

Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720

## Crystal and Molecular Structures of Thorium and Uranium Tetrakis(hexafluoroacetylpyrazolide) Complexes<sup>1</sup>

KARL VOLZ, ALLAN ZALKIN, and DAVID H. TEMPLETON\*

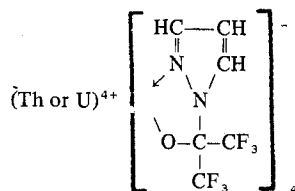
Received February 12, 1976

AIC60109P

Triclinic crystals of thorium(IV) and uranium(IV) tetrakis(hexafluoroacetylpyrazolide) are isostructural, with space group  $P\bar{1}$  and  $Z = 2$ . At 23 °C for Th(C<sub>6</sub>H<sub>3</sub>ON<sub>2</sub>F<sub>6</sub>)<sub>4</sub>  $a = 11.282$  (5) Å,  $b = 16.245$  (7) Å,  $c = 10.836$  (5) Å,  $\alpha = 90.14$  (5)°,  $\beta = 108.75$  (5)°, and  $\gamma = 107.07$  (5)°. For the uranium compound  $a = 11.302$  (5) Å,  $b = 16.377$  (8) Å,  $c = 11.000$  (5) Å,  $\alpha = 87.85$  (5)°,  $\beta = 111.02$  (5)°, and  $\gamma = 109.95$  (5)°. X-ray diffraction data were measured with a scintillation counter,  $\theta$ - $2\theta$  scans, and Mo K $\alpha$  radiation. For thorium the conventional  $R$  value is 0.026 for 2966 unique data with  $I > \sigma(I)$ , and for uranium it is 0.027 for 4125 unique data with  $I > 3\sigma(I)$ . The full-matrix least-squares refinement of the 598 parameters of each structure included anisotropic thermal parameters for the 61 nonhydrogen atoms and isotropic ones for the 12 hydrogen atoms. The actinide ion is at the center of an irregular polyhedron of four oxygen and four nitrogen atoms. The average Th-O, Th-N, U-O, and U-N distances are 2.291 (4), 2.637 (5), 2.237 (3), and 2.574 (5) Å. The molecules are packed in a manner which resembles cubic closest packing but which is more nearly analogous to the body-centered tetragonal structure of protactinium metal.

### Introduction

Polymeric pyrazolide compounds of the type M(pz)<sub>n</sub> can be formed in the reaction of pyrazole (HN<sub>2</sub>C<sub>3</sub>H<sub>3</sub> or Hpz) with ions of transition metals, lanthanides, and actinides. In 1966 Mahler<sup>2</sup> discovered that hexafluoroacetone (hfa) can react with the pyrazolide compounds to yield metal-pyrazolide-hexafluoroacetone complexes M(hfapz)<sub>n</sub>. Several actinide (hfapz)<sub>4</sub> compounds were synthesized by Andruchow and Karraker.<sup>3</sup> We studied two of these with x-ray diffraction methods to verify their composition and to establish their molecular structure, which can be represented as



### Experimental Section

Crystalline samples of Th(C<sub>6</sub>H<sub>3</sub>ON<sub>2</sub>F<sub>6</sub>)<sub>4</sub> and U(C<sub>6</sub>H<sub>3</sub>ON<sub>2</sub>F<sub>6</sub>)<sub>4</sub> were kindly provided by D. G. Karraker. The thorium crystals were well-formed colorless prisms which did not require recrystallization. The dark violet uranium crystals after recrystallization from toluene were fragile hexagonal plates. Crystals of both compounds are air stable and were mounted on glass fibers for x-ray diffraction study. Each exhibited sharp extinction under polarized light. Investigations with oscillation, Weissenberg, and precession photography indicated that the crystals were triclinic. The space group  $P\bar{1}$  was assumed and is confirmed by the subsequent refinement of the structure. Unit cell dimensions were obtained in each case by a least-squares analysis of the setting angles for 12 carefully centered reflections with  $2\theta > 37^\circ$ , using resolved Mo K $\alpha_1$  peaks ( $\lambda$  0.709 26 Å) with a Picker automated four-circle diffractometer and a graphite monochromator. Intensities were measured for both compounds using a  $\theta$ - $2\theta$  scan technique. Data for the thorium crystal were collected out to  $2\theta = 40^\circ$  at a scan rate of  $1^\circ/\text{min}$ ; data for the uranium crystal were measured to  $2\theta = 50^\circ$  at a scan rate of  $2^\circ/\text{min}$ . For thorium, reflections were scanned from  $0.8^\circ$  below the calculated K $\alpha_1$  position to  $0.8^\circ$  above K $\alpha_2$ ; for uranium, the range in each direction was  $0.9^\circ$ . Background was counted for 4 s at positions offset  $0.9^\circ$  from each end of the scan. Copper-foil attenuators were inserted when necessary to reduce the maximum counting rate below 10 000 counts/s. All the reflections within the spheres of reciprocal space delineated by the above  $2\theta$  limits were measured. Reflections (300), (060), and (003) for the thorium crystal and (500), (0,10,0), and (003) for the uranium crystal were measured at intervals of 200 measurements to monitor radiation damage and instrumental stability. Corrections calculated from the average change of the three standards were applied to the data; they ranged from 1.0 to 1.03. The widths of half-maximum of the scans increased an average

Table I. Crystal Data

	Th(C <sub>6</sub> H <sub>3</sub> - ON <sub>2</sub> F <sub>6</sub> ) <sub>4</sub>	U(C <sub>6</sub> H <sub>3</sub> ON <sub>2</sub> F <sub>6</sub> ) <sub>4</sub>	
Fw	1164.4	1170.4	
Space group	$P\bar{1}$	$P\bar{1}$	
$a$ , Å	11.282 (5)	11.302 (5) <sup>a</sup>	11.295 (5) <sup>b</sup>
$b$ , Å	16.245 (7)	16.377 (8)	16.393 (8)
$c$ , Å	10.836 (5)	11.000 (5)	10.999 (5)
$\alpha$ , deg	90.14 (5)	87.85 (5)	87.98 (5)
$\beta$ , deg	108.75 (5)	111.02 (5)	110.82 (5)
$\gamma$ , deg	107.07 (5)	109.95 (5)	109.79 (5)
$d_{\text{calcd}}$ (23 °C), g/cm <sup>3</sup>	2.163	2.186	
$d_{\text{measd}}$ (23 °C), <sup>c</sup> g/cm <sup>3</sup>	2.16	2.18	
$\mu$ , cm <sup>-1</sup> (Mo K $\alpha$ )	44.38	44.49	

<sup>a</sup> Original measurements. <sup>b</sup> Measurements after data collection was completed, made because setting angle discrepancies had developed. The change is attributed to radiation damage. <sup>c</sup> Measured by flotation.

of  $0.05^\circ$  for each crystal during the experiment.

