

substituent (Fig. 2) shows that three energetically favourable orientations of this group, with torsions of about ± 60 and 180° , are possible for both (1) and (2). The benzyl-group location above N(7) is the most energetically favourable and close to the orientation found in molecules (1B) and (2) in the crystal. The third possible conformation with $\tau \approx 180^\circ$ and an *anti* orientation of the benzyl-group with respect to the metal atom is unfavourable: the barrier to rotation around the N(1)–C(19) bond, characterized by the angle τ , does not exceed *ca* 21 kJ mol⁻¹ in molecules (1) and (2). This indicates the possibility of a fairly free rotation of the benzyl-group in the isolated molecules of (1) and (2). However, in solution the relative content of the conformer with $\tau \approx 180^\circ$ should be greater for (1) than for (2) (Fig. 2), in good agreement with the experimental data (Belokon' *et al.*, 1984).

It is interesting to note that the previous conformational calculations for conformers of various compounds coexisting in crystals (Yelagin, Timofeeva & Zorki, 1980) generally show one rather broad and flat minimum for U_{conf} corresponding to different conformers, despite substantial geometric differences between them. The case of molecules (1A) and (1B) considered here is the first example of conformers which are characterized by different minima of U_{conf} separated by a well defined barrier coexisting in a crystal.

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A Trivalent-Uranium Thioether Coordination Compound

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Abstract. Tris(methylcyclopentadienyl)(tetrahydrothiophene)uranium(III), $[\text{U}(\text{C}_5\text{H}_5)_3(\text{C}_4\text{H}_8\text{S})]$, $M_r = 563.57$, orthorhombic, *Pbca*, $a = 15.146$ (5), $b = 27.598$ (8), $c = 9.911$ (4) Å, $V = 4143$ (4) Å³, $Z = 8$, $D_x = 1.81$ g cm⁻³, *Mo Kα*, $\lambda(\alpha_1) = 0.70930$ Å, $\mu = 75.3$ cm⁻¹, $F(000) = 2152$, $T = 296$ K, $R = 0.035$ for 1382 observed reflections. 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 tetrahydrothiophene molecule. The average U–C distance is 2.81 ± 0.04 Å and the U–S distance is 2.986 (5) Å.

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, Zalkin, Ruben & Templeton, 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 $(\text{C}_5\text{H}_5)_3\text{U}(\text{SC}_4\text{H}_8)$.

Experimental. Red, air-sensitive needles of the tetrahydrothiophene complex were prepared by adding SC_4H_8 to a toluene solution of $(\text{C}_5\text{H}_5)_3\text{U}(\text{OC}_4\text{H}_8)$

(Brennan & 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 $0.10 \times 0.21 \times 0.34$ mm with nine faces; modified Picker automatic diffractometer, graphite monochromator; cell dimensions from 14 reflections, $21 < 2\theta < 33^\circ$; analytical absorption correction, range 2.08 to 4.32; max. $(\sin\theta)/\lambda = 0.59 \text{ \AA}^{-1}$, $h0$ to 17, $k0$ to 32, $l-11$ to 11; three standard reflections, 4% variation in intensities from average, intensities adjusted accordingly; 7028 data, 3642 unique [including 2260, $F^2 < 2\sigma(F^2)$], $R_{\text{int}} = 0.083$; 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 $F^2 > 2\sigma(F^2)$, $wR = 0.035$, $S = 1.05$; $w = [\sigma(F)]^{-2}$, $p = 0.04$ in calculation of $\sigma(F^2)$; max. $(\text{shift}/\sigma) = 0.01$; no correction for extinction; max. and min. of ΔF synthesis 2.9 and -3.0 e \AA^{-3} ; atomic f for neutral U, S and C, and spherical bonded H from *International Tables for X-ray Crystallography* (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, 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 reflections 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.

Discussion. Atomic parameters are listed in Table 1,* selected bond distances and angles in Table 2.

