Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes (50 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Part 31 of the series "Pentacoordinated Molecules." Presented in part at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March, 1978; Abstract No. INOR 196. (b) Part 30: P. F. Meunier, R. O. Day, J. R. Devillers, and R. R. Holmes, *Inorg. Chem.*, preceding paper in this issue.
(2) (a) This work in part represents a portion of the Ph.D. thesis of Richard K. Brown, University of Massachusetts, Amherst, Mass. (b) Visiting Professor at the University of Massachusetts, 1977–78, from the Chemical Institute, University of Bergen, Norway.
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Contribution from the Chemical Technology Division,
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Crystal and Molecular Structure of Trimeric Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)dioxouranium(VI)

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The deep red crystals of the title compound $[UO_2(hfa)_2]_3$ are monoclinic, space group $P2_1/c$, with $a = 16.526$ (11) Å, $b = 15.470$ (11) Å, $c = 22.277$ (15) Å, $\beta = 103.00$ (1)°, $Z = 4$, $V = 5549$ Å^3, and $d_{calcd} = 2.457$ g/cm^3. X-ray diffraction data were collected for 3239 independent reflections to $2\theta = 36°$ on an automatic X-ray diffractometer with Mo Kα radiation, and the structure was refined to $R = 0.095$. The three uranium atoms in the asymmetric unit form an equilateral triangle with edges 4.2 Å in length and are bridged by half the uranyl oxygen atoms; the other uranyl oxygen atoms are terminal. The six hfa molecules in the asymmetric unit are bidentate and complete pentagonal-bipyramidal coordination about U(1), U(2), and U(3). The crystal is thus an assembly of $[UO_2(hfa)_2]_3$ trimeric molecules. The CF_3 groups are disordered. This compound is unique in uranyl structural chemistry, being the first example of a uranyl trimer.

Experimental Section

$[UO_2(hfa)_2]_3$ is extremely reactive and air sensitive. A sample was prepared by a method described elsewhere,[1] and crystals were grown in a quartz capillary by the technique of Edwards et al.[2] A suitable crystal was removed from its neighbors by vibration and wedged in a tapered section of the tube by careful tapping. The crystal was not in an orientation suitable for Weissenberg lineup, so the crystal data including cell dimensions were found directly on the automatic four-circle diffractometer. The symmetry was found to be monoclinic, space group $P2_1/c$, with $a = 16.526$ (11) Å, $b = 15.470$ (11) Å, $c = 22.277$ (15) Å, $\beta = 103.00$ (1)°, and $V = 5549$ Å^3. From the effective atomic volumes in other hfa complexes it was deduced that the unit cell held twelve $UO_2(hfa)_2$ units; this indicated a complex structure, probably trimeric. The unit cell contents were confirmed in the following structural analysis. The calculated density is 2.457 g cm^{-3}. Complete three-dimensional data were collected to $2\theta = 36°$ with Mo Kα radiation (λ 0.7107 Å). A total of 3698 reciprocal lattice points were measured with a Si(Li) solid-state detector, and after averaging of equivalent reflections (which were measured for low-angle data only) 3239 reflections were available for the analysis. A standard reflection was measured every 20 reflections, and a 50% decline was observed in the standard over the period of the experiment (several weeks). The intensities were normalized to the standard reflection, corrected for absorption ($\mu = 54$ cm^{-1} for Mo Kα, minimum and maximum transmission factors 13% and 24%), and reduced to $F(hkl)$ values.[3] The crystal faces were ±(100), ±(011), (0,1,–1), (1,0,–1), (2,–1,3), (–1,0,1), and (–1,–1,1), with distances from the crystal center of 250, 250, 157, 157, 330, 320, 300, 330, and 330 × 10^{-4} cm, respectively. The morphology was determined on the diffractometer with a calibrated microscope.

Structural Analysis

In the three-dimensional Patterson synthesis, 20 major peaks were observed as probable U–U vectors. This was consistent with the theoretical number of 9 (i–i)- and 12 (i–j)-type vectors for 3 independent uranium atoms U(1), U(2), and U(3) in $P2_1/c$. The (x, y, z) coordinates of U(1), U(2), and U(3) were deduced from the vectors by trial and error. The uranium atoms lay on the corners of an equilateral triangle of side 4.2 Å, confirming the trimeric nature of the molecule.