The thorium (uranium) crystal had six (eight) faces and dimensions  $0.07 \times 0.085 \times 0.17$  mm ( $0.057 \times 0.10 \times 0.28$  mm). Absorption corrections were calculated by analytical integration<sup>4</sup> and checked for each data set as follows. Several test reflections were measured at regular intervals of the azimuthal angle  $\psi$  corresponding to rotation of the crystal around the direction of the diffraction vector.<sup>5</sup> These intensities reveal variations in the absorption effect for each reflection, and plots as a function of  $\psi$  before and after correction indicated the efficacy of the correction. The correction factors ranged from 1.294 to 1.447 for the thorium crystal and from 1.213 to 1.594 for uranium. After this correction the agreement of pairs of equivalent reflections is indicated by  $R_s = \sum |I - I_{av}| / \sum I = 0.03$  (0.05) for the thorium (uranium) crystal. Standard deviations were assigned to the average intensities according to counting statistics or the scatter, whichever gave the larger result, and corresponding values of  $\sigma(F)$  were derived. These data sets included 3359 (6291) unique reflections for the thorium (uranium) crystal, of which 2966 with  $I > \sigma(I)$  for thorium and 4125 with  $I > 3\sigma(I)$  for uranium were given weight in the final least-squares refinements,  $w = (\sigma(F))^{-2}$ . The crystal data are listed in Table I.

### Determination and Refinement of Structure

The coordinates of the thorium atom were readily obtained from the Patterson function. After least-squares refinement of that one atom, a  $\Delta F$  Fourier map revealed the locations of the remaining 60 nonhydrogen atoms. Refinement of the 61 atoms with anisotropic thermal parameters for thorium resulted in  $R = \sum |\Delta F| / \sum |F_o| = 0.06$ . The 12 hydrogen atoms were introduced at calculated positions, and further refinement of all 73 atoms reduced  $R$  to 0.05. Finally, with isotropic thermal parameters for hydrogen and anisotropic parameters for all other atoms (598 parameters in all)  $R$  was reduced to 0.026 for 2966 reflections with  $I > \sigma(I)$ . The weighted residual  $R_2 = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$  was 0.013, and  $R$  including zero-weight data

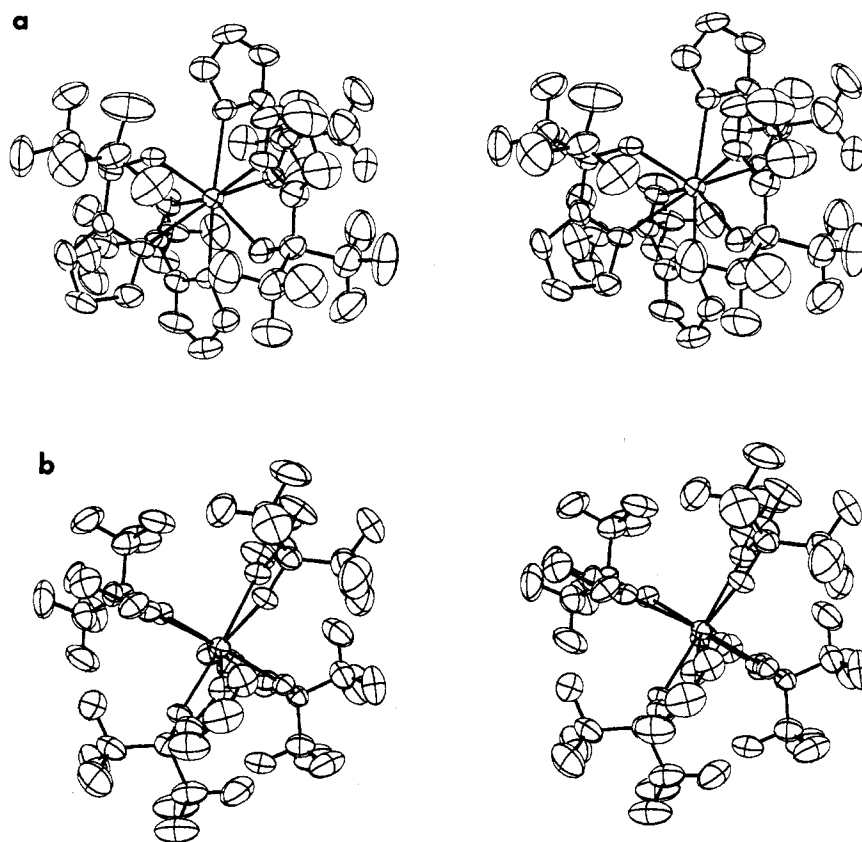


Figure 1. Stereoscopic views of the molecular structure of the thorium complex: (a) down the  $c^*$  axis; (b) down the  $b^*$  axis. The hydrogen atoms are omitted.

