

Structure of Tris(cyclopentadienyl)fluorouranium(IV), $(C_5H_5)_3UF$

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Abstract: The single-crystal X-ray structure of tris(cyclopentadienyl)fluorouranium(IV), $(C_5H_5)_3UF$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The structure is rhombohedral, $R\bar{3}m$, with hexagonal dimensions $a = 13.698$ (4) and $c = 5.980$ (2) Å, and contains Cp_3UF monomers having C_{3v} symmetry. The uranium and fluorine atoms lie on the crystallographic threefold axis. Two uranium atoms are separated by the length of the c axis (5.98 Å) with a fluorine atom located very asymmetrically between them, at the short U-F bond distance of 2.11 Å and the intermolecular F-U distance of 3.87 Å. The three symmetry-equivalent cyclopentadienyl rings are disordered across mirror planes and comprise, with the fluorine atom, a flattened tetrahedral arrangement with a F-U-Cp centroid angle of 99.7° and a centroid-U-centroid angle of 117.2°. Suspected dimer formation via uranium-fluorine-uranium bridging was not confirmed. However, the Cp rings are tipped toward the fluorine in the adjacent molecule at a distance appropriate for hydrogen bonding. The refinement model included hydrogens. The average C-C and U-C distances are 1.41 and 2.74 Å, respectively; the U-Cp (centroid) distance is 2.46 Å.

Tris(cyclopentadienyl)fluorouranium(IV), Cp_3UF ($Cp = C_5H_5$), is one of a class of organometallic compounds which is common with the d transition elements but is still relatively rare in the case of actinides even though Cp_3UCl was first reported in 1956.² (See also ref 3, 4, and 5.) More recently U(IV) compounds of the type Cp_3UR , containing σ -bonded alkyl and aryl groups, have been made.⁶

Cp_3UF was apparently first prepared⁷ in 1965. In 1970 workers at Karlsruhe studied the four halides, Cp_3UX ($X = F, Cl, Br, I$), and reported that only Cp_3UF has unusual properties.^{8a} In benzene solution, Cp_3UF is associated (dimeric), has a smaller dipole moment than would be expected in comparison with Cp_3UCl , and generally behaves as if it were fluoride bridged.^{8a} A propensity toward fluoride bridging was further suggested by 1:1 adduct formation between Cp_3UF and $Yb(Cp)_3$.^{8b} The vapor, however, is monomeric,^{8a,c} and magnetic data were interpreted as suggesting less marked association in the solid than in solution. The single-crystal X-ray structures of Cp_3UCl ,⁹ and of the benzyl-substituted Cp derivative,¹⁰ have been reported, but no comparable information was available on the fluoride. We therefore undertook a single-crystal study of Cp_3UF .

Experimental Section

The bulk material was prepared by the method of Laubereau,⁷ and a small yield of crystalline product was obtained by slow sublimation at 180°, in vacuo. Fragile blunt needles of this air- and moisture-sensitive compound were separated from the sublimed material and sealed in Pyrex capillaries under argon. Crystals were immobilized using Kel-F fluorocarbon grease. X-Ray powder diffraction patterns obtained from the single crystals and of the bulk material were identical. Crystals are pleochroic and give parallel extinction. Precession and Weissenberg photographs showed rhombohedral extinctions and $3m$ symmetry, indicating that the space group is $R\bar{3}m$, $R3m$, or $R32$. The hexagonal cell constants as determined by least-squares refinement to the setting angles of 12 high order reflections (as measured on a FACS-I, Mo $K\alpha_1$, λ 0.70930 Å) are $a = 13.698$ (4) and $c = 5.980$ (2) Å. The corresponding rhombohedral constants are $a = 8.156$ Å and $\alpha = 114.23^\circ$. The formula weight of Cp_3UF is 452.3, $d_x = 2.32$ g/cm³, giving an absorption coefficient of 187.2 cm⁻¹ for molybdenum radiation. The structure is characterized by weak forces perpendicular to the c axis and cleaves so readily, parallel to the U-F bonds along c , that great care was needed in manipulation of the crystals. Attempts to shorten needles caused splintering. Most crystals were rejected as unsuitable and it was necessary to accept crystals for data collection that were larger than optimum.