A structure factor calculation with the program LINUS,[4] with U(1),

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Table I. Positional and Thermal Parameters and Fluorine Occupancy Factors in $[UO_2(hfa)_2]_3$[a]

atom	% occ	*x*	*y*	*z*	*B*, Å^2	atom	% occ	*x*	*y*	*z*	*B*, Å^2
U(1)	100	2559 (1)	6715 (1)	1845 (1)		F(63)	50	254 (3)	673 (4)	−87 (2)	54 (11)
U(2)	100	4364 (1)	5537 (1)	1077 (1)		F(43)′	50	290 (5)	717 (6)	−93 (4)	130 (26)
U(3)	100	1931 (1)	4621 (1)	0628 (1)		F(53)′	50	370 (4)	661 (4)	−132 (3)	88 (16)
O(1)	100	211 (2)	583 (2)	137 (1)	69 (8)	F(63)′	50	290 (4)	586 (5)	−96 (3)	107 (19)
O(2)	100	296 (2)	757 (2)	231 (2)	72 (9)	O(14)	100	546 (2)	554 (2)	192 (1)	60 (7)
O(3)	100	381 (2)	619 (2)	147 (1)	45 (7)	O(24)	100	428 (2)	441 (2)	168 (2)	82 (9)
O(4)	100	488 (2)	488 (2)	69 (1)	45 (7)	C(14)	100	692 (9)	540 (10)	274 (7)	138 (43)
O(5)	100	302 (2)	480 (2)	67 (1)	67 (8)	C(24)	100	589 (3)	502 (4)	230 (2)	70 (12)
O(6)	100	91 (2)	442 (3)	63 (2)	85 (10)	C(34)	100	563 (3)	421 (4)	240 (3)	78 (14)
O(11)	100	336 (2)	587 (2)	264 (2)	75 (9)	C(44)	100	475 (3)	386 (4)	210 (3)	71 (14)
O(21)	100	177 (2)	632 (2)	249 (2)	72 (9)	C(54)	100	450 (5)	300 (5)	229 (4)	106 (19)
C(11)	100	410 (7)	528 (9)	363 (6)	136 (31)	F(14)	75	681 (3)	505 (3)	321 (3)	157 (14)
C(21)	100	330 (4)	565 (4)	321 (3)	90 (16)	F(24)	75	662 (5)	601 (6)	290 (4)	156 (27)
C(31)	100	257 (4)	580 (4)	339 (3)	91 (17)	F(34)	75	701 (5)	586 (6)	233 (4)	161 (26)
C(41)	100	188 (4)	603 (4)	304 (3)	70 (14)	F(14)′	75	725 (5)	478 (5)	261 (4)	146 (26)
C(51)	100	112 (7)	597 (7)	333 (5)	250 (30)	F(44)	50	496 (4)	285 (4)	293 (3)	100 (18)
F(11)	60	473 (4)	588 (5)	357 (3)	108 (18)	F(54)	50	383 (4)	290 (4)	220 (3)	76 (15)
F(21)	60	423 (5)	454 (6)	344 (4)	119 (22)	F(64)	50	488 (5)	246 (5)	191 (4)	125 (22)
F(31)	60	405 (4)	512 (5)	416 (3)	109 (18)	F(44)′	50	505 (4)	255 (4)	250 (3)	73 (14)
F(11)′	60	466 (6)	517 (7)	332 (4)	146 (25)	F(54)′	50	423 (4)	262 (4)	172 (3)	87 (15)
F(21)′	60	433 (7)	592 (8)	400 (6)	186 (37)	F(64)′	50	390 (7)	319 (7)	260 (6)	138 (35)
F(41)	100	68 (4)	544 (4)	304 (3)	173 (18)	O(15)	100	208 (2)	317 (2)	56 (1)	74 (8)
F(51)	100	68 (4)	666 (5)	320 (3)	226 (22)	O(25)	100	208 (2)	408 (2)	161 (1)	71 (8)
F(61)	100	126 (4)	578 (4)	386 (3)	179 (18)	C(15)	100	197 (7)	157 (6)	61 (5)	133 (26)
O(12)	100	275 (2)	756 (2)	106 (1)	56 (8)	C(25)	100	190 (3)	252 (3)	93 (2)	63 (12)
O(22)	100	142 (2)	758 (2)	155 (2)	69 (8)	C(35)	100	182 (3)	254 (3)	152 (2)	63 (11)
C(12)	100	298 (6)	882 (7)	48 (4)	111 (23)	C(45)	100	187 (3)	334 (4)	180 (3)	72 (13)