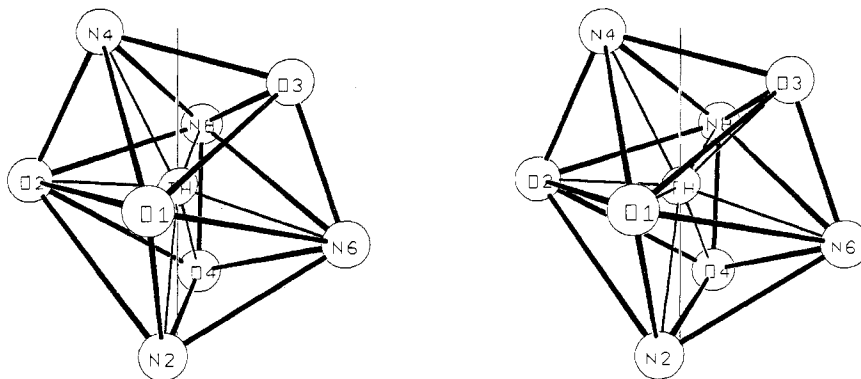


Figure 2. Stereoscopic view of the dodecahedral geometry of the eight atoms coordinated to thorium.

was 0.037. In the last cycle no parameter of hydrogen shifted more than  $0.17\sigma$  and for other atoms the largest shift was  $0.11\sigma$ . The standard deviation of an observation of unit weight was 0.99. In a final  $\Delta F$  Fourier map the largest peak,  $0.66 e/\text{\AA}^3$ , was near the thorium atom. The final coordinates are listed in Table II.<sup>6</sup>

The two compounds were known to be nearly isostructural on the basis of similar film data. Refinement of the uranium compound was started with the final parameters for the thorium one and converged with little change. The final refinement reduced  $R$  to 0.027 for the 4125 reflections with  $I > 3\sigma(I)$ ;  $R_2$  was 0.013;  $R$  was 0.059 including the zero-weight data. The standard deviation of an observation of unit weight was 1.01. The ten largest peaks in the final  $\Delta F$  map ranged from 1.40 to  $0.76 e/\text{\AA}^3$ . Most of them were near uranium or fluorine atoms. The final coordinates are listed in Table III.<sup>6</sup> In the last cycle none of these changed more than  $0.12\sigma$ , and no thermal parameter changed more than  $0.19\sigma$ .<sup>7</sup>

The scattering factors used were those of Doyle and Turner<sup>8</sup> for neutral carbon, nitrogen, oxygen, and fluorine and those of Cromer and Waber<sup>9</sup> for neutral thorium and uranium, in each case corrected for dispersion according to Cromer and Liberman.<sup>10</sup> Polarized hydrogen scattering factors from Stewart, Davidson, and Simpson<sup>11</sup>

were used with Olson's<sup>12</sup> modified version of our least-squares program, LESQ. Other calculations were done with our unpublished programs MAGPIK, INCOR, ORDER, MORPH, DISMAT, DISTAN, LSPLAN, LIST, and LISTAP, L. K. Templeton's absorption correction program ABSOR, and Johnson's<sup>13</sup> ORTEP.

### Discussion

These compounds crystallize as discrete molecular complexes (Figure 1) and are essentially isostructural except for an average difference of  $0.06 \text{\AA}$  in the actinide-ligand bond lengths as a result of the actinide contraction. Bond lengths and angles are listed in Tables IV–VII. The four ligands are arranged in a roughly tetrahedral fashion with approximately the symmetry of a twofold axis in the direction of  $c^*$  (Figure 1a). A pair of chelate rings is nearly coplanar (Figure 1b), and the planes of two of these pairs have a dihedral angle of  $88^\circ$ . The molecules in each of these planes are arranged in a trans configuration.

The coordination polyhedron about the actinide atom consists of four oxygen atoms and four nitrogen atoms at

Table II. Atomic Coordinates and Standard Deviations in Thorium Tetrakis(hexafluoroacetylpyrazolide)