The complex $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}(\text{SC}_4\text{H}_8)$ is monomolecular in the solid state. The uranium atom is coordinated to three cyclopentadienyl (Cp) groups and

* Lists of structure factors, anisotropic thermal and H-atom positional parameters, deviations from least-squares planes and distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42216 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
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 (\AA) and angles ($^\circ$)

U-S	2.986 (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 *	2.540
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)		
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		

* Cp₁, Cp₂ and Cp₃ represent the centers of atom groups C(1)-C(5), C(7)-C(11) and C(13)-C(17), respectively.

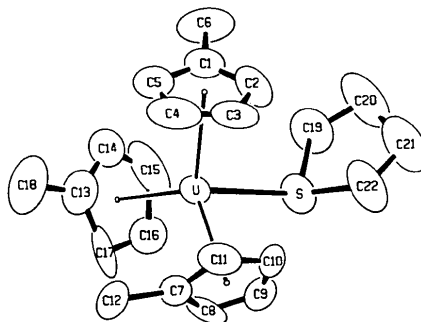


Fig. 1. ORTEP drawing of the title compound; thermal ellipsoids are at the 50% probability level.

to the sulfur atom of the tetrahydrothiophene ligand in a distorted tetrahedral array shown in Fig. 1. The shortest interligand C—C distance is 3.26 Å.

The structures of $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}(\text{SC}_4\text{H}_8)$ and $(\text{C}_5\text{H}_5)_3\text{U}(\text{OC}_4\text{H}_8)$ (Wasserman, Zozulin, Moody, Ryan & Salazar, 1983) are similar. The lack of planarity of the three atoms bonded to the sulfur atom in the tetrahydrothiophene 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 2.986 (5) and 2.55 (1) Å respectively.

A comparison of the structures of $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}(\text{SC}_4\text{H}_8)$ and $(\text{CH}_3\text{C}_5\text{H}_4)_3\text{U}\{\text{P}(\text{CH}_3)_3\}$ (Brennan & Zalkin, 1985) shows some geometrical differences. The Cp—U—Cp angles in the tetrahydrothiophene complex are all within 0.4° from 118°, a small 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 tetrahydrothiophene 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 tetrahydrothiophene and the trimethylphosphine complexes are 2.54 (1) and 2.52 (2) Å respectively. The U—S and U—P distances in the two structures are 2.986 (5) and 2.972 (6) Å respectively.

The U^{III}—S distance reported here [2.986 (5) Å] is similar to the U^{VI}—S distance [2.94 (1) Å] found in the

uranium thioether coordination complex, *cis*-dichloro-*[meso-bis(trans-2-hydroxycyclohexyl) sulfide-O,O,S]-dioxouranium(VI)* (Baracco *et al.*, 1975), and the difference in the above distances is much smaller than expected. For a coordination number of six, the estimated ionic radius of U^{III} is 0.295 Å larger than that for U^{VI} (Shannon, 1976); and the difference is even larger when the effect of a larger coordination number of the U^{III} complex (ten *vs* seven) is considered.

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Refinement of Trimethylammonium Trichlorocuprate(II) Dihydrate, $[\text{NH}(\text{CH}_3)_3][\text{CuCl}_3] \cdot 2\text{H}_2\text{O}$

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Abstract. $M_r = 266.05$, monoclinic, $P2_1/c$, $a = 7.5066$ (8), $b = 7.8873$ (5), $c = 16.758$ (1) Å, $\beta = 91.914$ (9)°, $V = 991.6$ (3) Å³, $Z = 4$, $D_x = 1.781$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 29.76$ cm⁻¹, $F(000) = 540$, $T = 297$ K, $R = 0.028$ for 2655 observed independent reflections. The previous determination [Losee, McElearney, Siegel, Carlin, Kahn, Roux & James (1972). *Phys. Rev. B*, **6**, 4342–

4348] is confirmed and improved. All H atoms are located. The two independent square-planar $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ subunits have significantly different bond lengths due to distortions by long Cu—Cl contacts. The Cl⁻ anion is involved in four hydrogen bonds of intermediate strength with the hydrate groups. The cation is connected by a very weak bifurcated hydrogen bond to the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ chains.