C(22)	100	252 (3)	833 (4)	84 (2)	51 (12)	C(55)	100	182 (6)	338 (6)	250 (4)	115 (21)
C(32)	100	180 (3)	874 (4)	90 (3)	75 (14)	F(15)	75	122 (5)	162 (5)	20 (4)	173 (23)
C(42)	100	132 (3)	834 (4)	128 (2)	69 (13)	F(25)	75	188 (4)	170 (4)	0 (3)	143 (19)
C(52)	100	44 (8)	877 (7)	134 (6)	239 (29)	F(35)	75	162 (3)	102 (3)	85 (2)	100 (12)
F(12)	60	296 (4)	836 (4)	−7 (2)	87 (17)	F(15)′	75	264 (4)	137 (4)	59 (3)	126 (16)
F(22)	60	384 (4)	874 (4)	79 (3)	95 (15)	F(45)	50	254 (8)	348 (10)	281 (6)	178 (43)
F(32)	60	271 (3)	952 (4)	20 (3)	86 (14)	F(55)	50	141 (4)	269 (5)	258 (3)	90 (16)
F(12)′	60	344 (6)	934 (6)	73 (4)	163 (27)	F(65)	50	100 (4)	350 (5)	242 (3)	84 (18)
F(22)′	60	338 (6)	837 (5)	18 (4)	139 (24)	F(45)′	50	212 (5)	259 (5)	276 (3)	98 (17)
F(42)	75	55 (5)	885 (5)	196 (4)	139 (26)	F(55)′	50	229 (7)	395 (7)	279 (4)	106 (26)
F(52)	75	−11 (5)	832 (5)	127 (4)	131 (26)	F(65)′	50	144 (8)	396 (7)	263 (5)	140 (29)
F(62)	75	58 (6)	956 (7)	131 (5)	142 (36)	O(16)	100	168 (2)	442 (2)	−41 (1)	65 (8)
F(42)′	75	8 (4)	912 (4)	77 (2)	195 (19)	O(26)	100	155 (2)	596 (2)	10 (1)	73 (8)
O(13)	100	514 (2)	662 (2)	86 (2)	73 (8)	C(16)	100	115 (6)	421 (7)	−158 (4)	129 (24)
O(23)	100	373 (2)	607 (2)	14 (2)	69 (8)	C(26)	100	123 (3)	474 (4)	−92 (3)	72 (13)
C(13)	100	602 (6)	769 (7)	48 (5)	128 (26)	C(36)	100	92 (3)	557 (4)	−92 (2)	73 (13)
C(23)	100	522 (3)	705 (3)	39 (2)	65 (12)	C(46)	100	103 (3)	611 (3)	−45 (2)	61 (12)
C(33)	100	469 (3)	702 (4)	−23 (3)	80 (14)	C(56)	100	75 (7)	718 (6)	−27 (4)	130 (26)
C(43)	100	394 (3)	657 (3)	−29 (2)	69 (13)	F(16)	75	98 (5)	466 (5)	−194 (4)	170 (24)
C(53)	100	332 (4)	648 (5)	−96 (3)	89 (18)	F(26)	75	106 (4)	339 (5)	−138 (3)	165 (19)
F(13)	60	661 (4)	711 (5)	32 (4)	119 (20)	F(36)	75	180 (6)	386 (6)	−154 (4)	205 (28)
F(23)	60	590 (4)	830 (5)	20 (3)	100 (16)	F(16)′	75	34 (5)	397 (5)	−158 (3)	166 (21)
F(33)	60	617 (4)	805 (4)	98 (3)	104 (15)	F(46)	60	130 (3)	758 (3)	−31 (2)	55 (10)
F(13)′	60	654 (5)	739 (6)	84 (4)	141 (23)	F(56)	60	27 (3)	701 (3)	8 (2)	60 (10)
F(23)′	60	612 (5)	771 (5)	−14 (4)	150 (22)	F(66)	60	15 (3)	709 (3)	−95 (2)	58 (10)
F(43)	50	362 (4)	719 (4)	−128 (3)	86 (16)	F(46)′	60	109 (11)	732 (10)	−88 (8)	326 (65)
F(53)	50	333 (3)	577 (4)	−115 (2)	58 (13)	F(56)′	60	23 (9)	704 (9)	−50 (7)	209 (50)

atom		β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U(1)	59 (1)	60 (1)	31 (1)	−5(1)	12 (1)	−8 (1)	U(3)	58 (1)	49 (1)	35 (1)	−6 (1)	6 (1)	−1 (1)
U(2)	48 (1)	54 (1)	29 (1)	6 (1)	5 (1)	3 (1)							

