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The crystal structure of tris(indenyl)uranium (β,β,β-trifluoroethanolate)

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Abstract

The title compound was obtained by reaction of the methyl tris(indenyl) uranium complex with trifluoroethanol. A crystal structure reveals that there are two symmetrically independent molecules in the unit cell. The coordination geometry about the uranium atom is a flattened tetrahedron with three π-bonded indenyl rings and one σ-bonded trifluoroethanol oxygen atom. The U–O bonds are remarkably short. The U–C distances indicate trihapto mode of bonding of the indenyl rings. Variation of the ligand X in the $U(C_9H_7)_3X$ class of complexes would not affect the stereochemistry about the U atom.

1. Introduction

The characterization of the title complex by single crystal X-ray diffraction forms part of our investigations on the bonding and stereochemistry in organoactinide complexes of the indenyl ligand. Structural data for halogeno [$U(C_9H_7)_3X$] complexes have been previously reported ([$U(C_9H_7)_3Cl$] [1], [$U(C_9H_7)_3Br$] [2], [$U(C_9H_7)_3I$] [3]) but no structural information was available for indenyl complexes with a ligand containing an oxygen donor atom. The title compound was prepared and its structure determined in order to confirm that its geometry was consistent with that of the halogeno species.

2. Experimental details

2.1. Preparation

The alkoxide [$U(C_9H_7)_3]OCH_2CF_3$ was prepared by treatment of a solution of methyl(trisindenyl)-uranium [4] in toluene with trifluoroethanol. Extraction followed by recrystallisation from toluene gave single crystals suitable for X-rays analysis. A selected specimen ($0.30 \times 0.25 \times 0.25$ mm) was sealed in a thin-walled glass capillary under an inert atmosphere.

2.2. Structural studies

The X-ray diffraction data were obtained with an Enraf-Nonius CAD4 diffractometer (using graphite-monochromated Mo Kα radiation: 0.71073 Å) at room temperature. The unit cell parameters and standard deviations were calculated from the setting angles of 25 reflections with $4° \times 2\theta \times 23°$. The space group $P2_1/c$ was indicated by the systematic absences.

Crystal data: $UOC_{30}F_3H_{23}$, $M_r = 1365.06$, $a = 21.735(9)$, $b = 9.339(4)$, $c = 31.95(10)$ Å, $\beta = 132.1063(6)°$, $V = 4812(6)$ Å^3, $Z = 8$ (two symmetrically independent molecular units), $D_{calcd} = 1.884$ g cm^{-3}, μ(Mo Kα) = 63.78 cm^{-1}, $F(000) = 2592$. The intensities of 5527 reflections with $I > 2\sigma(I)$ were measured by the θ–2θ scan technique in the range $4° \leqslant \theta \leqslant 26°$ (h $0 \rightarrow 24$, k $10 \rightarrow -10$, l $26 \rightarrow -26$). They averaged to 2963 unique reflections with $R_{int} = 0.031$. The intensities of three standard reflections were measured at 30 min intervals and showed slight changes during data collection; the data were rescaled to correct for this (minimum correction 0.944, maximum correction 1.070). Data were corrected for Lorentz-polarization and absorption effects, the latter by the empirical method DIFABS [5]. The transmission factors range from 0.6481 to 1.2913. The structure was solved by direct methods and Fourier techniques and refined by full matrix least-squares minimizing $\Sigma w(|F_o| - |F_c|)^2$. A weight-

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ing scheme based on counting statistics was used: $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma^2(I) + (0.06)^2]^{1/2}Lp$. Refinement was carried out on 2917 reflections with $I > 2\sigma(I)$. The non-hydrogen atoms were treated isotropically except for the U atoms, which were treated anisotropically. H atoms were not included in refinement. A secondary-extinction coeffi-

