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CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLOPENTADIENYLTETRAHYDROFURANURANIUM(III), $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$

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Summary

Tricyclopentadienyltetrahydrofuranuranium(III), $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$, crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a 8.248(3), b 24.322(17), c 8.357(4) Å, β 101.29(5)°, V 1644.0 Å^3 and ρ(calc) 2.04 g cm^{-1} for $Z = 4$ and mol.wt. 595.0. Diffraction data (Mo-K_α, 2θ(max) 45°) were collected on an Enraf–Nonius CAD4 diffractometer and the structure was refined to $R_w(F)$ 4.7% for those 1530 reflections having $I > 2\sigma(I)$. The molecule consists of a distorted tetrahedral arrangement of THF and $(\eta^5\text{-}C_5H_5)$ ligands with Cp–U–Cp angles in the range 110.4–122.4° and Cp–U–O angles between 90.2 and 106.0°. Individual uranium–carbon distances range from 2.76(2) to 2.82(2) Å and average 2.79[1] Å. The uranium–oxygen distance of 2.551(10) Å suggests a 10-coordinate U^{3+} radius of 1.20 Å in this class of compounds.

Introduction

The organometallic chemistry of uranium has received considerable attention in recent years [1], and while the primary emphasis has been on the tetravalent state, there has also been renewed interest in the organometallic chemistry of trivalent uranium. Yet only a few organometallic uranium(III) complexes have been characterized by single crystal X-ray diffraction. The earliest structural example of this type was $U(\eta^6\text{-}C_6H_6)(AlCl_4)_3$ [2], while more recently, investigations utilizing substituted cyclopentadienyl ligands have resulted in structural reports for tris(indenyluranium(III)) [3] and for two pentamethylcyclopentadienyl complexes, $\{U[\eta^5\text{-}(CH_3)_5C_5]_2(\mu\text{-}Cl)\}_3$ [4] and $U[\eta^5\text{-}(CH_3)_5C_5]_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]H$ [5]. A preliminary report of the structure of a related borohydride uranium(III) complex, $U(BH_4)_3$(THF)(MTHFE) where MTHFE = methyltetrahydrofurfuryl ether, has also been presented [6].

One of the first reports describing organometallic uranium(III) chemistry presented the synthesis of UCp_3 and its Lewis base adducts, among which was included $UCp_3(THF)$ [7]. While improved syntheses of $UCp_3(THF)$ have been reported [8], structural data have not previously been available due to difficulties experienced in obtaining single crystals suitable for X-ray diffraction studies.

Suitable crystals of $UCp_3(THF)$ were recently obtained in our laboratories and we describe herein the crystal and molecular structure of this complex including a comparison of observed structural parameters with those of related organometallic uranium(III) complexes.

Experimental

Crystals of the title complex were obtained from the reaction of one mmol of crude $U[N(SiEt_3)_2]Cl_2$ [9] with two equivalents of NaCp in THF, followed by filtration, concentration to 15 ml, and cooling to −10°C for several days. A thin plate-like crystal of approximate dimensions 0.03 × 0.12 × 0.36 mm was sealed, using epoxy, into a thin-walled glass capillary under inert atmospheric conditions. After mounting on the goniostat of the Enraf–Nonius CAD4 diffractometer, the crystal was kept at −48(2)°C with use of the Nonius Universal Low Temperature cooling system. Crystal parameters and experimental data are summarized in Table 1.

The structure was found to be isomorphous with that of $(\eta^5\text{-}C_5H_5)_3Gd \cdot OC_4H_8$ [10,11]. Full-matrix least-squares refinement minimizing the function $\Sigma w(\Delta F)^2$ led to $R(F)$ 5.1%, $R_w(F)$ 4.7% and goodness of fit 2.45. Only those data for which $I > 2.0\sigma(I)$ were included. Attempts at refining anisotropic thermal parameters for the cyclopentadienyl carbon atoms were not wholly successful and were abandoned. The final model included an isotropic correction for the effects of secondary extinction [12]. No attempt was made to include the contribution of hydrogen atoms.

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$

(A) Crystal parameters at − 48(2)°C	
Crystal System: Monoclinic	Space Group: $P2_1/n$
a 8.248(3) Å	V 1644.0 Å^3
b 24.322(17) Å	mol wt 595.0
c 8.357(4) Å	ρ(calc) 2.04 g cm^{-1}
β 101.29(5)°	$Z = 4$

(B) Data collection

Diffractometer: Enraf–Nonius CAD-4
Radiation: Graphite-monochromatized Mo-K_α (λ 0.710690 Å)
2θ Range: 3.5–45°
Reflections measured: $+h +k \pm l$
scan type: θ(crystal)–2θ(counter)
scan range: $2.0 + 0.347 \tan\theta$
scan speed: variable, 1.8° min^{-1}–10.0° min^{-1}
Reflections collected: 2715 total
yielding 2136 independent;
1530 with $I > 2.0\sigma(I)$
absorption coefficient: 93.6 cm^{-1}
crystal faces; distance from origin, mm: {100}; 0.059 {010}; 0.018 {001}; 0.18