[a] The coordinates are $\times 10^3$ (except for U, which are $\times 10^4$), and the *B*'s are $\times 10$ (except for U, where $10^4\beta_{ij}$'s are given). The temperature factor expression is $TF = \exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$ for anisotropic uranium atoms and $TF = \exp[-(B(\sin^2\theta)/\lambda^2)]$ for all other atoms.

U(2), and U(3) alone, gave $R_1 = \sum(|F_o| - |F_c|)/\sum(|F_o|) = 0.30$ with isotropic temperature factors. The hfa molecules were located in further cycles of difference synthesis–structure factor calculations (six cycles). The Fourier syntheses showed the CF_3 groups to be disordered, and more than three fluorine density peaks were observed for most of the CF_3 groups as the fluorine distribution in the disordered CF_3 groups was doughnut shaped. The CF_3 groups also had high thermal motion. This disorder and high thermal motion made the coordinates in the CF_3 groups of lower accuracy than those of the other atoms. Instead of refining 87 independent atoms for an ordered structure, it was necessary to refine 108 atoms in the asymmetric unit, to include partial fluorine locations. LINUS was enlarged to handle the large number of atoms. The uranium atoms were given anisotropic thermal parameters with all other atoms isotropic. The neutral atom scattering factors were taken from ref 5, and the curve for uranium was corrected for anomalous dispersion ($\Delta f' = -8$ e, $\Delta f'' = 8$ e).[6] A unit weighting scheme was used. The final discrepancy factor *R* was 0.095 over the 3239 reflections. The final positional parameters are given in Table I; the interatomic distances and angles in Table II. A table of observed and calculated structure amplitudes is given as supplementary material.

Discussion

The trimeric structure found here for $[UO_2(hfa)_2]_3$ is quite unique, being the first trimeric uranyl coordination complex to be reported. Even dimeric complexes are rare for uranium.[7]

