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Structure and Disorder in Crystals of Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)uranium(IV), [$U(C_5H_4F_3O_2)_4$]

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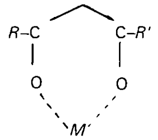
Abstract. $M_r = 850$, monoclinic, $C2/c$, $a = 24·917$ (5), $b = 6·430$ (2), $c = 21·232$ (6) Å, $\beta = 125·69$ (2)°, $V = 2763$ (3) Å^3, $Z = 4$, $D_x = 2·042$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å, $\mu = 56·8$ cm^{-1}, $F(000) = 1600$, $T = 294$ K. Affected by a stacking disorder along the c axis, this structure has been solved discarding the l-odd reflexions and refined on F to $R = 0·076$ for 930 remaining observations with $I > 3\sigma(I)$. The uranium atom lies on the diad axis and is eight-coordinated by oxygen atoms from four bidentate ligands (U—O, 2·36–2·40 Å) in a square-antiprism configuration. The asymmetric ligands span the lateral edges of the polyhedron corresponding to the D_4 (*llll*) stereoisomer [Hoard & Silverton (1963). *Inorg. Chem.* **2**(2), 235–243].

Introduction. The structure of the title compound, also known as U(tfaa)$_4$, tetrakis[(trifluoro)acetylacetonato]-uranium(IV), was investigated as part of a systematic study of the eight-coordination of uranium(IV) in β-diketonates: identical or different substituents R and R' on the pseudo cycle, the presence of electronegative fluorinated or aromatic groups may influence the geometry of ligands around the metal atom. We first reported the structure of U(tfba)$_4$, tetrakis[(trifluoro)-benzoylacetonato]uranium(IV), (Navaza, de Rango & Charpin, 1980) and showed that the polyhedron around the uranium atom was a dodecahedron belonging to the subclass S_4 (*gggg*) of possible stereoisomers (Hoard & Silverton, 1963). The ligand in U(tfaa)$_4$ is also a dissymmetric one: $R = CF_3$, $R' = CH_3$.



Experimental. Crystals grown by slow evaporation of solutions of the compound either in benzene or ethanol; preliminary examinations by Weissenberg method leading to space group $C2/c$ or Cc, and showing the coexistence of sharp and broadened spots, respectively $l = 2n$ and $l = 2n + 1$, broadening affecting more severely crystals obtained from ethanol; crystal (0·050 × 0·100 × 0·200 mm) selected from the least disordered ones, kept in Lindemann-glass capillary to avoid rapid decomposition in ambient atmosphere; D_m not measured; data collected on a CAD-4 Nonius diffractometer with Mo graphite-monochromatized radiation; cell dimensions from 25 centered reflexions; intensities measured in one quadrant of the reciprocal sphere between 1·5 and 25° θ in the $\omega/2\theta$ scan mode ($0 < h < 29$, $0 < k < 7$, $-20 < l < 20$), corrected for Lorentz and polarization effects, but not for absorption; standard reflexions $20\bar{2}$, $\bar{4}0\bar{2}$ and $1\bar{1}\bar{4}$ with 0, 3·6 and 6% intensity variation, respectively; 1442 unique reflexions with $I > 3\sigma(I)$ in the hkl and $hk\bar{l}$ octants; structure solved with *SDP* chain programs (Frenz, 1983), using the heavy-atom method; atomic scattering factors from *International Tables for X-ray Crystallography* (1974) corrected for anomalous dispersion ($f'_U = -10·673$, $f''_U = 9·654$); no correction for secondary extinction.

The position of the uranium atom given by the Patterson method, 0, y, $\frac{1}{4}$, led us to prefer the centrosymmetric group $C2/c$ rather than Cc and to locate the heavy atom on the twofold axis. The subsequent difference synthesis clearly showed the effect of disorder with the presence of a pseudo-uranium atom, at 0, $\bar{y}$, $\frac{1}{4}$, given by a pseudo symmetry plane, parallel to the glide plane c. At this point, the solution of the structure was only possible by excluding from the data set the l-odd reflexions strongly affected by the packing disorder along the c axis: 930 l-even reflexions were thus left to solve the structure. All atoms were located in general positions: final atomic positional and equivalent or isotropic thermal parameters are given in Table 1. The labeling of atoms with bond lengths and angles is given by two drawings of the two independent acetylacetonate rings of the molecule (Fig. 1*a*,*b*). Difficulties were encountered in positioning the