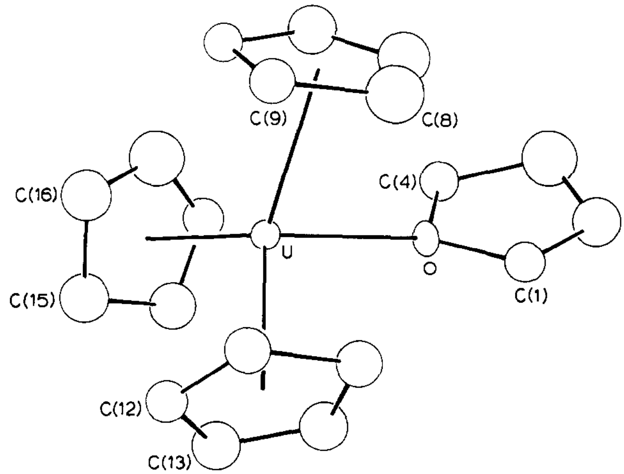

Fig. 1. Atomic labeling scheme in the $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$ molecule (ORTEPII diagram).

The Los Alamos Crystal Structure Solution Package, due principally to A.C. Larson, was used for all computations [13]. Analytical neutral atom scattering factors [14a], modified by both real and imaginary components of anomalous dispersion [14b] were used. Final positional and thermal parameters are listed in Table 2.

Figure 1 shows the atomic labeling scheme in the $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$ molecule.

Discussion

Important interatomic distances and angles, with their associated estimated standard deviations, are tabulated in Table 3. The structure of $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$ is a member of the isostructural series $(\eta^5\text{-}C_5H_5)M \cdot OC_4H_8$ (M = Y [11], Gd [10], U, La [11]). The gross molecular configuration of these species is related closely to such other $(\eta^5\text{-}C_5H_5)_3M(\eta^1\text{-ligand})$ complexes as $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ [15], $(\eta^5\text{-}C_5H_5)_3U[CH_3C(CH_2)_2]$ [16] and $(\eta^5\text{-}C_5H_5)_3U[C{\equiv}CH]$ [17]. The geometry about the uranium atom is best described as distorted tetrahedral, with Cp–U–Cp [18] angles ranging from 110.4 to 122.4°. The corresponding Cp–U–O(THF) angles are smaller, falling in the range 90.2–106.0°.

The uranium–oxygen(THF) linkage in the $(\eta^5\text{-}C_5H_5)_3U \cdot OC_4H_8$ molecule is 2.551(10) Å which compares well with the value of 2.55(3) Å we have observed in $U(BH_4)_3$(THF)(MTHFE) [6]. Although comparison with higher oxidation state species is less meaningful, we note that known U^{IV}– and U^{VI}–O(THF) bond lengths include U–O 2.347(14) Å in seven-coordinate pentagonal bipyramidal $UO_2[(CF_3CO)_2CH]_2 \cdot$ THF [19], U–O (average) 2.450(8) Å in eight-coordinate $[\eta^1\text{-}C_5(CH_3)_5]UCl_3 \cdot$ 2THF [20] and the single unique U–O distance of 2.42(2) Å in $UO_2(NO_3)_2 \cdot$ 2THF [21]. We have also determined U^{VI}– and U^{V}–O(THF) linkages of 2.42(2) and 2.53(2) Å, respectively, in a mixed-valent uranium phenoxide species [22]. While the THF ligand in the present molecule maintains its "puckered" nature, its mean least-squares plane [23] subtends an angle of 157° with the U–O vector.

TABLE 2

FINAL POSITIONAL AND THERMAL PARAMETERS

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U(1)[a]	0.91759(7)	0.14460(3)	0.05296(7)	2.067(33)	2.575(36)	2.041(34)	−0.139(82)	0.738(40)	−0.332(95)
O(1)	1.1104(12)	0.0816(5)	0.2473(12)	3.46(61)	3.56(78)	1.91(59)	0.78(112)	−0.72(95)	0.15(116)
Atom	X	Y	Z	B	Atom	X	Y	Z	B
C(1)	1.0907(23)	0.0700(9)	0.4142(23)	4.12(42)	C(11)	0.6109(22)	0.1644(8)	0.1280(24)	3.81(42)
C(2)	1.2594(28)	0.0486(11)	0.5064(30)	6.40(60)	C(12)	0.5765(21)	0.1356(8)	−0.0124(21)	3.58(39)
C(3)	1.3668(33)	0.0683(13)	0.4141(34)	8.11(73)	C(13)	0.6291(26)	0.0794(10)	0.0054(28)	5.46(53)
C(4)	1.2865(23)	0.0723(10)	0.2299(24)	4.39(45)	C(14)	0.6957(25)	0.0736(11)	0.1624(28)	5.46(52)
C(5)	1.0183(21)	0.2527(8)	0.0373(21)	3.23(37)	C(15)	0.8461(28)	0.1146(11)	−0.2710(29)	5.64(54)
C(6)	1.1649(27)	0.2227(10)	0.1198(29)	5.78(55)	C(16)	0.9654(27)	0.0678(11)	−0.1889(28)	5.83(54)
C(7)	1.1359(29)	0.2090(11)	0.2695(31)	6.30(61)	C(17)	1.1085(25)	0.0946(10)	−0.1532(25)	4.65(47)
C(8)	0.9817(31)	0.2256(12)	0.2999(32)	7.19(66)	C(18)	1.1061(35)	0.1459(14)	−0.1972(34)	8.02(68)
C(9)	0.9087(21)	0.2554(8)	0.1476(23)	3.62(40)	C(19)	0.9627(30)	0.1595(11)	−0.2633(30)	6.17(60)
C(10)	0.6921(23)	0.1260(9)	0.2528(25)	4.16(45)					

