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URANIUM(III)THIOPHENE $(CH_3C_5H_4)_3U(SC_4H_8)$

A. Zalkin and J.G. Brennan

April 1985

DISCLAIMER

STRUCTURE OF

TRIS(METHYLCYCLOPENTADIENYL)URANIUM(III)THIOPHENE

$$(CH_3C_5H_4)_3U(SC_4H_8)$$

By Allan Zalkin & John G. Brennan

Materials and Molecular Research Division

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Berkeley, California 94720 USA

Abstract. M_r = 563.57, orthorhombic, Pbca, a = 15.146(5), b = 27.598(8), c = 9.911(4) A, V = 4143(4) A^3, Z = 8, D_x = 1.81 g cm^{-3}, Mo Kα, λ($α_1$) = 0.70930 A, μ = 75.3 cm^{-1}, F(000) = 2152, T = 296 K, R = 0.035 for 1382 reflections (F^2>2σ). The structure consists of uranium centered monomolecular units in which the uranium atom is coordinated to three cyclopentadiene rings and to the sulfur atom of a thiophene molecule. The average U-C distance is 2.81 ± 0.04 A and the U-S distance is 2.986(5) A.

Introduction. The numbers of structurally characterized complexes with U-S bonds are far fewer than those with U-O bonds. Several uranyl thiocarbamate and thiocarboxylate complexes as well as a uranyl disulfide complex have been reported (Perry et al, 1982 and references therein); the structure of a uranyl thioether has also been reported (Baracco et al, 1975). No structurally characterized U(III) sulfur complexes have been reported to date.

As part of a study of the synthesis and characterization of trivalent uranium coordination compounds (Brennan & Zalkin, 1985), we report here the structure of $(CH_3C_5H_4)_3U \cdot SC_4H_8$.

Experimental. Red, air-sensitive needles of the thiophene complex were prepared by adding SC_4H_4 to a toluene solution of $(CH_3C_5H_4)_3U-OC_4H_8$ (Brennan and Andersen, 1985) and crystallizing from ether at 253 K. Crystals were sealed inside quartz capillaries because of their reactivity in the atmosphere, and no measured density is reported for the same reason. Crystal 0.10 x 0.21 x 0.34 mm with 9 faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 14 reflections, $21° < 2\theta < 33°$; analytical absorption correction, range 2.08 to 4.32; max. $(\sin\theta)/\lambda = 0.59$ $Å^{-1}$, h 0 to 17, k 0 to 32, ℓ -11 to 11; three standard reflections, 4% variation in intensities from average, intensities adjusted accordingly; 7028 data, 3642 unique (including 2260, $F^2 < 2\sigma$), $R_{int} = 0.083$; structure solved by Patterson and Fourier methods; refined on F, 217 parameters; non-methyl hydrogen atoms in calculated positions with estimated isotropic thermal parameters, methyl hydrogen atoms not included; anisotropic thermal parameters for non-hydrogen atoms; R = 0.20 for 3642 data, R = 0.035 for 1382 reflections for which $F^2 > 2\sigma$, wR = 0.035, S = 1.05; w = $[\sigma(F)]^{-2}$, p = 0.04 in calc. of $\sigma(F^2)$; max. (shift/σ) =

0.01; no correction for extinction; max. and min. of ΔF synthesis 2.9 and -3.0 e Å^{-3}; atomic f for neutral U, S and C, and spherical bonded H from International Tables (1974); local unpublished programs and ORTEP (Johnson, 1965).

The large R factor (for all the data) reported above is due to a large number of unobserved reflections. The uranium atom dominates the intensities, particularly at the higher diffraction angles, and the coordinates of the uranium atom are such, that with certain indices whole groups of intensities are depleted. For example the uranium atom y parameter is very near to 1/8 which, for this space group, means that the uranium atom contributes very little to reflections of the types (ℓ odd, k=4n) and (ℓ even, k=4n+2) which are a quarter all the reflections. To increase the data-to-parameter ratio, all of the planes within the hkℓ ranges indicated above were collected to a 2θ angle of 50°, resulting in a high proportion of unobserved data. Approximately half of the data occur between 39 and 50° of 2θ, and less than a quarter of these were observed; of the lower-angle half of the data, over half were observed.

Atomic parameters are listed in Table 1.[*]

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[*]Lists of structure factors, anisotropic thermal and H-atom positional parameters, deviations from least-squares planes, distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No.   (** pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The complex $(CH_3C_5H_4)_3U \cdot SC_4H_8$ is monomolecular in the solid state. The uranium atom is coordinated to three cyclopentadienyl groups and to the sulfur atom of the tetrahydrothiophene ligand in a distorted tetrahedral array. The shortest interligand C-C distance is 3.26 A.