TABLE 1. Positional and thermal parameters with estimated standard deviations

Atom	x	y	z	B (Å^2)
U1	0.72157(5)	0.23334(9)	0.42652(3)	4.53(3) [a]
U2	0.16280(4)	0.25551(9)	0.23870(3)	3.69(2) [a]
F1	0.613(1)	−0.078(3)	0.479(1)	15.3(9)
F2	0.592(2)	−0.189(3)	0.408(1)	18(1)
F3	0.511(1)	−0.146(3)	0.4037(9)	15.7(9)
F4	0.442(1)	0.248(2)	0.4675(8)	12.6(7)
F5	0.381(1)	0.092(3)	0.404(1)	15.9(9)
F6	0.432(1)	0.254(3)	0.399(1)	18(1)
O1	0.6339(9)	0.098(2)	0.4110(6)	6.1(4)
O2	0.2552(9)	0.276(2)	0.3242(6)	5.8(4)
C1	0.723(1)	0.050(3)	0.364(1)	5.5(7)
C2	0.772(1)	0.158(3)	0.368(1)	7.2(8)
C3	0.856(1)	0.174(3)	0.431(1)	8.3(9)
C4	0.929(1)	−0.007(3)	0.5124(9)	6.2(7)
C5	0.910(2)	−0.121(3)	0.528(1)	7.3(8)
C6	0.833(2)	−0.188(4)	0.491(1)	8.5(9)
C7	0.765(2)	−0.150(4)	0.433(1)	9(1)
C8	0.783(1)	−0.025(3)	0.4208(9)	5.2(6)
C9	0.865(2)	0.051(3)	0.457(1)	7.6(8)
C10	0.822(1)	0.177(3)	0.5355(8)	4.9(6)
C11	0.869(2)	0.275(3)	0.536(1)	7.7(8)
C12	0.831(1)	0.415(3)	0.521(1)	7.3(8)
C13	0.711(1)	0.522(3)	0.510(1)	7.0(7)
C14	0.658(2)	0.472(3)	0.514(1)	8.6(9)
C15	0.646(2)	0.343(4)	0.522(1)	10(1)
C16	0.696(2)	0.221(4)	0.528(1)	10(1)
C17	0.758(1)	0.263(3)	0.5283(9)	5.8(6)
C18	0.765(1)	0.406(3)	0.5192(9)	5.2(6)
C19	0.609(1)	0.445(3)	0.379(1)	5.9(7)
C20	0.677(1)	0.505(2)	0.3920(8)	4.4(6)
C21	0.689(1)	0.462(3)	0.3571(9)	5.3(6)
C22	0.596(1)	0.308(3)	0.266(1)	7.8(9)
C23	0.529(1)	0.234(3)	0.235(1)	6.4(7)
C24	0.482(2)	0.219(3)	0.247(1)	8.0(9)
C25	0.497(1)	0.276(3)	0.292(1)	7.0(8)
C26	0.574(1)	0.362(2)	0.3309(8)	4.0(5)
C27	0.620(1)	0.366(3)	0.3163(9)	5.2(6)
C28	0.558(2)	0.026(4)	0.387(1)	10(1)
C29	0.582(2)	−0.078(4)	0.424(1)	11(1)
C30	0.008(1)	0.211(3)	0.199(1)	6.7(7)
C31	0.029(1)	0.087(3)	0.185(1)	5.5(6)
C32	0.092(1)	0.009(2)	0.2353(8)	4.6(5)
C33	0.162(1)	0.041(3)	0.341(1)	6.8(8)
C34	0.160(1)	0.125(3)	0.372(1)	6.2(7)
C35	0.113(2)	0.254(3)	0.352(1)	7.7(8)
C36	0.061(1)	0.296(3)	0.2952(9)	5.8(7)
C37	0.057(1)	0.205(2)	0.2593(8)	4.6(5)
C38	0.111(1)	0.078(2)	0.2810(8)	3.8(5)
C39	0.257(1)	0.236(3)	0.211(1)	6.3(7)

TABLE 1 (Continued)

Atom	x	y	z	B (Å^2)
C40	0.302(1)	0.152(3)	0.261(1)	6.1(6)
C41	0.246(1)	0.029(3)	0.2446(9)	6.0(7)
C42	0.118(1)	−0.074(3)	0.147(1)	6.0(7)
C43	0.060(1)	−0.038(3)	0.095(1)	7.2(8)
C44	0.058(2)	0.085(3)	0.070(1)	7.1(8)
C45	0.125(1)	0.187(3)	0.104(1)	7.2(8)
C46	0.182(1)	0.162(3)	0.1620(9)	5.6(6)
C47	0.182(1)	0.029(3)	0.187(1)	5.7(6)
C48	0.077(1)	0.506(3)	0.2147(9)	5.7(6)
C49	0.057(1)	0.466(3)	0.1652(9)	6.1(7)
C50	0.137(1)	0.488(3)	0.1757(9)	5.7(7)
C51	0.280(1)	0.582(3)	0.261(1)	6.6(7)
C52	0.329(2)	0.642(3)	0.318(1)	7.3(8)
C53	0.284(1)	0.662(3)	0.336(1)	7.8(8)
C54	0.206(2)	0.625(3)	0.313(1)	7.1(8)
C55	0.157(1)	0.558(2)	0.2564(9)	5.1(6)
C56	0.194(1)	0.544(3)	0.232(1)	6.8(7)
C57	0.313(1)	0.308(3)	0.384(1)	5.8(6)
C58	0.381(2)	0.237(3)	0.407(1)	9(1)