Table II. Interatomic Angles (deg) and Distances (Å) in $[UO_2(hfa)_2]_3$

Angles			
Uranyl Group			
O(1)-U(1)-O(2)	178 (1)	O(5)-U(3)-O(6)	177 (1)
O(3)-U(2)-O(4)	178 (1)		
Pentagonal Ring			
O(11)-U(1)-O(21)	71 (1)	O(5)-U(2)-O(23)	69 (1)
O(21)-U(1)-O(22)	77 (1)	O(23)-U(2)-O(13)	72 (1)
O(22)-U(1)-O(12)	72 (1)	O(16)-U(3)-O(26)	69 (1)
O(12)-U(1)-O(3)	70 (1)	O(26)-U(3)-O(1)	70 (1)
O(3)-U(1)-O(11)	73 (1)	O(25)-U(3)-O(1)	71 (1)
O(13)-U(2)-O(14)	78 (1)	O(25)-U(3)-O(15)	73 (1)
O(14)-U(2)-O(24)	70 (1)	O(15)-U(3)-O(16)	78 (1)
O(24)-U(2)-O(5)	72 (1)		
Distances			
U-U			
U(1)-U(2)	4.178 (3)	U(3)-U(1)	4.202 (3)
U(2)-U(3)	4.167 (3)		
Uranyl Group			
U(1)-O(1)	1.79 (3)	U(2)-O(4)	1.68 (3)
U(1)-O(2)	1.72 (3)	U(3)-O(5)	1.81 (3)
U(2)-O(3)	1.72 (3)	U(3)-O(6)	1.71 (3)
Pentagonal Ring			
U(1)-O(3)	2.54 (3)	U(2)-O(13)	2.22 (3)
U(2)-O(5)	2.48 (3)	U(2)-O(23)	2.27 (3)
U(3)-O(1)	2.47 (3)	U(2)-O(14)	2.30 (3)
U(1)-O(11)	2.35 (3)	U(2)-O(24)	2.22 (3)
U(1)-O(21)	2.23 (3)	U(3)-O(15)	2.27 (3)
U(1)-O(12)	2.27 (3)	U(3)-O(25)	2.29 (3)
U(1)-O(22)	2.28 (3)	U(3)-O(16)	2.28 (3)
		U(3)-O(26)	2.40 (3)
hfa Molecules 1 and 2			
O(11)-C(21)[a]	1.34 (5)	O(12)-C(22)[a]	1.31 (4)
C(11)-C(21)	1.55 (9)	O(22)-C(42)[a]	1.32 (5)
C(21)-C(31)	1.37 (6)	C(12)-C(22)	1.42 (7)
C(31)-C(41)	1.28 (6)	C(22)-C(32)	1.39 (5)
C(41)-C(51)	1.55 (9)	C(32)-C(42)	1.43 (6)
O(21)-C(41)[a]	1.27 (5)	C(42)-C(52)	1.64 (9)
C(11)-F(11)	1.42 (11)	C(12)-F(12)	1.41 (9)
C(11)-F(21)	1.26 (11)	C(12)-F(22)	1.44 (9)
C(11)-F(31)	1.22 (10)	C(12)-F(32)	1.29 (8)
C(11)-F(11)′	1.28 (11)	C(12)-F(12)′	1.16 (9)
C(11)-F(21)′	1.29 (12)	C(12)-F(22)′	1.24 (9)
C(51)-F(41)	1.19 (9)	C(52)-F(42)	1.35 (10)
C(51)-F(51)	1.29 (9)	C(52)-F(52)	1.13 (9)
C(51)-F(61)	1.20 (9)	C(52)-F(62)	1.24 (10)
hfa Molecules 3 and 4			
O(13)-C(23)[a]	1.28 (4)	O(14)-C(24)[a]	1.26 (5)
O(23)-C(43)[a]	1.34 (5)	O(24)-C(44)[a]	1.38 (5)
C(13)-C(23)	1.63 (8)	C(14)-C(24)	1.85 (11)
C(23)-C(33)	1.46 (5)	C(24)-C(34)	1.37 (6)
C(33)-C(43)	1.39 (5)	C(34)-C(44)	1.55 (6)
C(43)-C(53)	1.61 (6)	C(44)-C(54)	1.49 (7)
C(13)-F(13)	1.42 (9)	C(14)-F(14)	1.23 (12)
C(13)-F(23)	1.12 (8)	C(14)-F(24)	1.15 (13)
C(13)-F(33)	1.22 (8)	C(14)-F(34)	1.20 (12)
C(13)-F(13)′	1.14 (9)	C(14)-F(14)′	1.17 (13)
C(13)-F(23)′	1.43 (9)		
C(53)-F(43)	1.46 (7)	C(54)-F(44)	1.48 (8)
C(53)-F(53)	1.19 (6)	C(54)-F(54)	1.07 (7)
C(53)-F(63)	1.39 (8)	C(54)-F(64)	1.43 (9)
C(53)-F(43)′	1.27 (8)	C(54)-F(44)′	1.16 (7)
C(53)-F(53)′	1.15 (8)	C(54)-F(54)′	1.37 (8)
C(53)-F(63)′	1.17 (8)	C(54)-F(64)′	1.37 (9)
hfa Molecules 5 and 6			
O(15)-C(25)[a]	1.36 (5)	O(16)-C(26)[a]	1.31 (5)
O(25)-C(45)[a]	1.29 (5)	O(26)-C(46)[a]	1.34 (5)
C(15)-C(25)	1.65 (9)	C(16)-C(26)	1.65 (8)
C(25)-C(35)	1.36 (5)	C(26)-C(36)	1.38 (6)
C(35)-C(45)	1.38 (6)	C(36)-C(46)	1.32 (6)
C(45)-C(55)	1.59 (8)	C(46)-C(56)	1.79 (9)
C(15)-F(15)	1.36 (9)	C(16)-F(16)	1.05 (8)
C(15)-F(25)	1.35 (9)	C(16)-F(26)	1.36 (9)
C(15)-F(35)	1.21 (8)	C(16)-F(36)	1.19 (9)
C(15)-F(15)′	1.16 (8)	C(16)-F(16)′	1.38 (9)
C(55)-F(45)	1.24 (11)	C(56)-F(46)	1.12 (8)
C(55)-F(55)	1.30 (8)	C(56)-F(56)	1.26 (9)
C(55)-F(65)	1.34 (9)	C(56)-F(66)	1.62 (8)
C(55)-F(45)′	1.38 (9)	C(56)-F(46)′	1.60 (16)
C(55)-F(55)′	1.25 (9)	C(56)-F(56)′	0.93 (13)
C(55)-F(65)′	1.18 (9)		

[a] Carbonyl atoms.