Atom	x	y	z
Th	0.007 88 (3)	0.248 70 (2)	0.197 33 (2)
O(1)	-0.171 3 (4)	0.221 9 (2)	0.010 4 (3)
O(2)	0.148 4 (4)	0.277 9 (2)	0.079 6 (3)
O(3)	-0.071 0 (4)	0.331 7 (2)	0.302 1 (4)
O(4)	0.118 4 (4)	0.163 7 (2)	0.325 1 (4)
N(1)	-0.223 0 (6)	0.072 4 (4)	-0.014 1 (5)
N(2)	-0.104 8 (5)	0.089 2 (3)	0.084 5 (5)
N(3)	0.186 2 (5)	0.426 3 (4)	0.085 6 (5)
N(4)	0.098 6 (5)	0.409 8 (4)	0.151 3 (5)
N(5)	-0.222 5 (5)	0.219 3 (4)	0.354 9 (5)
N(6)	-0.171 1 (5)	0.169 6 (4)	0.301 6 (5)
N(7)	0.277 3 (6)	0.272 5 (4)	0.481 9 (6)
N(8)	0.215 0 (5)	0.324 2 (4)	0.409 0 (5)
C(1)	-0.258 1 (7)	0.149 9 (4)	-0.066 0 (6)
C(2)	-0.251 2 (9)	0.152 0 (5)	-0.204 1 (7)
C(3)	-0.399 1 (7)	0.141 4 (5)	-0.068 1 (8)
C(4)	-0.089 (1)	0.012 2 (6)	0.108 8 (9)
C(5)	-0.193 (1)	-0.053 5 (6)	0.026 (1)
C(6)	-0.275 (1)	-0.013 1 (6)	-0.051 0 (9)
C(7)	0.212 5 (6)	0.349 6 (4)	0.039 7 (6)
C(8)	0.167 3 (9)	0.342 1 (5)	-0.111 0 (7)
C(9)	0.363 4 (8)	0.365 0 (6)	0.097 1 (9)
C(10)	0.089 3 (9)	0.486 3 (6)	0.178 0 (8)
C(11)	0.170 (1)	0.551 6 (6)	0.133 5 (9)
C(12)	0.228 1 (9)	0.511 9 (6)	0.074 5 (8)
C(13)	-0.158 7 (7)	0.314 9 (4)	0.364 6 (6)
C(14)	-0.264 4 (8)	0.357 9 (5)	0.304 4 (8)
C(15)	-0.087 4 (8)	0.345 0 (5)	0.512 3 (7)
C(16)	-0.235 3 (8)	0.088 3 (6)	0.313 1 (7)
C(17)	-0.325 8 (8)	0.087 2 (6)	0.375 0 (7)
C(18)	-0.315 9 (8)	0.170 4 (7)	0.398 9 (8)
C(19)	0.221 5 (7)	0.178 6 (4)	0.432 9 (7)
C(20)	0.331 4 (9)	0.150 6 (6)	0.409 0 (9)
C(21)	0.178 2 (8)	0.129 7 (6)	0.541 8 (8)
C(22)	0.278 2 (9)	0.401 3 (5)	0.471 7 (9)
C(23)	0.379 (1)	0.401 2 (8)	0.585 (1)
C(24)	0.377 9 (9)	0.317 5 (8)	0.588 9 (9)
F(1)	-0.341 2 (4)	0.084 7 (3)	-0.289 1 (3)
F(2)	-0.134 2 (5)	0.151 1 (3)	-0.204 0 (4)
F(3)	-0.271 1 (5)	0.222 8 (3)	-0.255 6 (4)
F(4)	-0.435 2 (4)	0.207 0 (3)	-0.116 8 (4)
F(5)	-0.404 4 (4)	0.138 2 (3)	0.052 1 (4)
F(6)	-0.488 4 (4)	0.069 2 (3)	-0.138 3 (4)
F(7)	0.229 0 (5)	0.410 0 (3)	-0.158 0 (4)
F(8)	0.040 0 (5)	0.335 9 (3)	-0.156 9 (4)
F(9)	0.179 5 (5)	0.273 0 (3)	-0.160 3 (4)
F(10)	0.392 4 (4)	0.296 6 (3)	0.067 0 (5)
F(11)	0.400 0 (4)	0.374 8 (3)	0.227 4 (5)
F(12)	0.436 8 (4)	0.433 8 (3)	0.063 5 (5)
F(13)	-0.357 6 (4)	0.339 9 (3)	0.356 9 (5)
F(14)	-0.320 8 (4)	0.330 1 (3)	0.178 9 (5)
F(15)	-0.213 2 (4)	0.442 0 (3)	0.313 9 (4)
F(16)	-0.013 7 (5)	0.424 1 (3)	0.534 9 (4)
F(17)	-0.008 5 (4)	0.297 1 (3)	0.563 8 (3)
F(18)	-0.168 2 (4)	0.335 4 (3)	0.580 1 (4)
F(19)	0.437 8 (4)	0.162 8 (3)	0.512 8 (5)
F(20)	0.368 2 (4)	0.193 3 (3)	0.318 0 (5)
F(21)	0.289 1 (5)	0.067 3 (3)	0.363 6 (5)
F(22)	0.128 0 (4)	0.045 6 (3)	0.504 2 (4)
F(23)	0.087 1 (5)	0.155 1 (3)	0.564 6 (4)
F(24)	0.275 2 (4)	0.139 9 (3)	0.654 1 (4)
H(1)	-0.003 (6)	0.012 (4)	0.166 (6)
H(2)	-0.218 (7)	-0.113 (4)	0.018 (6)
H(3)	-0.358 (6)	-0.035 (4)	-0.118 (6)
H(4)	0.030 (5)	0.490 (4)	0.219 (5)
H(5)	0.166 (5)	0.612 (4)	0.135 (5)
H(6)	0.303 (6)	0.535 (4)	0.031 (6)
H(7)	-0.223 (6)	0.037 (4)	0.276 (5)
H(8)	-0.383 (5)	0.038 (4)	0.396 (5)
H(9)	-0.357 (5)	0.193 (3)	0.447 (5)
H(10)	0.250 (4)	0.448 (3)	0.446 (4)
H(11)	0.454 (7)	0.451 (5)	0.639 (8)
H(12)	0.442 (9)	0.291 (5)	0.647 (8)

Table III. Atomic Coordinates and Standard Deviations in Uranium Tetrakis(hexafluoroacetylpyrazolide)