[a] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. U_{ij}'s in the table are multiplied by 10^2.

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å), AND ANGLES (deg) WITH e.s.d.'s FOR $(\eta^5\text{-}C_5H_5)_3U\cdot OC_4H_8$

(A) Uranium–carbon distances			
U–C(5)	2.77(2)	U–C(14)	2.80(2)
U–C(6)	2.76(2)	U–C(15)	2.75(2)
U–C(7)	2.77(3)	U–C(16)	2.84(2)
U–C(8)	2.82(3)	U–C(17)	2.83(2)
U–C(9)	2.81(2)	U–C(18)	2.84(3)
U–C(10)	2.77(2)	U–C(19)	2.76(2)
U–C(11)	2.77(2)	U–Cp(1)	2.51
U–C(12)	2.77(2)	U–Cp(2)	2.52
U–C(13)	2.82(2)	U–Cp(3)	2.54
(B) Uranium–oxygen distance			
U–O	2.551(10)		
(C) Selected angles about the uranium atom			
Cp(1)–U–O	95.9	Cp(1)–U–Cp(2)	118.5
Cp(2)–U–O	101.2	Cp(1)–U–Cp(3)	116.0
Cp(3)–U–O	99.7	Cp(2)–U–Cp(3)	118.3

The THF ligand is symmetrically disposed about the U–O bond, with U–O–C(1) 123.4(9)° and U–O–C(4) 121.4(10)°. Distances and angles within the THF ligand are unexceptional [24].

The observed uranium–oxygen distance suggests a radius for the U^{3+} ion in this class of compounds of about 1.20 Å [based upon r(oxygen) ~ 1.35 Å] [25].

Table 4 presents a comparison of important metrical parameters in $(\eta^5\text{-}C_5H_5)_3M\cdot OC_4H_8$ complexes. Our calculation of the U^{3+} radius indicates that U^{3+} lies between Gd^{3+} and La^{3+} while previous structural compilations indicate that the radii of La^{3+} and U^{3+} should be very nearly the same [26]. We point out that the previous structural results for this series are not consistent with the reported ionic radii for the metal atoms. That is, while Raymond's [27] estimate of 1.64 ± 0.04 Å for Cp results in reasonable estimates for the M–C bond distances in the Y and Gd complexes of 2.72 and 2.75 Å respectively, the La–C distance is predicted to be ca. 0.1 Å longer than the observed distance. Although the present data are not inconsistent with a major deviation from purely ionic bonding, we feel that a definitive statement on this important question should await further structural information.

TABLE 4

COMPARISON OF IMPORTANT BOND LENGTHS (Å) IN $(\eta^5\text{-}C_5H_5)_3M\cdot OC_4H_8$ COMPLEXES

M	M^{3+} radius	M–O	M–C (avg)	M–Cp (avg)	Ref.
Y	1.08 [a]	2.451(4)	2.71(1)	2.448	11
Gd	1.11 [a]	2.494(7)	2.74(1)	2.483	10
U	1.20 [b]	2.551(10)	2.79(1)	2.523	This
	1.19 [c]				work
La	1.27 [a]	2.57(1)	2.82(1)	2.576	11

[a] M^{3+} radii were taken from the compilation of Shannon; see ref. 29. [b] Based upon r(oxygen) ~ 1.35 Å. See text. [c] Based upon $r(C_5H_5)$ ~ 1.60 Å.

The three (η^5-C_5H_5) ligands bond to the uranium atom with equivalent U–Cp distances of 2.51, 2.52 and 2.54 Å. Individual uranium–carbon distances average 2.79[1] Å [28], with a range of 2.76(2)–2.82(2) Å. Similar values were obtained for tris(indenyluranium(III)) [3], in which uranium carbon distances range 2.73–2.85(2) Å, and for two pentamethylcyclopentadienyluranium(III) species, viz., U–C (average) 2.768(11) Å in the eight-coordinate trimeric complex $[U(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Cl)]_3$ [4] and U–C (average) 2.79(3) Å in $U[\eta^5\text{-}(CH_3)_5C_5]_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]H$ [5].

Further structural investigations on U^{III} species, especially borohydride complexes, are currently in progress.

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