The structures of $(CH_3C_5H_4)_3U \cdot SC_4H_8$ and $(C_5H_5)_3U \cdot OC_4H_8$ (Wasserman et al., 1983), are similar. The lack of planarity of the three atoms bonded to the sulfur atom in the thiophene complex and to the oxygen atom in the tetrahydrofuran complex suggests but one lone pair of electrons in the U-S and U-O bonds. The U-S and U-O distances are 2.997(1) and 2.55(1) A respectively.

A comparison of the structures of $(CH_3C_5H_4)_3U \cdot SC_4H_4$ and $(CH_3C_5H_4)_3U \cdot P(CH_3)_3$ (Brennan and Zalkin, 1985), show some geometrical differences. The Cp-U-Cp angles in the thiophene complex average 118±1°, a small 2° distortion from what would be expected for the base free complex, whereas the comparable angles in the trimethylphosphine complex (106.0°, 119.8° and 119.4°) indicate considerable distortion. The thiophene ligand, with its polarizable lone pair of electrons instead of a methyl group, could be sterically less restricting than the trimethylphosphine ligand, thus decreasing ligand-cyclopentadienyl repulsive interactions. The average U-Cp distances in the thiophene and the trimethylphosphine complexes are 2.54(1) A and 2.52(2) A, respectively. The U-S and U-P distances in the two structures are 2.997(1) A and 2.972(6) A, respectively.

The U(III)-S distance reported here (2.997(1) A) is similar to the U(VI)-S distance (2.94(1) A) found in the uranium thioether coordination complex, cis-dichloro-[meso-bis(trans-2-hydroxycyclohexyl) sulphide-OOS]dioxouranium(VI) (Baracco et al., 1975), and the difference in the above

distances is much smaller than expected. For a coordination number of 6, the estimated ionic radius of U(III) is 0.295 A larger than that for U(VI), (Shannon, 1976); and the difference is even larger when the effect of a larger cooordination number of the U(III) complex (10 vs 7) is considered.

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Table 1. Atomic parameters for

Tris(methylcyclopentadienyl)uranium(III)thiophene

$$B_{eq} = \sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j / 3, \ \text{Å}^2.$$

Atom	x	y	z	B_{eq}
U	0.17692(4)	0.12615(2)	0.15991(5)	3.55
S	0.3423(3)	0.13410(17)	-0.0024(5)	5.36
C(1)	0.0793(13)	0.0975(8)	-0.0770(20)	5.20
C(2)	0.1022(17)	0.1462(9)	-0.0953(21)	5.36
C(3)	0.0542(19)	0.1750(8)	-0.0026(25)	7.48
C(4)	0.0063(16)	0.1444(10)	0.0800(26)	7.55
C(5)	0.0212(14)	0.0959(9)	0.0380(23)	6.74
C(6)	0.1072(17)	0.0572(7)	-0.1611(27)	8.46
C(7)	0.1627(14)	0.1871(6)	0.3878(17)	4.46
C(8)	0.2566(17)	0.1790(12)	0.364(3)	6.85
C(9)	0.2858(21)	0.2002(8)	0.2587(26)	5.30
C(10)	0.2186(20)	0.2234(7)	0.1974(22)	4.87
C(11)	0.1402(15)	0.2165(7)	0.2779(22)	5.44
C(12)	0.0995(14)	0.1707(7)	0.5000(22)	6.82
C(13)	0.1408(19)	0.0426(7)	0.3122(28)	6.52
C(14)	0.1626(18)	0.0245(8)	0.1860(25)	6.35
C(15)	0.2513(24)	0.0308(12)	0.153(3)	9.70
C(16)	0.2875(24)	0.0564(8)	0.273(3)	6.60
C(17)	0.2246(24)	0.0623(8)	0.378(3)	5.65
C(18)	0.0531(17)	0.0371(8)	0.3845(26)	9.99
C(19)	0.3594(16)	0.0930(8)	-0.1479(23)	7.85
C(20)	0.3481(18)	0.1257(11)	-0.2701(21)	10.31
C(21)	0.3821(19)	0.1744(11)	-0.2389(27)	9.46
C(22)	0.3443(16)	0.1898(7)	-0.0999(21)	7.55