Two crystals were used. Crystal I, a long needle, had dimensions $\approx 0.17 \times 0.17 \times 0.6$ mm; crystal II had dimensions $\approx 0.14 \times 0.16 \times 0.36$. Well-developed faces were present and identified as $[1\bar{2}0, 120]$. ω -Scans on crystal I (mounted on the c axis) showed no splitting so data were taken to $2\theta \leq 70^\circ$ using 2θ scans. A complete data set ($2\theta \leq 70^\circ$) for reflections of the type $hkil$ were obtained, and data were obtained for $hkil$ reflections to $2\theta \leq 20^\circ$, in order to test the enantiomorph, in case the correct space group proved to be polar. Crystal II showed splitting of spots: a unique set of data was taken to $2\theta \leq 50^\circ$ only with ω -scans. Structures refined on the ω data were in essential agreement with those obtained from the 2θ data with somewhat larger standard errors, and only the results of refinements on the 2θ data are presented here. Data were collected on crystal II only after the structure had been solved using data from crystal I. This was done to provide an independent check on the unusually short U-F distance found on refinement using data set I. Data were collected using a Picker FACS-I system equipped with a graphite monochromator. Periodic examination of two standard reflections indicated no appreciable deterioration of the sample during data collection; on long standing substantial deterioration occurred.

The Patterson function could be interpreted simply (if the correct space group was assumed to be $R\bar{3}m$) and the structure was outlined directly from it. The U-F bond lies on the crystallographic threefold axis, and the three Cp rings are arranged pseudo-tetrahedrally.

Equivalent reflections related by $3m$ were averaged, yielding 763 unique reflections which were used in the refinements. Refinements of the structure where carbon positional parameters were refined independently resulted in Cp ring distances and angles which varied over an unacceptable range. Subsequent refinements were carried out using rigid body constraints for the Cp ring. In addition to the usual translational and rotational degrees of freedom, the internal symmetry coordinate which is totally symmetric (A_1) in the point group D_{3h} was refined using Strouse's method¹¹ (i.e., the C-H distance was fixed at 1.0 Å and the average C-C distance was allowed to vary). Four structural models were refined. (a) The structure was refined in the space group $R\bar{3}$. (b) Refinement in $R\bar{3}m$ with one carbon atom on the mirror plane (i.e., an ordered model). (c) A disordered model was used in which two Cp rings (each having a carbon atom on the mirror) related to each other by a 180° rotation about the Cp plane normal. In this refinement a population factor was included for each Cp ring (constrained so that the sum of the population factors was 1.0) and the same "size" parameter was applied to both rings. The ring for which the apical carbon atom was pointing toward the fluorine atom in the next molecule was favored by a population parameter of 67%. (d) The rotation angle about the Cp normal was allowed to refine so that the "disorder" was described by two half-weight Cp rings related by the crystallographic mirror plane.

Table I. Fractional Coordinates and Thermal Parameters (all $\times 10^4$)^a

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	0	0	5000	38 (0.2)	38 (0)	273 (2)	38 (0)	0	0
				<i>B</i> ^b					
F	0	0	1479 (20)	4.8 (2)					
C ₁	-1236 (2)	627 (12)	7534 (19)	3.9 (2)		(population factor 0.5) mirror related			
C ₂	-1901 (2)	153 (7)	5610 (6)	3.3 (2)		(population factor 0.5) mirror related			
C ₃	-1351 (1)	881 (4)	3800 (6)	4.7 (3)		(population factor 0.5) mirror related			
C ₄	-277 (7)	1648 (5)	6914 (26)	4.8 (3)		(population factor 0.5) mirror related			
C ₅	-348 (7)	1805 (5)	4606 (20)	4.5 (3)		(population factor 0.5) mirror related			
H ₁	-1415 (2)	296 (18)	9072 (14)	9.3 (4)		(population factor 0.5) mirror related			
H ₂	-2633 (2)	-572 (6)	5541 (1)	9.3 (4)		(population factor 0.5) mirror related			
H ₃	-1626 (1)	763 (11)	2220 (7)	9.3 (4)		(population factor 0.5) mirror related			
H ₄	345 (8)	2168 (9)	7933 (30)	9.3 (4)		(population factor 0.5) mirror related			
H ₅	215 (7)	2458 (9)	3699 (26)	9.3 (4)		(population factor 0.5) mirror related			

^a Thermal parameters are defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. Extinction factor, $g = 5.9 \times 10^{-6}$. ^b *B*'s are not multiplied by 10^4 .

Of the four refinements, both (a) and (b) resulted in a distinctly poorer fit to the data than did (c) or (d). Refinements c and d are indistinguishable in terms of comparisons between goodness of fit parameters. Consideration of the H...F distances makes refinement d slightly more appealing than (c). Refinement c results in a distance of 2.40 Å between the hydrogen atom on the mirror plane and the fluorine atom in the adjacent Cp₃UF molecule while the corresponding distance for model d has the more acceptable value of 2.60 Å. The actual structure may contain a Cp ring which undergoes hindered rotation.

