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Structure of Tetrakis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)uranium

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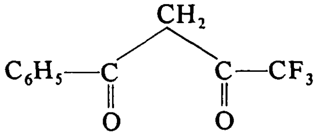
Abstract. [U($C_{10}H_6F_3O_2$)$_4$], $C_{40}H_{24}F_{12}O_8U$, tetragonal, $I4_1/a$, $a = 17{\cdot}70\,(2)$, $c = 12{\cdot}67\,(4)$ Å, $Z = 4$, $M_r = 1098$, $V = 3969\,(17)$ Å^3. The uranium atom lies on an inversion tetrad axis and is surrounded by eight oxygen atoms forming a double-tetrahedral arrangement. The two U—O distances are 2·326 (7) and 2·355 (8) Å. The overall packing is such as to allow van der Waals bonds between F atoms from CF_3 groups along the 4_1 axis.

Introduction. We present here the structure of the title compound {tetrakis[(trifluoro)benzoylacetonato]uranium(IV)} {[U(tfba)$_4$] in the following}; this structure was investigated as part of a study on highly symmetric uranium(IV) compounds, in order to obtain a better understanding of their electronic spectra. The compound was first reported by Folcher, Paris, Plurien, Rigny & Soulié (1974), who have shown that this chelate can be used as an NMR chemical-shift reagent.



Crystals of [U(tfba)$_4$] suitable for X-ray work were grown by slow evaporation of a solution of the compound in butanol. Preliminary results were obtained from photographs. Space group $I4_1/a$ (No. 88) was inferred from the following systematic extinctions: hkl: $h + k + l \neq 2n$; $hk0$: h, $(k) \neq 2n$; $00l$: $l \neq 4n$. The calculated density is 1·84 (1) Mg m^{-3} for $Z = 4$. The U atom must then occupy the only special position on the fourfold axis ($\bar{4}$): either 4(a) or equivalent set 4(b).

The structure was solved from intensity data collected on a Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Since the linear absorption coefficient is not very high (3·8 mm^{-1}) and the crystal small and nearly equidimensional, an absorption correction was omitted.

Table 1. *Atomic coordinates (with e.s.d.'s in parentheses) and isotropic thermal parameters* (Å^2)

$\bar{U}$ is the average of the three eigenvalues of each anisotropic vibration tensor.

	x	y	z	$\bar{U}/U$ ($\times 10^2$)
U	0·5000	0·7500	0·1250	5·94
O(1)	0·5972 (4)	0·8234 (4)	0·1939 (6)	5·07
O(2)	0·4543 (4)	0·8176 (5)	0·2719 (6)	5·30
C(1)	0·5590 (6)	0·8656 (6)	0·3638 (9)	4·72
C(2)	0·6098 (6)	0·8535 (6)	0·2852 (9)	4·40
C(3)	0·4798 (6)	0·8481 (6)	0·3543 (8)	4·38
C(4)	0·6894 (7)	0·8724 (7)	0·3020 (9)	5·36
F(1)	0·7178 (5)	0·9146 (6)	0·2275 (8)	10·83
F(2)	0·7328 (5)	0·8168 (5)	0·3131 (10)	12·21
F(3)	0·7015 (5)	0·9130 (6)	0·3878 (8)	11·86
C(5)	0·4265 (6)	0·8658 (6)	0·4409 (8)	4·08
C(6)	0·3511 (7)	0·8486 (7)	0·4289 (9)	5·31
C(7)	0·2988 (7)	0·8650 (7)	0·5042 (10)	6·04
C(8)	0·3220 (7)	0·9001 (7)	0·5960 (10)	6·02
C(9)	0·3939 (8)	0·9186 (8)	0·6100 (10)	6·80
C(10)	0·4468 (7)	0·9000 (7)	0·5328 (10)	6·08
H(1)	0·5782	0·8888	0·4326	4·30
H(6)	0·3341	0·8212	0·3611	5·30
H(7)	0·2429	0·8520	0·4926	6·00
H(8)	0·2832	0·9116	0·6535	6·00
H(9)	0·4103	0·9470	0·6770	6·00
H(10)	0·5029	0·9120	0·5453	6·00

Of 2696 reflexions, 2000 were observed. The structure was solved by the heavy-atom method: the U atom was indeed located on the fourfold axis; all other atoms were located from successive Fourier difference syntheses, phased on the heavy atom. Neutral-atom scattering factors were used for atoms other than U; the tetravalent scattering factor was used for uranium. These were calculated from the coefficients of the analytical approximation to the scattering factors.

All atoms other than U are in general positions: final atomic positions and isotropic U values are given in Table 1 (note origin on $\bar{1}$, at $0,\frac{1}{4},\frac{1}{8}$ from $\bar{4}$). The final R factor is 0·049, including H atoms.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34886 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. The asymmetric unit given in Fig. 1 is repeated around the U atom by the $\bar{4}$ axis. In this way the environment of the U atom in this chelate is formed by eight O atoms belonging to two distinct tetrahedra (Fig. 2), one being flattened along the $\bar{4}$ axis [O(1)], the other elongated [O(2)].