Table 2. Selected distances and angles

Distances

Atoms		d(A)	Atoms		d(A)
U	- S	2.9865(5)	U	- C(13)	2.809(22)
U	- C(1)	2.886(18)	U	- C(14)	2.824(20)
U	- C(2)	2.826(22)	U	- C(15)	2.863(29)
U	- C(3)	2.806(21)	U	- C(16)	2.789(24)
U	- C(4)	2.750(23)	U	- C(17)	2.880(28)
U	- C(5)	2.779(20)	U	- Cp_1[a]	2.536
U	- C(7)	2.823(15)	U	- Cp_2	2.538
U	- C(8)	2.774(28)	U	- Cp_3	2.554
U	- C(9)	2.802(24)	S	- C(19)	1.853(20)
U	- C(10)	2.782(18)	S	- C(22)	1.815(19)
U	- C(11)	2.809(17)			

Angles

Atoms		deg	Atoms		deg
S	- U - Cp_1	104.9	Cp_2	- U - Cp_3	118.4
S	- U - Cp_2	92.8	C(19)	- S - C(22)	95.8(11)
S	- U - Cp_3	95.4	U	- S - C(19)	119.4(8)
Cp_1	- U - Cp_2	117.8	U	- S - C(22)	111.3(7)
Cp_1	- U - Cp_3	118.4			

[a] Cp_1, Cp_2, and Cp_3 represents the centers of atom groups C(1)-C(5), C(7)-C(11) and C(13)-C(17) respectively.

Figure caption

Fig 1. ORTEP drawing of tris(methylcyclopentadienyl)uranium(III)-

thiophene; thermal ellipsoids at 50% probability level.
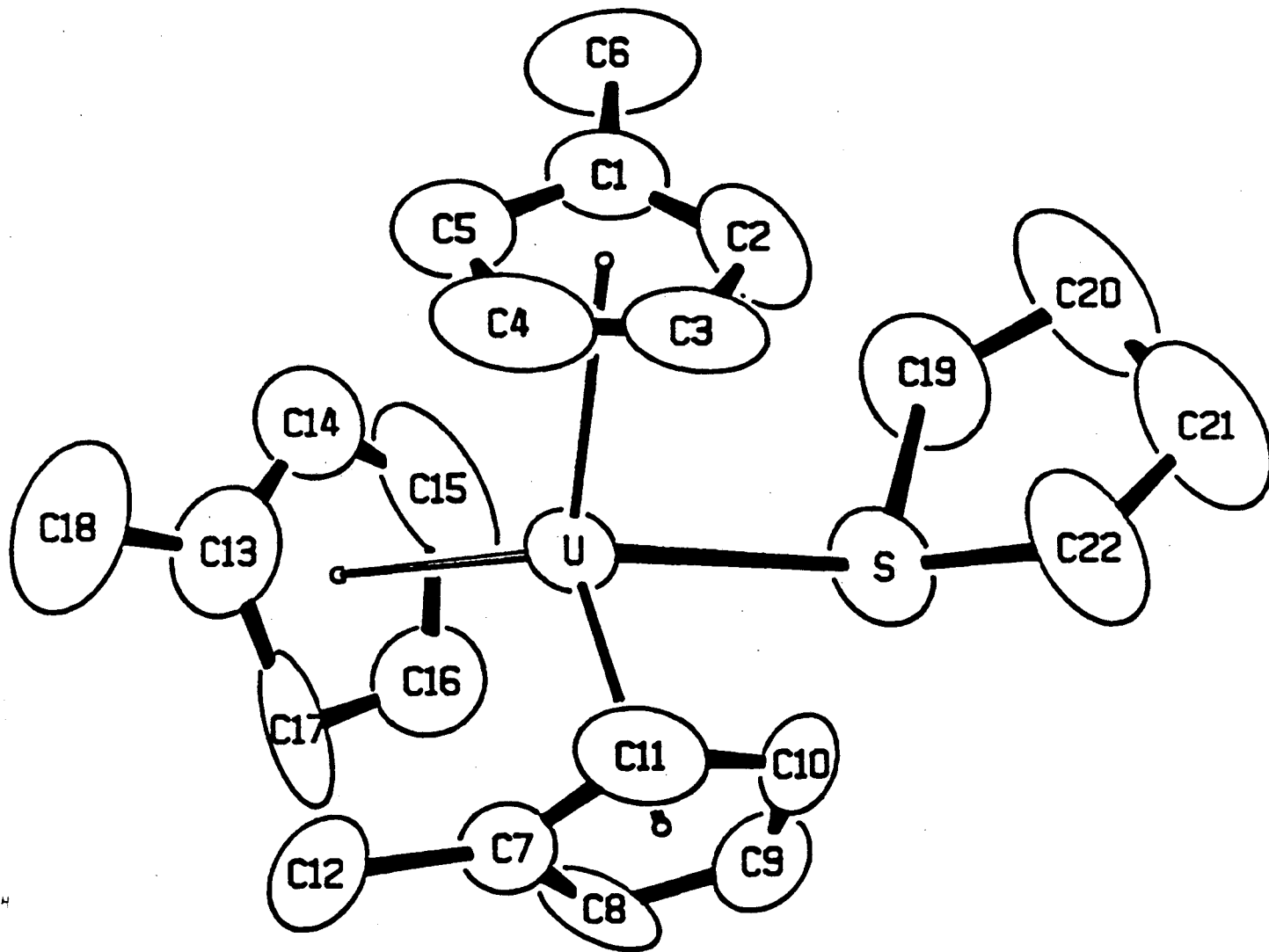
Supplemental Material