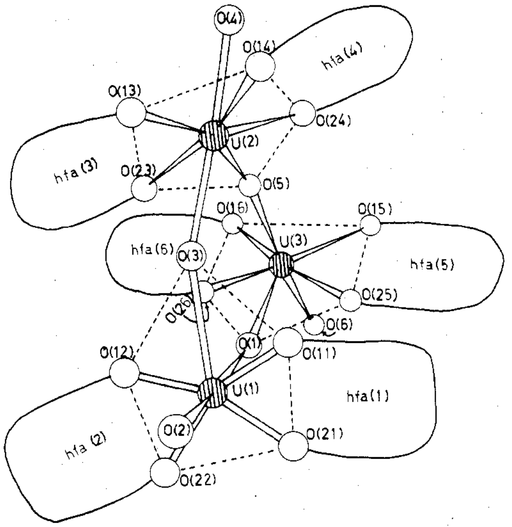

Figure 1. Schematic diagram of the $[UO_2(hfa)_2]_3$ trimeric molecule.

A trimeric U(IV) compound $U_3(CH_3NCH_2CH_2NCH_3)_6$ has recently been described,[7] while $UO_2(acac)_2$ has been reported[8] to be dimeric in benzene solution. The present trimer structure allows the U(VI) atom to retain a pentagonal-bipyramidal configuration with a linear uranyl group at right angles to a reasonably planar pentagonal ring.

A diagram illustrating the main features of the trimeric molecule is given in Figure 1, and a stereoview of the molecule, calculated by ORTEP,[9] in Figure 2. The three uranium atoms in the trimer form an equilateral triangle, of side 4.2 Å, and the uranium atoms are bridged by uranyl oxygen atoms; the three remaining uranyl oxygen atoms are terminal. Each uranium atom in the trimer has pentagonal-bipyramidal coordination by oxygen atoms. Each pentagonal ring of oxygens is made up of four carbonyl oxygen atoms from two bidentate hfa units and one uranyl oxygen from a neighboring uranium atom. The environments of the three uranium atoms in the trimer are equivalent.

The bond lengths and angles in the trimeric molecule are normal, Table II. The terminal uranyl bond distances (~1.70 Å) are shorter than the bridging uranyl bonds (~1.80 Å). The U–O distances in the pentagonal ring are 2.2–2.5 Å. Despite the tight trimeric configuration, the uranyl groups are nearly linear, and the pentagonal angles in the rings are close to 72°. Strains arising from the trimerization are more evident in the lack of planarity of the pentagonal rings (see below). The interatomic distances in the hfa molecules are normal.

Figure 3 is a stereoview of the contents of one unit cell and illustrates the packing of the trimer molecules in the crystal structure. The intermolecular contacts are mainly between

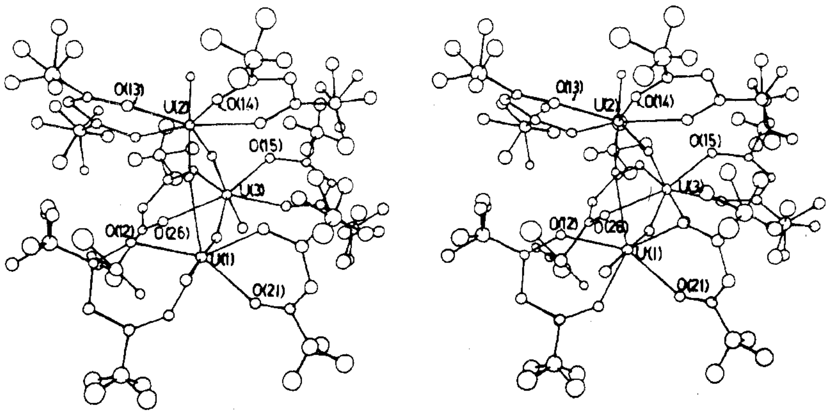

Figure 2. Stereo diagram of the $[UO_2(hfa)_2]_3$ trimeric molecule. The disordered CF_3 groups as found in the difference syntheses are shown.