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Table 1. *Atomic positional and equivalent or isotropic thermal parameters*

	x	y	z	B(Å^2)
U	0	0·1224 (3)	$\frac{1}{4}$	2·58 (3)*
Ligand *A*				
O(1)	0·0943 (6)	−0·008 (12)	0·2621 (7)	3·5 (3)
C(1)	0·1352 (12)	0·077 (5)	0·2510 (14)	4·5 (7)
C(2)	0·2021 (12)	−0·039 (7)	0·2959 (14)	5·9 (8)
F(21)	0·1906 (10)	−0·241 (4)	0·2786 (11)	8·0 (7)
F(22)	0·2332 (9)	−0·015 (14)	0·3702 (10)	10·1 (6)
F(23)	0·2385 (9)	0·032 (7)	0·2734 (10)	10·1 (7)
C(3)	0·1288 (14)	0·251 (5)	0·2075 (16)	4·6 (7)
C(4)	0·0701 (11)	0·368 (6)	0·1690 (13)	4·1 (6)
C(5)	0·0611 (13)	0·542 (7)	0·1148 (15)	6·3 (9)
O(2)	0·0234 (7)	0·343 (3)	0·1776 (9)	4·0 (4)
Ligand *B*				
O(3)	0·0579 (6)	−0·008 (13)	0·3778 (7)	3·8 (3)
C(6)	0·1035 (11)	0·075 (4)	0·4431 (13)	3·8 (6)
C(7)	0·1100 (18)	−0·025 (17)	0·5132 (21)	10·5 (13)
F(71)	0·1103 (11)	−0·231 (5)	0·5075 (13)	9·6 (8)
F(72)	0·1657 (10)	0·038 (7)	0·5783 (11)	10·8 (7)
F(73)	0·0601 (10)	0·039 (7)	0·5141 (12)	11·6 (8)
C(8)	0·1436 (14)	0·253 (6)	0·4660 (16)	5·0 (8)
C(9)	0·1366 (11)	0·371 (6)	0·4059 (13)	4·1 (6)
C(10)	0·1853 (14)	0·550 (6)	0·4285 (16)	6·5 (9)
O(4)	0·0893 (1)	0·355 (3)	0·3310 (8)	3·7 (3)

* $B_{eq} = \frac{4}{3}\sum_i \sum_j \mathbf{a}_i . \mathbf{a}_j \beta_{ij}$.

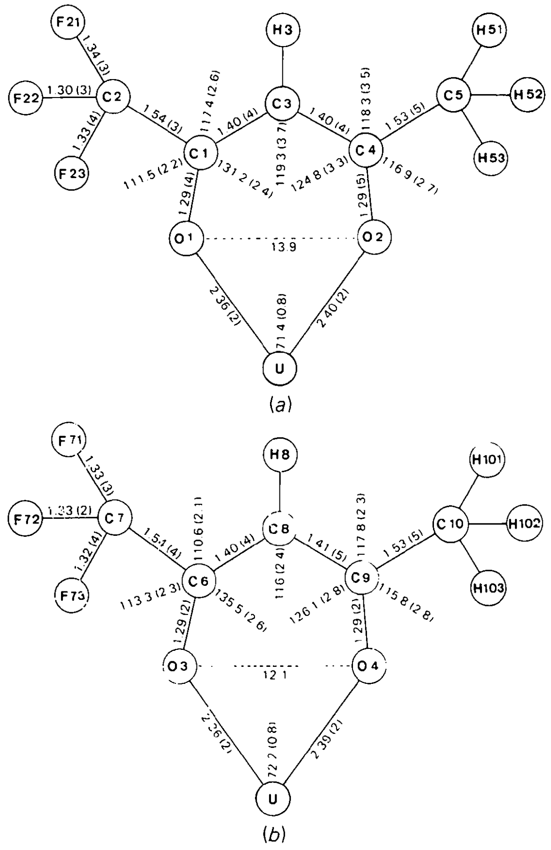

Fig. 1. Labeling of atoms and bond distances (Å) and angles (°) in (*a*) ligand *A*, (*b*) ligand *B*.

fluorine atoms of the CF_3 groups, particularly the group C(7)F(71)F(72)F(73), which is implicated both in rotational and packing disorders. Attempts to assign annex positions failed, due to the lack of crystal perfection. Another difficulty arose from the pseudo symmetry plane mentioned above, and concerned the large number of atoms lying near $y = 0$, the y coordinates of these atoms being difficult to refine: this is, of course, reflected in the accuracy of bond lengths and angles. Hydrogen atoms were introduced in calculated positions and not refined (C—H = 0·95 Å). Final R 0·076,* wR 0·092 (unit weights), S 12·1. Max. values of Δ/σ 0·55 [y O(1)], 0·34 [y O(2)]. Max. peak in final ΔF map 2·37 e Å^{-3} at 0·99 Å from uranium atom.