Atom	x	y	z
U	0.024 15 (2)	0.247 45 (1)	0.186 28 (2)
O(1)	-0.159 6 (3)	0.225 5 (2)	0.003 5 (3)
O(2)	0.159 6 (3)	0.272 1 (2)	0.072 4 (3)
O(3)	-0.041 1 (3)	0.332 9 (2)	0.280 4 (3)
O(4)	0.128 1 (3)	0.161 9 (2)	0.310 9 (3)
N(1)	-0.222 0 (4)	0.075 0 (3)	-0.021 5 (4)
N(2)	-0.099 3 (4)	0.092 0 (3)	0.078 5 (4)
N(3)	0.210 4 (4)	0.421 1 (3)	0.073 7 (5)
N(4)	0.123 3 (4)	0.406 1 (3)	0.138 0 (4)
N(5)	-0.192 7 (4)	0.225 0 (3)	0.345 8 (4)
N(6)	-0.151 7 (4)	0.171 6 (3)	0.292 4 (4)
N(7)	0.294 7 (4)	0.268 1 (3)	0.468 8 (4)
N(8)	0.236 5 (4)	0.322 4 (3)	0.392 5 (4)
C(1)	-0.251 8 (5)	0.154 3 (4)	-0.073 3 (5)
C(2)	-0.246 2 (7)	0.157 7 (5)	-0.211 9 (6)
C(3)	-0.394 0 (6)	0.145 2 (4)	-0.078 9 (6)
C(4)	-0.091 0 (6)	0.013 3 (4)	0.099 6 (6)
C(5)	-0.203 0 (7)	-0.053 4 (5)	0.016 1 (7)
C(6)	-0.282 7 (7)	-0.011 4 (4)	-0.059 5 (7)
C(7)	0.231 1 (5)	0.343 5 (4)	0.033 9 (6)
C(8)	0.183 8 (8)	0.335 8 (6)	-0.118 3 (7)
C(9)	0.384 7 (6)	0.357 9 (5)	0.097 4 (8)
C(10)	0.116 6 (6)	0.482 1 (4)	0.159 6 (6)
C(11)	0.199 8 (8)	0.548 0 (5)	0.110 3 (8)
C(12)	0.256 1 (7)	0.507 5 (5)	0.056 3 (7)
C(13)	-0.122 3 (5)	0.319 4 (3)	0.348 9 (5)
C(14)	-0.231 8 (7)	0.360 1 (4)	0.284 3 (7)
C(15)	-0.038 8 (7)	0.355 5 (5)	0.492 5 (6)
C(16)	-0.221 8 (6)	0.091 8 (4)	0.310 3 (6)
C(17)	-0.303 4 (7)	0.093 6 (6)	0.376 8 (7)
C(18)	-0.284 8 (7)	0.178 1 (6)	0.395 7 (7)
C(19)	0.234 4 (5)	0.175 3 (3)	0.423 3 (6)
C(20)	0.343 1 (6)	0.148 0 (5)	0.400 8 (6)
C(21)	0.188 5 (6)	0.125 2 (4)	0.529 5 (6)
C(22)	0.304 8 (6)	0.400 4 (5)	0.458 2 (7)
C(23)	0.408 9 (8)	0.399 6 (6)	0.573 1 (8)
C(24)	0.398 6 (7)	0.315 1 (5)	0.576 5 (7)
F(1)	-0.344 5 (4)	0.092 0 (2)	-0.297 1 (3)
F(2)	-0.130 3 (4)	0.155 1 (3)	-0.208 4 (3)
F(3)	-0.259 3 (4)	0.230 6 (2)	-0.262 3 (3)
F(4)	-0.425 8 (3)	0.213 2 (2)	-0.125 4 (3)
F(5)	-0.396 5 (3)	0.141 6 (2)	0.041 0 (4)
F(6)	-0.491 9 (3)	0.074 0 (2)	-0.148 6 (3)
F(7)	0.257 9 (4)	0.402 5 (3)	-0.162 9 (4)
F(8)	0.057 3 (4)	0.335 2 (3)	-0.167 5 (3)
F(9)	0.185 6 (4)	0.263 8 (3)	-0.163 6 (4)
F(10)	0.407 3 (4)	0.289 2 (3)	0.067 8 (4)
F(11)	0.420 7 (3)	0.367 3 (2)	0.226 6 (4)
F(12)	0.463 2 (3)	0.427 5 (3)	0.066 3 (4)
F(13)	-0.319 0 (4)	0.349 4 (3)	0.341 3 (4)
F(14)	-0.299 9 (3)	0.328 2 (2)	0.161 8 (4)
F(15)	-0.173 4 (4)	0.445 9 (3)	0.282 2 (3)
F(16)	0.047 2 (4)	0.435 2 (3)	0.500 1 (4)
F(17)	0.035 4 (3)	0.306 9 (2)	0.548 4 (3)
F(18)	-0.112 3 (4)	0.356 8 (3)	0.561 3 (3)
F(19)	0.453 1 (3)	0.161 6 (3)	0.506 1 (4)
F(20)	0.379 7 (3)	0.189 4 (2)	0.307 1 (4)
F(21)	0.296 3 (4)	0.063 7 (3)	0.362 6 (4)
F(22)	0.126 0 (3)	0.041 2 (2)	0.488 6 (3)
F(23)	0.100 9 (4)	0.153 1 (2)	0.551 3 (3)
F(24)	0.288 0 (3)	0.132 5 (2)	0.641 1 (3)
H(1)	-0.009 (4)	0.004 (2)	0.182 (4)
H(2)	-0.211 (6)	-0.115 (4)	0.020 (6)
H(3)	-0.370 (4)	-0.033 (3)	-0.127 (4)
H(4)	0.052 (4)	0.487 (3)	0.209 (4)
H(5)	0.211 (5)	0.612 (4)	0.123 (5)
H(6)	0.338 (6)	0.530 (4)	0.025 (6)
H(7)	-0.202 (4)	0.043 (3)	0.279 (4)
H(8)	-0.367 (5)	0.047 (3)	0.395 (5)
H(9)	-0.321 (4)	0.213 (3)	0.438 (4)
H(10)	0.287 (5)	0.456 (3)	0.424 (5)
H(11)	0.465 (6)	0.453 (4)	0.630 (6)
H(12)	0.447 (5)	0.277 (3)	0.637 (5)

**Table IV.** Bond Distances (Å) and Standard Deviations for the Thorium Compound

	Ligand I	Ligand II	Ligand III	Ligand IV
Th-O(1) <sup>a</sup>	2.286 (4)	2.286 (4)	2.291 (4)	2.300 (4)
Th-N(2)	2.623 (5)	2.628 (5)	2.637 (5)	2.661 (6)
O(1)-C(1)	1.347 (7)	1.333 (6)	1.335 (6)	1.318 (6)
C(1)-C(2)	1.523 (9)	1.539 (9)	1.525 (9)	1.532 (9)
C(1)-C(3)	1.548 (9)	1.554 (9)	1.545 (8)	1.552 (9)
C(2)-F(1)	1.348 (7)	1.320 (7)	1.311 (8)	1.318 (8)
C(2)-F(2)	1.324 (8)	1.332 (8)	1.316 (8)	1.312 (8)
C(2)-F(3)	1.327 (8)	1.305 (8)	1.308 (7)	1.329 (8)
C(3)-F(4)	1.304 (7)	1.314 (8)	1.281 (7)	1.322 (8)
C(3)-F(5)	1.323 (8)	1.333 (8)	1.342 (7)	1.304 (8)
C(3)-F(6)	1.333 (7)	1.312 (8)	1.320 (7)	1.320 (7)
C(1)-N(1)	1.487 (7)	1.482 (7)	1.494 (7)	1.490 (7)
N(1)-C(6)	1.342 (8)	1.351 (8)	1.343 (8)	1.352 (9)
N(1)-N(2)	1.365 (6)	1.361 (6)	1.345 (6)	1.349 (6)
N(2)-C(4)	1.331 (8)	1.317 (9)	1.335 (8)	1.304 (8)
C(4)-C(5)	1.383 (11)	1.378 (11)	1.387 (10)	1.380 (11)
C(5)-C(6)	1.355 (11)	1.332 (11)	1.340 (10)	1.357 (12)
C(4)-H(1)	0.96 (6)	0.93 (5)	0.99 (5)	0.92 (4)
C(5)-H(2)	0.93 (6)	1.00 (5)	0.95 (5)	0.99 (7)
C(6)-H(3)	0.95 (5)	1.07 (6)	0.94 (5)	1.00 (8)

<sup>a</sup> For each ligand the atoms are numbered as in Figure 3. For ligand I this corresponds to the numbering in Table II. Similar numbering is used in Tables V-VII.