With the exception of the rigid body constraints all details of the intensity measurements and refinements were carried out in the usual manner.¹² Neutral scattering factors were used for H, C, and F atoms and the scattering factor used for uranium was U⁴⁺ with the appropriate dispersion terms.¹³ Refinement of the two possible enantiomorphs resulted in an *R* factor of 3.04% for the model reported here and 3.7% for the other, without producing substantial changes in the U-F distances, 2.106 (12) and 2.111 (16) Å, respectively.

Models for which the H atoms were included exhibited a significant improvement in the goodness of fit parameters. The final unweighted *R* value is 3.04%. Final parameters are reported in Table I. Table II compares observed and calculated intensities and Table III contains some distances and angles. Table II will appear only in the microfilm edition; see paragraph at end of paper regarding supplementary material.

Discussion of the Structure

The value of the U-F distance found is 2.11 (1) Å. In a recent accurate study¹⁰ of (BzI Cp)₃UCl the U-Cl bond distance is found to be 2.627 (2) Å, significantly longer than the U-Cl distance reported⁹ (though known less accurately) for Cp₃UCl = 2.56 (1.6) Å. The ionic radii of F⁻ = 1.33 Å, and of Cl⁻ = 1.81 Å yield a difference of 0.48 Å;¹⁴ the difference in covalent radii (0.99 - 0.64) is only 0.35 Å.¹⁵ Using the ionic radii difference, 0.48 Å, the U-F bond distance in Cp₃UF can be approximated as 2.08 Å from the U-Cl distance in Cp₃UCl, 2.56 Å. The U-Cl distance of 2.63 Å in (BzI Cp)₃UCl would give 2.15 Å as a larger estimate for the U-F bond length. The point to be made is that the U-F bond in Cp₃UF should be substantially longer than the 2.11 Å we observe, were the fluorine actually bonded to two uranium atoms in the structure. While there are no U(IV) fluorides connected by single bridging fluorides, tetragonal UF₅ contains linear chains along the *c* axis in which the U-U distance is 4.46 Å, connected by individual shared fluorines at U-F bond distances of 2.23 Å (ref 16). In Cp₃UF the U-U distance is 5.98 Å. We conclude that the U-F distance of 2.11 Å, and the F-U distance of 3.87 Å are so disparate that it can safely be said that the structure is monomeric in nature and that strong intermolecular association through U-F bridges is not supported by this structural study.

Although we find absent *strong* association of Cp₃UF via

Table III. Some Bond Distances (Å) and Angles (deg) in Cp₃UF

F-U	2.106 (12)
F-(U) nonbonded	3.87
F-C ₃	3.01
U-C ₁	2.71 (1)
U-C ₂	2.74 (1)
U-C ₃	2.76 (1)
U-C ₄	2.72 (1)
U-C ₅	2.75 (1)
	(av U-C = 2.74)
U-Cp ring center	2.456 (5)
α^a	20.4 (3)
β^b	11.1 (5)
C-H	1.00 (fixed)
H-F	2.60 (2)
C-C	1.408 (7)
F-U-Cp center	99.7 (2)
Cp center-U-Cp center	117.2 (1)

^a α is the angle of rotation about the ring normal (from the crystallographic mirror plane). ^b β is the angle of rotation about the vector perpendicular to both the α axis and *z*.

Table IV. Some Distances (Å) and Angles (deg) in Cp₃UF and Comparable Compounds

(BzI Cp) ₃ UCl ¹⁰	Cl-U-Cp center	100
Cp ₃ UCl ⁹	Cl-U-Cp center	101
Cp ₃ UF	F-U-Cp center	99.7
(BzI Cp) ₃ UCl ¹⁰	Cp center-U-Cp center	117.1
Cp ₃ UCl ⁹	Cp center-U-Cp center	116.7
Cp ₃ UF	Cp center-U-Cp center	117.2
(BzI Cp) ₃ UCl ¹⁰	U-C av	2.734
Cp ₃ UCl ⁹	U-C (av)	2.74
Cp ₃ UF	U-C (av)	2.74

U-F-U bridging which might have been suspected based on its dimeric behavior in benzene solution, hydrogen bonding distances from Cp rings on one molecule to the next fluorine in the chain are 2.6 Å, and likely contribute considerably to the packing forces. Indeed, the point can be made that the Cp rings need to be disordered off the mirror to provide a reasonable hydrogen bonding distance; if they were not (and the observed U-U distance were maintained), the H-F distance would be shortened from 2.6 to 2.4 Å. Thus a cooperative stacking arrangement is necessary. The H-F distance could be accommodated without disorder if the U-U distance (*c* axis) were longer. Opposing this lengthening of the U-U distance may be laid to some attractive force, even at 3.9 Å, between the uranium in one molecule and the next fluorine in the chain, supplementing the hydrogen bonding forces just mentioned.