Such an environment can be thought of as derived from a cube arbitrarily decomposed into two independent tetrahedra. However, the best interpretation leads to the dodecahedral configuration described fully by Hoard & Silverton (1963). In their nomenclature, the three specific parameters, if M stands for U, A for O(2) and B for O(1), are the angles θ_A, θ_B made by the bonds MA and MB with the $\bar{4}$ axis, and the ratio of the bond lengths. Here: $\theta_A = 37, 80°$, $\theta_B = 67, 94°$, $MA/MB = 1{\cdot}012$. The polyhedron is also characterized by unequal edge lengths: $a = 2{\cdot}89\,(1)$ Å (AA), $g = 2{\cdot}72\,(1)$ Å (AB), $m = 2{\cdot}83\,(1)$ Å (AB') and $b = 3{\cdot}51\,(1)$ Å (BB'), where A and B refer to the upper atoms, and A' and B' to the atoms below the U atom (Fig. 3).

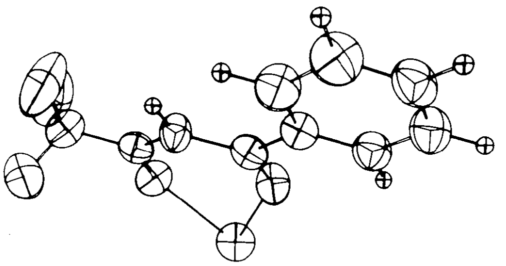

Fig. 1. The asymmetric [U(tfba)$_4$] unit.

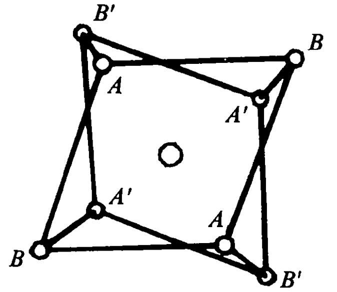

Fig. 2. The environment of the U atom.

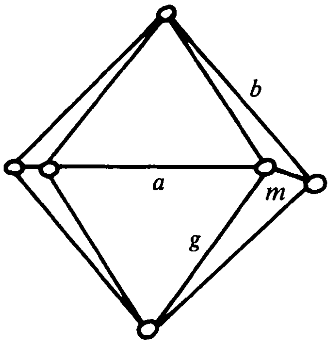

Fig. 3. The U polyhedron.

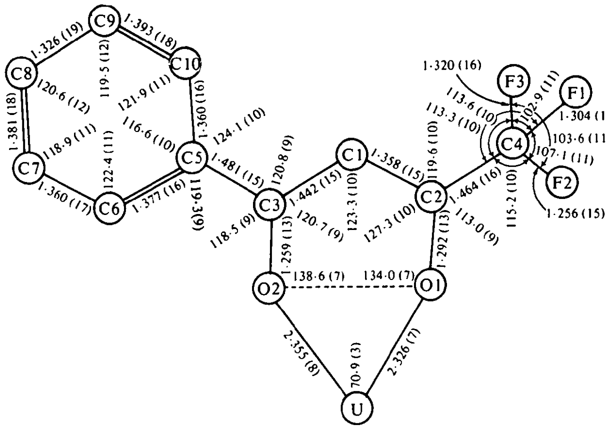

Fig. 4. Bond distances (Å) and angles (°) in [U(tfba)$_4$].

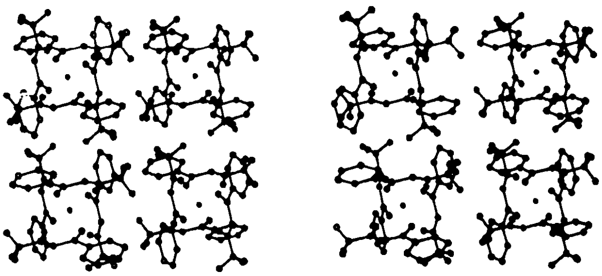

Fig. 5. A stereoview of the packing arrangement in [U(tfba)$_4$].

[U(tfba)$_4$] has four bidentate ligands described in the dodecahedral subclass *gggg*.

The chelate ring is not flat, but folded through about 16° along the line joining the O atoms.

The bond angles and bond distances in the asymmetric unit are given in Fig. 4.

Within the CF_3 group, the C—F distances and F—C—F angles are as expected, except for the rather short C—F(2); however, high thermal parameters affect the F positions.

The phenyl group has the usual planar regular hexagon configuration, with C—C distances lying between 1·33 and 1·39 Å, and C—C—C angles very close to 120° within the error limits.

All H atoms have been located in theoretical positions and not refined.

An interesting feature of the structure is that as a result of the packing there is a tendency for contacts to be realized between F atoms belonging to different units: the distance between F(1) of one CF_3 group and F(3) of another is only 2·80 Å, and infinite chains of the type $[F(1)\cdots F(3)][F(1)\cdots F(3)][F(1)\cdots F(3)]_n$ are formed along the 4_1 axis (Fig. 5).

References

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