for

STRUCTURE OF

TRIS(METHYLCYCLOPENTADIENYL)URANIUM(III)THIOPHENE
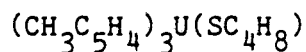
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Table A. Anisotropic Thermal Parameters (A^2)[a]

Atom	B11	B22	B33	B12	B13	B23
U	4.190(26)	3.419(21)	3.053(20)	0.42(4)	-0.38(4)	-0.03(3)
S	5.7(3)	5.71(27)	4.67(21)	1.15(24)	0.87(20)	0.35(20)
C(1)	4.0(11)	6.7(13)	4.9(12)	0.7(10)	-2.2(10)	0.2(10)
C(2)	8.3(16)	6.9(13)	3.9(10)	1.5(11)	0.8(11)	0.8(9)
C(3)	10.9(21)	5.8(13)	5.7(15)	-0.1(12)	-5.0(14)	0.3(10)
C(4)	7.1(16)	8.9(18)	6.6(14)	2.7(12)	-2.8(12)	-2.7(12)
C(5)	4.9(12)	9.8(17)	5.6(13)	-1.3(12)	-1.4(11)	-0.0(12)
C(6)	9.5(16)	6.8(12)	9.1(14)	1.6(11)	-2.1(15)	-4.7(13)
C(7)	4.8(13)	5.0(9)	3.6(8)	-0.8(9)	1.0(8)	-1.4(7)
C(8)	7.9(21)	11.1(23)	1.5(12)	-1.6(12)	0.5(9)	-1.9(13)
C(9)	5.4(14)	5.1(11)	5.4(14)	-1.7(11)	0.1(13)	-0.2(10)
C(10)	6.8(12)	3.5(9)	4.3(13)	-2.3(10)	1.1(12)	-0.3(8)
C(11)	6.9(14)	4.4(10)	5.0(11)	1.8(10)	-0.9(10)	-1.7(9)
C(12)	7.9(14)	6.6(12)	5.9(13)	-3.6(10)	3.3(11)	-2.7(9)
C(13)	8.8(17)	3.2(9)	7.6(17)	-0.2(9)	1.3(14)	-0.3(10)
C(14)	8.7(17)	4.7(9)	5.7(15)	-0.4(11)	-1.5(13)	1.5(9)
C(15)	16.8(37)	7.1(17)	5.2(17)	4.0(16)	2.6(19)	2.8(14)
C(16)	7.1(18)	5.3(13)	7.4(18)	-0.5(13)	-3.7(16)	3.3(12)
C(17)	8.0(14)	4.2(12)	4.7(16)	2.9(12)	4.2(13)	2.6(9)
C(18)	7.5(16)	9.2(16)	13.3(22)	-1.4(12)	3.9(15)	0.6(14)
C(19)	8.8(15)	9.1(14)	5.6(12)	0.5(11)	3.7(13)	-2.6(12)
C(20)	14.1(23)	12.4(17)	4.4(10)	4.0(22)	4.3(12)	-0.4(16)
C(21)	9.9(18)	11.7(18)	6.8(15)	4.6(16)	1.6(15)	3.2(15)
C(22)	10.5(19)	6.7(12)	5.4(10)	3.9(12)	2.6(12)	1.3(9)

