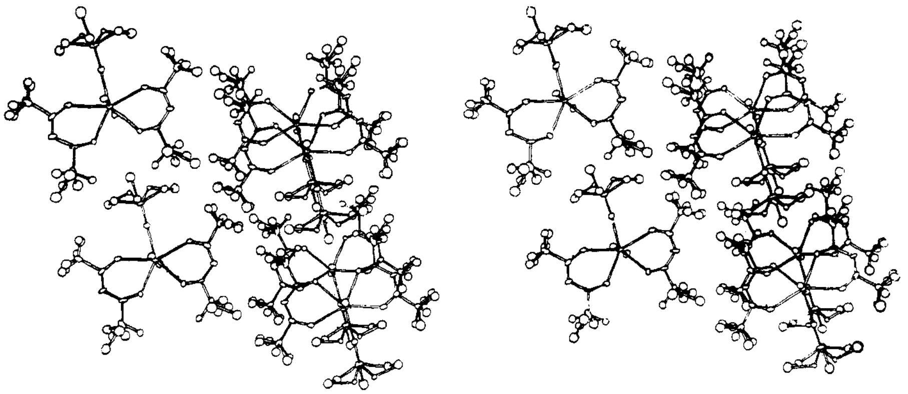

FIGURE 3 Stereoview of α-$[UO_2(hfpd)_2\{PO(OMe)_3\}]$

---

[8] W. C Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' W. A. Benjamin, New York, 1968, p. 16.

uranyl oxygen atoms. The i.r. uranyl-stretch band for the β form has a shoulder which is not present in its spectrum of the α form;[1] this must be due to the different uranyl environments in the two forms.

We thank Dr. G. W. Cox of the Applied Mathematics and Computing Section, A.A.E.C.R.E., for computing the ORTEP diagrams.

[6/2220 *Received, 3rd December, 1976*]