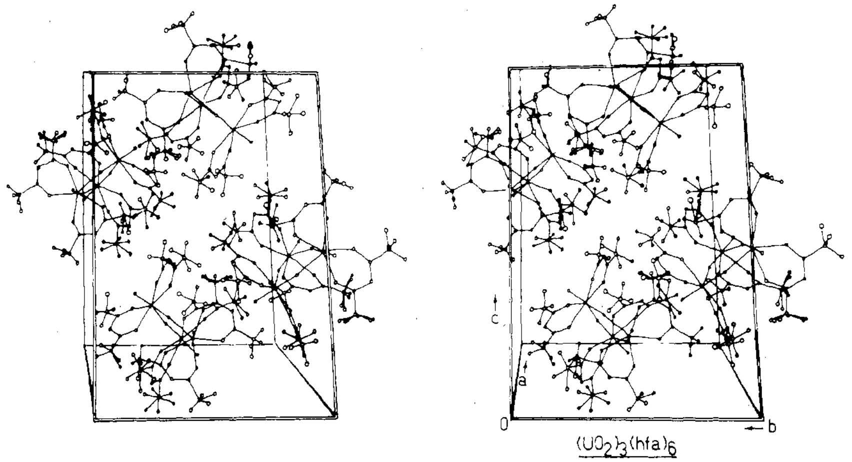

Figure 3. Stereo diagram of one unit cell in the crystal structure of $[UO_2(hfa)_2]_3$, illustrating the molecular packing.

Table III. Least-Squares Planes[a]

plane	A	B	C	D
hfa 1	0.239	0.922	0.300	18.27
hfa 2	0.503	0.449	0.730	12.03
hfa 3	−0.415	0.771	0.383	9.71
hfa 4	−0.402	0.398	0.825	4.79
hfa 5	0.987	−0.117	0.116	1.90
hfa 6.	0.826	0.372	−0.426	8.38
U(1) pentagon	0.454	0.739	0.487	16.86
U(2) pentagon	−0.487	0.623	0.612	7.19
U(3) pentagon	0.977	0.098	−0.187	4.34
plane through U(1), U(2), U(3)	0.208	−0.635	0.744	−8.28

[a] The equations are in the form $AX' + BY + CZ = D$ referred to orthogonal axes with X' perpendicular to b and c, Y parallel to b, and Z parallel to c and are in the perpendicular form. In the monoclinic cell, $X = ax$, $Y = b(^1/_2 + y)$, and $Z = cz$.

III. Table IV shows that, within the experimental error, all hfa units are planar. Only one pentagonal ring, around U(2), appears to be close to planar; the nonplanarity of the pentagons is due to the bending out of the plane of the bridging uranyl oxygen atom. Table V and Figure 2 show that the hfa units are inclined at about 40° to each other around a given uranium atom in a boat configuration. The pentagonal planes are normal to the plane of the three uranium atoms and inclined at about 60° to each other. Owing to the boat configurations, CF_3 groups or between CF_3 groups and terminal uranyl oxygen atoms. They are mainly glide related. There are 22 contacts between 2.8 and 3.4 Å between trimers at (x, y, z) and $(1 - x, y - {}^1/_2, {}^1/_2 - z)$ and 23 between (x, y, z) and $(1 - x, {}^1/_2 + y, {}^1/_2 - z)$. There are 3 in this range for (x, y, z) and $(-x, y - {}^1/_2, {}^1/_2 - z)$ and 2 for (x, y, z) and $(-x, {}^1/_2 + y, {}^1/_2 - z)$.

The more important least-squares planes are given in Table the hfa units are inclined at about 70° to the plane of the three uranium atoms.