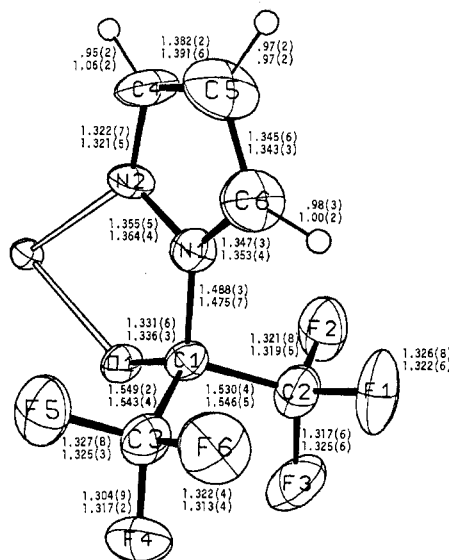
**Table V.** Bond Angles (deg) and Standard Deviations for the Thorium Compound

	Ligand I	Ligand II	Ligand III	Ligand IV
O(1)-Th-N(2)	61.7 (2)	62.0 (2)	61.6 (2)	61.3 (2)
Th-O(1)-C(1)	134.7 (4)	134.3 (4)	134.7 (4)	134.8 (4)
O(1)-C(1)-N(1)	109.7 (5)	110.8 (5)	110.0 (5)	111.4 (5)
C(1)-N(1)-N(2)	115.5 (6)	115.8 (6)	115.8 (6)	115.4 (6)
N(1)-N(2)-Th	117.0 (4)	117.0 (5)	117.3 (4)	117.2 (4)
N(1)-N(2)-C(4)	105.5 (6)	104.3 (6)	105.1 (6)	104.2 (6)
N(2)-C(4)-C(5)	110.9 (8)	112.2 (9)	110.4 (8)	112.7 (8)
C(4)-C(5)-C(6)	105.3 (8)	105.1 (8)	105.6 (8)	105.1 (9)
C(5)-C(6)-N(1)	108.5 (8)	108.3 (8)	107.9 (8)	106.2 (9)
C(6)-N(1)-N(2)	109.8 (7)	110.2 (7)	110.9 (6)	111.9 (7)
O(1)-C(1)-C(2)	110.1 (6)	110.2 (5)	110.2 (5)	111.2 (6)
O(1)-C(1)-C(3)	110.2 (6)	110.0 (5)	109.7 (6)	109.1 (6)
N(1)-C(1)-C(2)	106.9 (6)	108.0 (5)	109.1 (6)	107.3 (6)
N(1)-C(1)-C(3)	109.0 (6)	107.7 (6)	105.9 (5)	107.3 (6)
C(2)-C(1)-C(3)	110.9 (7)	110.1 (6)	111.8 (6)	110.6 (6)
C(1)-C(2)-F(1)	113.8 (6)	113.8 (6)	113.2 (6)	114.8 (7)
C(1)-C(2)-F(2)	111.0 (7)	108.7 (7)	108.9 (7)	109.9 (7)
C(1)-C(2)-F(3)	111.6 (7)	112.1 (6)	111.2 (7)	111.2 (7)
F(1)-C(2)-F(2)	106.8 (7)	106.3 (6)	107.2 (7)	107.2 (7)
F(1)-C(2)-F(3)	106.1 (6)	108.4 (7)	108.7 (7)	107.4 (7)
F(2)-C(2)-F(3)	107.3 (7)	107.2 (7)	107.4 (6)	105.9 (7)
C(1)-C(3)-F(4)	110.9 (6)	110.8 (7)	112.9 (6)	110.2 (7)
C(1)-C(3)-F(5)	110.4 (6)	108.4 (7)	109.2 (6)	110.6 (6)
C(1)-C(3)-F(6)	112.7 (7)	115.4 (7)	113.5 (6)	113.8 (7)
F(4)-C(3)-F(5)	108.6 (7)	106.1 (7)	106.5 (7)	107.4 (7)
F(4)-C(3)-F(6)	107.8 (6)	109.2 (7)	108.1 (7)	106.9 (6)
F(5)-C(3)-F(6)	106.3 (6)	106.5 (7)	106.1 (6)	107.7 (7)

average bond distances Th-O = 2.291 (4), Th-N = 2.637 (5), U-O = 2.237 (3), and U-N = 2.574 (5) Å. These eight atoms are at the vertices of an irregular dodecahedron (Figure 2) with the bidentate ligands spanning the "m" edges as designated by Hoard and Silverton.<sup>14</sup> The coordinating atoms have a "bite" on the metal atom averaging 2.54 Å with an average O-M-N angle of 61°. Much of the distortion of this polyhedron results from the difference in bond lengths to oxygen and nitrogen; if the shape is described by the bond angles at the central atom, changes of no more than 10° are required to reach the ideal shape. The arrangement of oxygen and nitrogen atoms on the polyhedron is in conflict with the ideal symmetry  $\bar{4}2m$ , and crowding of oxygen atoms with each other is correlated with the largest angular distortions from this symmetry. The shape of the coordination polyhedron is closer to the dodecahedron than to a square antiprism.