[a] These atoms were refined anisotropically. They are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$. For U1: $B_{1,1} = 4.95(3)$, $B_{2,2} = 4.40(4)$, $B_{3,3} = 3.98(3)$, $B_{1,2} = 1.04(3)$, $B_{1,3} = 2.89(2)$, $B_{2,3} = 0.37(3)$. For U2: $B_{1,1} = 3.33(2)$, $B_{2,2} = 4.11(4)$, $B_{3,3} = 3.97(2)$, $B_{1,2} = 0.06(3)$, $B_{1,3} = 2.59(1)$, $B_{2,3} = 0.03(3)$.

cient was refined to a value of $g = 6.52 \times 10^{-8}$, $\{F_c = F_c/[1 + g(F_c)^2Lp]\}$. The final agreement factors were $R = 0.056$, $R_w = 0.089$, $S = 2.35$. The number of variables refined in least squares was 284. The maximum shifts/e.s.d. in final cycle was 0.01. The highest peak in the final difference Fourier map, of 1.35 e Å^{-3}, was located near one U atom. Atomic scattering factors and anomalous-dispersion terms were taken from International Tables for X-ray Crystallography [6]. Calculations were performed with Enraf-Nonius SDP programs (1986) [7]. The atomic coordinates and thermal parameters are listed in Table 1. Observed and calculated structure factors are available on request from the authors.

3. Results and discussion

The molecular structure of the two independent molecules with the numbering scheme, are shown in Fig. 1. [8]. Corresponding bond lengths and angles are listed in Table 2. In each molecule the U atom is coordinated by the five-membered rings of three indenyls and by the oxygen atom of one trifluoroethanolate ligand. If the coordination polyhedron is considered to be formed by the centres of the indenyl five-membered rings and by the trifluoroethanol oxygen atom, the coordination about the uranium can be

considered to have approximate C_{3v} symmetry, with the indenyl at the base and the oxygen at the apex of a flattened tetrahedron. The distortion of the coordination polyhedron is reflected by the angles subtended at the U atom. The O-U-ind. angles are less than 109°, while the ind.-U-ind. angles are nearly identical and greater than 109° (Table 2).

The molecular parameters reported in Table 2 show a stereochemistry similar to that observed for the halogeno complexes $U(C_9H_7)_3X$. Thus substitution of the bulky halogen atom by an oxo donor ligand does not affect the structure of the $[U(C_9H_7)_3]^+$ moiety. The U-O distances, 2.05(1) and 2.04(1) Å, respectively, for the two independent molecular units (Table 2) are rather short, and indicate a strong metal-oxygen bond. For comparison, in the tris(η^5-cyclopentadienyl)pheno-
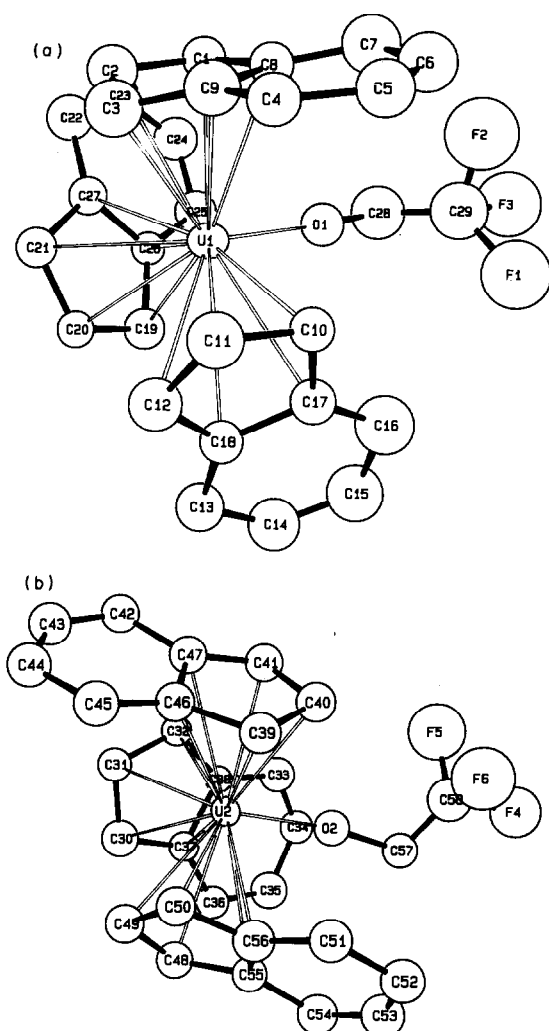

Fig. 1. The molecular structures of the two independent molecules showing the atom labelling. Thermal ellipsoids are at the 50% probability level.