Table I shows the thermal vibrations in the trimer are large, especially for the peripheral atoms. As mentioned above, most of the CF_3 groups are disordered, with a curvilinear fluorine density. Figure 2 shows the number of observed fluorine maxima in the CF_3 groups to be between 3 and 6. Occupancy factors estimated for partial fluorine locations are given in Table I. Because of the disorder and high thermal motion, the CF_3 groups could not be precisely determined. Disordered CF_3 groups were also found in α-$UO_2(hfa)_2$tmp (tmp = trimethyl phosphate).[10]

The present trimeric structure is unstable in the presence of molecules which could form a neutral ligand, e.g., H_2O, the trimer being destroyed with the formation of monomeric molecules. Thus, α- and β-$UO_2(hfa)_2$tmp,[10,11] whose structures have recently been determined, have monomeric molecular structures with pentagonal-bipyramidal coordination.

Polymeric forms of β-diketone complexes of other metals are not uncommon. Thus, $Pr(thd)_3$ (thd = anion of 2,2,-6,6-tetramethyl-3,5-heptanedione)[12] is dimeric in the solid state, $Ni(acac)_2$ is trimeric[13] (acac = anion of 2,4-pentadione), and $Co(acac)_2$ is tetrameric.[14] In these complexes, bridging occurs via the carbonyl oxygen atoms of the β-diketone ligand. $[UO_2(hfa)_2]_3$, however, remains a very novel compound, since it is the only reported uranyl trimer and the first uranyl chelate compound with uranyl oxygen bridging.

Registry No. $[UO_2(hfa)_2]_3$, 67761-38-0.

Supplementary Material Available: Observed and calculated

Table IV. Distances of Atoms from Least-Squares Planes

plane	deviations from plane, Å × 10^2						
hfa 1	O(11)	O(21)	C(11)	C(21)	C(31)	C(41)	C(51)
	−2(13)	−1(6)	12(6)	2(6)	−9(16)	−6(3)	3(3)
hfa 2	O(12)	O(22)	C(12)	C(22)	C(32)	C(42)	C(52)
	2(18)	0(5)	−2(6)	6(5)	−4(18)	−4(2)	2(4)
hfa 3	O(13)	O(23)	C(13)	C(23)	C(33)	C(43)	C(53)
	−5(4)	3(4)	6(11)	−1(5)	−7(6)	6(5)	−2(8)
hfa 4	O(14)	O(24)	C(14)	C(24)	C(34)	C(44)	C(54)
	1(3)	0(4)	4(17)	−2(17)	−8(7)	−1(7)	5(9)
hfa 5	O(15)	O(25)	C(15)	C(25)	C(35)	C(45)	C(55)
	−2(3)	8(3)	11(11)	−9(5)	−6(5)	−6(5)	4(9)
hfa 6	O(16)	O(26)	C(16)	C(26)	C(36)	C(46)	C(56)
	−8(3)	13(3)	12(10)	−8(6)	−6(5)	−3(5)	0(12)
U(1) pentagon	U(1)	O(3)	O(11)	O(21)	O(12)	O(22)	
	−2(1)	−31(3)	34(3)	−22(3)	21(3)	0(3)	
U(2) pentagon	U(2)	O(5)	O(13)	O(23)	O(14)	O(24)	
	3(0)	13(3)	0(4)	−9(4)	8(3)	−15(4)	
U(3) pentagon	U(3)	O(1)	O(15)	O(25)	O(16)	O(26)	
	4(0)	21(3)	9(3)	−21(3)	3(3)	−16(3)	

Table V. Dihedral Angles

plane 1	plane 2	dihedral angle, deg
hfa 1	hfa 2	41.1
hfa 3	hfa 4	37.8
hfa 5	hfa 6	43.8
U(1) pentagon	U(1), U(2), U(3) plane	90.7
U(2) pentagon	U(1), U(2), U(3) plane	92.4
U(3) pentagon	U(1), U(2), U(3) plane	90.0
U(1) pentagon	U(2) pentagon	57.5
U(1) pentagon	U(3) pentagon	64.9
U(2) pentagon	U(3) pentagon	58.1
U(1), U(2), U(3) plane	hfa 1	71.8
U(1), U(2), U(3) plane	hfa 2	68.7
U(1), U(2), U(3) plane	hfa 3	73.1
U(1), U(2), U(3) plane	hfa 4	73.9
U(1), U(2), U(3) plane	hfa 5	68.5
U(1), U(2), U(3) plane	hfa 6	67.6

structure factors for $UO_2(hfa)_2$ (11 pages). Ordering information is given on any current masthead page.

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