Distances and angles in Cp₃UF are compared in Table IV with those observed in Cp₃UCl and (BzI Cp)₃UCl.

In the cyclooctatetraene sandwich structures (C₈H₈)₂U,

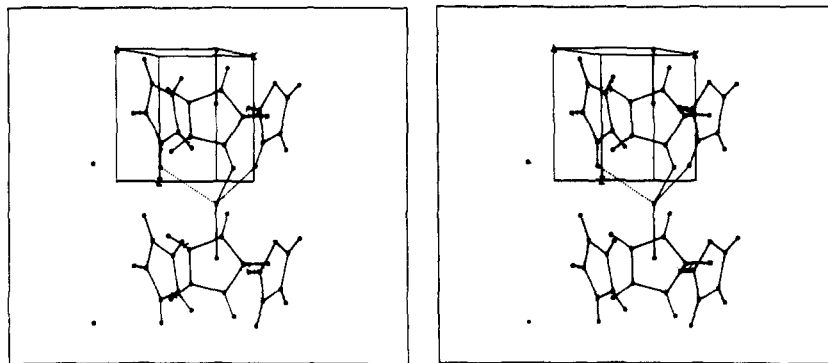


Figure 1. Stereoview of the structure of Cp_3UF normal to the xz plane.

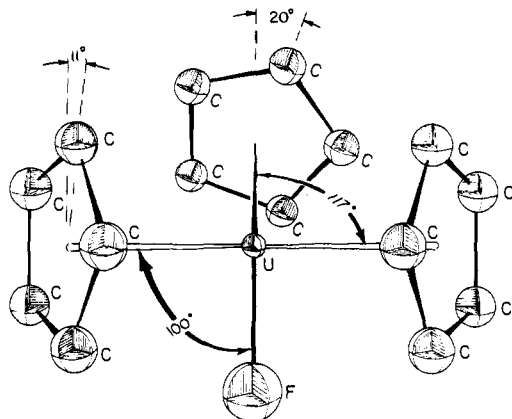


Figure 2. The molecular structure of tris(cyclopentadienyl)uranium fluoride.

and $[(\text{CH}_3)_4\text{C}_8\text{H}_4]_2\text{U}$, bond distances for U-C are respectively 2.65 and 2.66 Å (ref 17 and 18). For Cp and substituted-Cp compounds, U-C bond lengths are substantially longer. Known examples are (references in parentheses): $(\text{C}_5\text{H}_5)_3\text{UC}\equiv\text{CC}_6\text{H}_5$, 2.68 Å (19); $(\text{C}_6\text{H}_5\text{CH}_2\text{C}_3\text{H}_4)_3\text{UCl}$, 2.73 Å (10); $(\text{C}_5\text{H}_5)_3\text{UCl}$, 2.74 Å (9); $(\text{C}_9\text{H}_7)_3\text{UCl}$, 2.79 Å (20); $(\text{C}_5\text{H}_5)_4\text{U}$, 2.81 Å (21). The average U-C distance of 2.74 Å in Cp_3UF is comparable with the U-C distances of 2.73 Å in $(\text{BzCp})_3\text{UCl}$ or 2.74 Å in Cp_3UCl .

The U-F bond length of 2.11 Å is the shortest U(IV)-fluorine bond yet observed, being ~ 0.15 Å shorter than found in a variety of U(IV) fluorides.²² In the latter, high fluorine coordination numbers (8-9) are involved. Octahedral fluorine coordination is found in UF_6 and in CsUF_6 . With the smaller coordination (and higher charge), U-F distances of 2.05 and 2.047 Å, respectively,^{23,24} are found. In Cp_3UF the F-C distances are van der Waals distances or longer and there are no F-F repulsions: the unprecedented U(IV)-F distance of 2.11 Å is a consequence.

A general view of the structure is given in Figure 1, indicating hydrogen bonds by dotted lines. Figure 2 displays a projection of the molecular unit.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edi-

tion of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-4258.

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