**Table VI.** Bond Distances (Å) and Standard Deviations for the Uranium Compound

	Ligand I	Ligand II	Ligand III	Ligand IV
U-O(1)	2.244 (3)	2.235 (3)	2.222 (4)	2.246 (3)
U-N(2)	2.539 (5)	2.574 (5)	2.593 (5)	2.589 (5)
O(1)-C(1)	1.332 (5)	1.328 (5)	1.343 (5)	1.339 (5)
C(1)-C(2)	1.546 (8)	1.560 (8)	1.542 (7)	1.540 (7)
C(1)-C(3)	1.542 (7)	1.556 (8)	1.535 (7)	1.543 (7)
C(2)-F(1)	1.336 (7)	1.329 (7)	1.309 (7)	1.317 (6)
C(2)-F(2)	1.312 (7)	1.332 (7)	1.310 (6)	1.325 (6)
C(2)-F(3)	1.330 (6)	1.307 (8)	1.336 (7)	1.321 (7)
C(3)-F(4)	1.314 (6)	1.311 (7)	1.319 (7)	1.322 (6)
C(3)-F(5)	1.328 (6)	1.330 (7)	1.327 (6)	1.316 (6)
C(3)-F(6)	1.323 (6)	1.305 (6)	1.315 (7)	1.309 (6)
C(1)-N(1)	1.492 (6)	1.476 (6)	1.472 (6)	1.460 (6)
N(1)-C(6)	1.351 (7)	1.363 (7)	1.345 (7)	1.352 (7)
N(1)-N(2)	1.370 (5)	1.361 (5)	1.355 (5)	1.370 (5)
N(2)-C(4)	1.330 (6)	1.307 (6)	1.326 (6)	1.321 (7)
C(4)-C(5)	1.392 (8)	1.404 (8)	1.376 (9)	1.387 (8)
C(5)-C(6)	1.348 (8)	1.336 (9)	1.339 (9)	1.348 (9)
C(4)-H(1)	1.09 (4)	1.08 (4)	1.01 (4)	1.03 (5)
C(5)-H(2)	0.98 (6)	1.02 (5)	0.93 (4)	0.97 (6)
C(6)-H(3)	0.95 (4)	1.05 (6)	1.02 (4)	1.03 (5)



**Figure 3.** View of ligand I of the thorium compound. The thermal ellipsoids are scaled to include 30% probability. The size of the hydrogen atoms is arbitrary. In Tables II and III the next larger serial numbers of atoms are assigned in the same sequence to ligand II, then III, then IV. The distances (in Å) listed by each bond are averages for the four ligands for thorium (upper values) and for uranium (lower values). The standard deviation of the mean in each case is derived from the scatter of the individual values.

The eight hfapz molecules of the two complexes have very similar dimensions, and averages for the two crystals are listed in Figure 3. The values for the pyrazole ring are little different from those reported by Berthou, Elguero, and Rerat<sup>15</sup> for unsubstituted pyrazole. The atoms of these rings are accurately planar, with a maximum deviation of 0.01 Å, and the carbon and oxygen atoms of the chelate ring in the same ligand come within 0.07 Å of the same plane, on the average, and within 0.12 Å in the extreme case.<sup>6</sup> The five atoms of each chelate ring are less precisely planar, with the distance of the actinide ion from the mean plane of the other atoms ranging from 0.00 to 0.27 Å.

As is to be expected, the bonds of the trifluoromethyl groups are nearly *staggered* with respect to the bonds at atom C(1), Figure 3. The torsion angles for rotation around the C-C bonds, for the 16 examples, range from 0 to 13° with a mean of 4° from exactly *staggered* positions. The fluorine atoms have the largest amplitudes of anisotropic thermal motion in

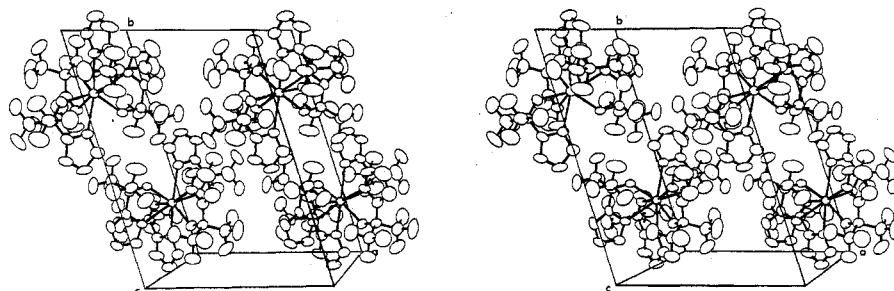


Figure 4. Stereoscopic view (for the thorium crystal) showing the unit cell and molecular packing. Hydrogen atoms are omitted.