[a] The anisotropic temperature factor has the form

$$\exp[-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots)].$$

Table B. Estimated Hydrogen Positional and Isotropic Thermal Parameters

Atom	x	y	z	B
H(1) (2)	0.1449	0.1588	-0.1609	10.0
H(2) C(3)	0.5430	0.2104	0.0034	10.0
H(3) C(4)	-0.0325	0.1543	0.1549	10.0
H(4) C(5)	-0.0032	0.0666	0.0802	10.0
H(5) C(8)	0.2938	0.1597	0.4520	10.0
H(6) C(9)	0.3474	0.1993	0.2265	10.0
H(7) C(10)	0.2215	0.2418	0.1132	10.0
H(8) C(11)	0.0816	0.2300	0.2587	10.0
H(9) C(14)	0.1200	0.0086	0.1260	10.0
H(10)C(15)	0.2825	0.0211	0.0703	10.0
H(11)C(16)	0.3487	0.0678	0.2807	10.0
H(12)C(17)	0.2322	0.0756	0.4684	10.0
H(13)C(19)	0.3151	0.0673	-0.1483	10.0
H(14)C(19)	0.4816	0.0790	-0.1459	10.0
H(15)C(20)	0.2855	0.1278	-0.2939	10.0
H(16)C(20)	0.3814	0.1122	-0.3462	10.0
H(17)C(21)	0.3623	0.1974	-0.3079	10.0
H(18)C(21)	0.4464	0.1739	-0.2353	10.0
H(19)C(22)	0.3830	0.2137	-0.0567	10.0
H(20)C(22)	0.2849	0.2030	-0.1090	10.0

[a] The isotropic temperature factor has the form $\exp[-B\sin^2\theta/\lambda]$.

Table C.   Deviations (A) from Least-Squares Planes

Plane 1, C(1) - C(5)

$$11.711 \ a - 2.088 \ b + 6.241 \ c = 0.2699$$

C(1)	0.026
C(2)	0.027
C(3)	-0.017
C(4)	0.001
C(5)	0.015
U	2.536
C(6)	-0.140

Plane 2, C(7) - C(11)

$$3.235 \ a + 22.576 \ b + 5.293 \ c = 6.804$$

C(7)	-0.003
C(8)	-0.003
C(9)	0.008
C(10)	-0.009
C(11)	0.007
U	-2.538
C(12)	0.018

Plane 3, C(13) - C(17)

$$3.297 \ a - 24.646 \ b + 3.903 \ c = 0.652$$

C(13)	-0.020
C(14)	0.005
C(15)	0.014
C(16)	-0.027
C(17)	0.028
U	-2.554
C(18)	0.109

Table D. Selected distances and angles to carbon

Distances

C(1)	– C(2)	1.400(25)		C(14)	– C(15)	1.39(3)
C(1)	– C(5)	1.441(28)		C(15)	– C(16)	1.49(4)
C(2)	– C(3)	1.417(29)		C(16)	– C(17)	1.42(4)
C(3)	– C(4)	1.383(30)		C(1)	– C(6)	1.453(26)
C(4)	– C(5)	1.420(27)		C(7)	– C(12)	1.536(24)
C(7)	– C(8)	1.458(26)		C(13)	– C(18)	1.52(3)
C(7)	– C(11)	1.400(25)		C(19)	– C(20)	1.52(3)
C(8)	– C(9)	1.28(4)		C(20)	– C(21)	1.47(3)
C(9)	– C(10)	1.35(4)		C(21)	– C(22)	1.55(3)
C(10)	– C(11)	1.44(3)		C(19)	– S	1.853(20)
C(13)	– C(14)	1.39(3)		C(22)	– S	1.815(19)
C(13)	– C(17)	1.53(4)				

Angles(°)

C(2)	– C(1)	– C(5)	106.5(21)		C(13)	– C(17)	– C(16)	102.0(28)
C(1)	– C(2)	– C(3)	109.1(23)		C(2)	– C(1)	– C(6)	126.0(24)
C(2)	– C(3)	– C(4)	108.1(22)		C(5)	– C(1)	– C(6)	127.5(23)
C(3)	– C(4)	– C(5)	108.6(26)		C(8)	– C(7)	– C(12)	132.7(33)
C(1)	– C(5)	– C(4)	107.4(22)		C(11)	– C(7)	– C(12)	125.6(21)
C(8)	– C(7)	– C(11)	101.6(20)		C(14)	– C(13)	– C(18)	126.7(28)
C(7)	– C(8)	– C(9)	113.5(28)		C(17)	– C(13)	– C(18)	124.3(24)
C(8)	– C(9)	– C(10)	109.0(30)		C(19)	– S	– C(22)	95.8(11)
C(9)	– C(10)	– C(11)	108.0(21)		S	– C(19)	– C(20)	103.9(15)
C(7)	– C(11)	– C(10)	107.9(18)		S	– C(22)	– C(21)	104.4(15)
C(14)	– C(13)	– C(17)	108.4(23)		C(19)	– C(20)	– C(21)	109.6(21)
C(13)	– C(14)	– C(15)	113.4(28)		C(20)	– C(21)	– C(22)	107.9(22)
C(14)	– C(15)	– C(16)	103.0(27)		C(19)	– S	– U	119.4(8)
C(15)	– C(16)	– C(17)	113.1(33)		C(22)	– S	– U	111.3(7)