TABLE 2. Selected bond distances (Å) and angles (°) in [$U(C_9H_7)_3$)(OCH$_2$CF$_3$)] (standard deviations are given in parentheses)

U1-O1	2.05(1)	U2-O2	2.04(1)
U1-C1	2.64(2)	U2-C30	2.72(2)
U1-C2	2.80(2)	U2-C31	2.68(2)
U1-C3	2.89(3)	U2-C32	2.73(2)
U1-C8	2.82(2)	U2-C37	2.83(2)
U1-C9	3.08(2)	U2-C38	2.81(2)
U1-Ind.I [a]	2.56(2)	U2-Ind.IV [a]	2.47(2)
U1-C10	2.64(2)	U2-C39	2.74(2)
U1-C11	2.77(3)	U2-C40	2.78(2)
U1-C12	2.83(2)	U2-C41	2.70(2)
U1-C17	2.80(2)	U2-C46	2.89(2)
U1-C18	2.92(2)	U2-C47	2.90(2)
U1-Ind.II [a]	2.52(2)	U2-Ind.V [a]	2.52(2)
U1-C19	2.69(2)	U2-C48	2.77(2)
U1-C20	2.68(2)	U2-C49	2.73(2)
U1-C21	2.80(2)	U2-C50	2.75(2)
U1-C26	2.82(2)	U2-C55	2.90(2)
U1-C27	2.89(2)	U2-C56	2.82(2)
U1-Ind.III [a]	2.51(2)	U2-Ind.VI [a]	2.51(2)
O1-U1-Ind.I	104.9(6)	O2-U2-Ind.IV	100.7(6)
O1-U1-Ind.II	104.9(6)	O2-U2-Ind.V	102.4(6)
O1-U1-Ind.III	102.1(6)	O2-U2-Ind.VI	101.5(6)
U1-O1-C28	165(2)	U2-O2-C57	171(1)
Ind.I-U1-Ind.II	113.6(6)	Ind.IV-U2-Ind.V	115.9(6)
Ind.I-U1-Ind.III	114.1(6)	Ind.IV-U2-Ind.VI	114.4(6)
Ind.II-U1-Ind.III	115.5(6)	Ind.IV-U2-Ind.VI	118.0(6)
O1-C28-C29	104(3)	O2-C57-C58	107(2)
C28-C29-F1	133(4)	C57-C58-F4	113(3)
C28-C29-F2	108(4)	C57-C58-F5	121(3)
C28-C29-F3	106(3)	C57-C58-F6	128(3)

[a] Ind. denotes the centre of the five-membered ring of the indenyl ligand.

latouranium(IV) [9], the length of the corresponding uranium-alkoxide oxygen bond is 2.119(7) Å, and in the complex $U(OC_6H_5)_42[(CH_3)_2P(CH_2)P(CH_3)_2]$ [10] it is 2.17(1) Å. To our knowledge that in the trifluoroethanolate is the shortest U-O IV bond ever observed, though a value of 2.057(1) Å has been observed for the U-O IV bridge bond in [{C_9H_7UBr(CH$_3$-CN)$_4$}$_2$O]$^{2+}$[UBr$_6$]$^{2-}$ [11]. As previously reported for other tris(indenyl)uranium [1-3] and tris(indenyl)thorium [see ref. 12 and references cited therein] complexes, the U-C shortest bond distances are those towards the non-bridging C atoms of the indenyl five-membered rings, suggesting a trihapto character of the metal-carbon bonding (Table 2).

The indenyl rings are planar within the limits of the standard deviations. The accuracy of some bond distances and angles is, of course, affected by the high thermal motion associated with the fluorine atoms as well as with some indenyl C atoms (Table 1).

The crystal is made up of discrete molecules with no significant intermolecular contacts.

References

1 J.M. Burns and P.G. Laubereau, *Inorg. Chem., 10* (1971) 2789.
2 M.-R. Spirlet, J. Rebizant and J. Goffart, *Acta Crystallogr., Sect. C, 34* (1987) 354.
3 J. Rebizant, M.-R. Spirlet, G. van den Bossche and J. Goffart, *Acta Crystallogr. Sect. C, 44* (1988) 1710.
4 J. Goffart, *Inorg. Nucl. Chem. Lett., 13* (1977) 189.
5 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.
6 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, 1974 (Present distributor Kluwer, Academic Publishers, Dordrecht).
7 Enraf-Nonius, *Structure Determination Package, Version 18,* Enraf-Nonius, Delft, The Netherlands, 1986.
8 C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, TN 1976.
9 M.-R. Spirlet, J. Rebizant, C. Apostolidis, G. van den Bossche and B. Kanellakopulos, *Acta Crystallogr. Sect. C, 46* (1990) 2318.
10 P.G. Edward, R.A. Anderson and A. Zalkin, *J. Am. Chem. Soc., 103* (1981) 7792.
11 W. Beeckman, J. Goffart, J. Rebizant and M. R. Spirlet, *J. Organomet. Chem., 307* (1986) 23.
12 M.-R. Spirlet, J. Rebizant, S. Bettonville and J. Goffart, *Acta Crystallogr. Sect. C, 46* (1990) 1234.