Table VII. Bond Angles (deg) and Standard Deviations for the Uranium Compound

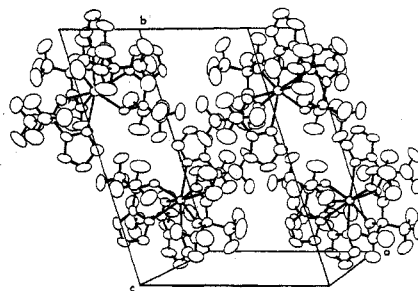
	Ligand I	Ligand II	Ligand III	Ligand IV
O(1)-U-N(2)	63.5 (1)	63.4 (1)	62.8 (1)	62.7 (1)
U-O(1)-C(1)	133.2 (2)	133.7 (3)	134.7 (2)	134.8 (2)
O(1)-C(1)-N(1)	110.2 (4)	110.7 (4)	109.7 (4)	109.5 (4)
C(1)-N(1)-N(2)	114.6 (4)	116.0 (4)	116.3 (4)	117.1 (4)
N(1)-N(2)-U	117.2 (2)	116.2 (3)	116.0 (2)	115.9 (2)
N(1)-N(2)-C(4)	103.5 (5)	105.8 (5)	104.6 (5)	104.7 (5)
N(2)-C(4)-C(5)	113.1 (5)	111.1 (6)	111.6 (6)	112.5 (6)
C(4)-C(5)-C(6)	103.9 (6)	105.4 (7)	105.2 (6)	104.1 (7)
C(5)-C(6)-N(1)	108.8 (5)	107.9 (7)	108.2 (6)	109.2 (6)
C(6)-N(1)-N(2)	110.6 (5)	109.9 (6)	110.3 (5)	109.5 (5)
O(1)-C(1)-C(2)	110.3 (4)	110.0 (5)	109.6 (4)	109.9 (4)
O(1)-C(1)-C(3)	110.1 (4)	110.2 (5)	110.4 (4)	110.2 (4)
N(1)-C(1)-C(2)	106.4 (4)	107.3 (5)	107.2 (4)	107.7 (4)
N(1)-C(1)-C(3)	108.8 (4)	108.1 (5)	107.8 (4)	108.0 (4)
C(2)-C(1)-C(3)	110.3 (4)	110.5 (6)	112.2 (5)	111.4 (5)
C(1)-C(2)-F(1)	113.3 (5)	113.1 (5)	115.1 (5)	113.7 (5)
C(1)-C(2)-F(2)	110.7 (5)	108.2 (5)	110.3 (5)	111.3 (5)
C(1)-C(2)-F(3)	111.2 (5)	111.6 (5)	109.8 (5)	111.0 (5)
F(1)-C(2)-F(2)	107.4 (5)	107.0 (5)	107.8 (5)	108.0 (4)
F(1)-C(2)-F(3)	106.1 (4)	108.2 (5)	107.4 (5)	106.1 (4)
F(2)-C(2)-F(3)	108.0 (4)	108.4 (5)	106.0 (4)	106.4 (4)
C(1)-C(3)-F(4)	111.2 (5)	110.2 (5)	110.4 (5)	109.9 (5)
C(1)-C(3)-F(5)	109.7 (4)	108.0 (5)	109.0 (5)	110.0 (5)
C(1)-C(3)-F(6)	114.4 (5)	114.5 (5)	113.9 (5)	113.7 (4)
F(4)-C(3)-F(5)	106.8 (4)	107.8 (5)	106.4 (4)	107.1 (4)
F(4)-C(3)-F(6)	108.3 (4)	109.4 (5)	108.6 (5)	107.8 (4)
F(5)-C(3)-F(6)	106.1 (4)	106.7 (4)	108.3 (4)	108.1 (4)

these crystals, and the directions of maximum amplitude correspond to torsional motion of the groups around these C-C bonds. The mean C-F bond length for both structures is 1.32 (1) Å (uncorrected) and 1.36 (1) Å after correction for thermal motion according to the riding model.<sup>16</sup> These values may be compared with an average of 1.334 (4) Å reported for some other polyfluoro paraffins.<sup>17</sup>

Figure 4 illustrates the arrangement of the molecules in the unit cell. Each molecule has 12 nearest neighbors for which, in the uranium case, the U-U distances are 8.98, 9.19, 10.45, 11.00 (twice), 11.05, 11.18, 11.24, 11.30 (twice), and 12.63 (twice) Å. The packing resembles the cubic closest packing of spheres, described by a pseudocell given by the matrix

$$\begin{bmatrix} 1 & 1/2 & 3/2 \\ 1 & 1/2 & -1/2 \\ 1 & -1/2 & 1/2 \end{bmatrix}$$

The dimensions of this cell, which contains four molecules, are  $a = 16.74$  Å,  $b = 14.25$  Å,  $c = 15.50$  Å,  $\alpha = 81.19^\circ$ ,  $\beta = 76.89^\circ$ , and  $\gamma = 90.08^\circ$ . A more precise description of the packing, which considers only the first ten neighbors to be



nearest neighbors, is given by the body-centered tetragonal structure described by Zachariasen<sup>18</sup> for protactinium metal. The corresponding pseudocell, containing two molecules and given by the matrix

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 1/2 & -1/2 \\ 0 & 1/2 & 1/2 \end{bmatrix}$$

has dimensions  $a = 12.63$  Å,  $b = 14.25$  Å,  $c = 10.03$  Å,  $\alpha = 96.86^\circ$ ,  $\beta = 85.47^\circ$ , and  $\gamma = 84.66^\circ$ . Neither of these cells is a true cell because the fact that there are two orientations of molecules requires a doubling of axes for strict periodicity. The molecular packing involves only weak forces which permit the molecules to sublime at  $140^\circ$  under vacuum.<sup>3</sup>

**Acknowledgment.** We thank Dr. D. G. Karraker for providing the compounds, Dr. G. Chapuis and Dr. L. K. Templeton for help with the absorption correction, and Mrs. H. W. Ruben for assistance with the calculations.

**Registry No.** Th(C<sub>6</sub>H<sub>3</sub>ON<sub>2</sub>F<sub>6</sub>)<sub>4</sub>, 12098-83-8; U(C<sub>6</sub>H<sub>3</sub>ON<sub>2</sub>F<sub>6</sub>)<sub>4</sub>, 40904-28-7.

**Supplementary Material Available:** Listings of thermal parameters, deviations of atoms from various least-squares planes, and structure factor amplitudes for each of these crystals (46 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) Work done in part under the auspices of the U.S. Energy Research and Development Authority.
- (2) W. Mahler, U.S. Patent 3 265 705 (Aug 9, 1966), assigned to E. I. du Pont de Nemours and Co., Inc.
- (3) W. Andruschow and D. G. Karraker, *Inorg. Chem.*, **12**, 2194 (1973).
- (4) L. K. Templeton and D. H. Templeton, Abstracts, American Crystallographic Association Proceedings, Series 2, Vol. 1, 1973, p 143.
- (5) G. Chapuis, D. H. Templeton, K. W. Volz, and A. Zalkin, Abstracts, American Crystallographic Association Proceedings, Series 2, Vol. 1, 1973, p 154.
- (6) Supplementary material.
- (7) The function minimized is  $\sum w|\Delta F|^2$ .
- (8) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
- (9) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18**, 104 (1965).
- (10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (12) A. J. Olson, Ph.D. Thesis, University of California, Berkeley, Calif., 1975.
- (13) C. K. Johnson, "ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
- (14) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
- (15) J. Berthou, J. Elguero, and C. Rerat, *Acta Crystallogr., Sect. B*, **26**, 1880 (1970).
- (16) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).
- (17) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions", Special Publication No. 11, Chemical Society, London, 1958, p S15.
- (18) W. H. Zachariasen, *Acta Crystallogr.*, **5**, 19 (1952).