Discussion. The uranium environment shown in Fig. 2 is clearly a square antiprism: the local symmetry is very close to a tetrad axis. However, the polyhedron is very peculiar in the sense that the two square faces are different in size: the larger one $S1$, which corresponds to O(1), O(1′), O(3), O(3′) on the CF_3 side of the ligands, has edges 3·12 Å, while the smaller one $S2$, formed by O(2), O(2′), O(4), O(4′) on the CH_3 side of the ligands, has edges only 2·71 Å. However, the distances between the uranium atom and its eight oxygen neighbors are maintained at about the same value, by locating the uranium just 0·84 Å above the $S1$ square and 1·40 Å beneath the $S2$ square.

The U—O distances involving oxygen atoms close to CF_3 groups are probably shorter (2·36 Å) than the others (2·40 Å) though within e.s.d.'s. The bite angles are quite normal (72°), with l edges of the same length (2·79 Å).

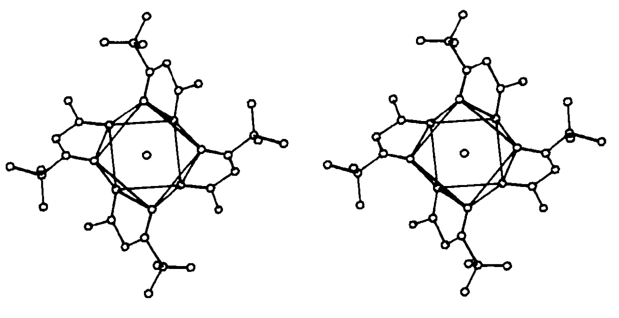

Fig. 2. Stereoscopic view of the molecular unit (*ORTEP*, Johnson, 1965).

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* Lists of observed and calculated structure factors, uranium anisotropic thermal parameters and coordinates of non-refined hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42269 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In such an antiprism configuration, this tetrakis bidentate chelate appears as representative of the subclass I*a* (*llll*) stereoisomer, fully described by Hoard & Silverton (1963) in their basic analysis of stereochemistry of discrete eight-coordinated complexes. To our knowledge, only one example of this configuration has been given for tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV) (Pinnavaia, Barnett, Podolsky & Tulinsky, 1975) with 'an idealized D_4 (*llll*) square-antiprism structure resembling a four-bladed propeller'. In the U(tfaa)$_4$ structure (Fig. 2) the dissymmetry of the ligand brings about a supplementary feature which does not break the nearly achieved D_4 symmetry: the ratio l/s no longer has a unique value, but two very different ones: 1·037 and 0·9058; the θ angle, between the molecular axis (here [010]) and the metal—oxygen bond also has two values, 54 and 69° respectively for CH_3 and CF_3 sides.

The two independent acetylacetonate rings are folded as usual along the O–O line by about 13°, the diketonate part of the rings being planar within 0·04 Å. No difference or marked double-bond character may be seen in the C—C bonds.

The crystal structure of U(tfaa)$_4$ consists of discrete molecules packed in such a way that intermolecular contacts between fluorine atoms are realized, as we have observed in the U(tfba)$_4$ structure, the shortest distance appearing between F(73) atoms (2·74 Å). The packing may also be understood as antiprisms linked by their square faces along the *b* axis, leading to a short U—U distance in this direction (6·43 Å), compared to others (12·87 and 10·74 Å).

The disorder affecting this structure concerns the packing of *ab* layers along the *c* axis, which is normally obtained by the glide plane *c*: it may be described as faults in translations which define ordered domains, the size of which are very dependent on the conditions of crystallization. Upon discarding the *l*-odd reflexions, the structure of the *ab* layers is obtained without the ordering by the glide plane. Such faults introduce a change of the origin by $c/2$ and lead to the superposition of atoms at $+y$ and $-y$. The contribution to the *hkl* structure factors is the same from the two kinds of domains for family reflexions ($l = 2n$) while they have contributions of opposite signs when $l = 2n + 1$. If the perturbation by frontier zones is considered as negligible, the structure may be reasonably solved using only the first group of reflexions.

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References

FRENZ, B. A. (1983). *Structure Determination Package*. College Station, Texas 77840, USA, and Enraf–Nonius, Delft, Holland.

HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**(2), 235–243.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

NAVAZA, A., DE RANGO, C. & CHARPIN, P. (1980). *Acta Cryst.* B**36**, 696–697.

PINNAVAIA, J., BARNETT, B. L., PODOLSKY, G. & TULINSKY, A. (1975). *J. Am. Chem. Soc.* **97**(10), 2712–2717.

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Structure du Complexe Bis(oxyde de triphénylphosphine)tétrakis(tétrahydroborato)uranium(IV) Solvaté avec le Benzène

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Abstract. $[U(BH_4)_4(C_{18}H_{15}OP)_2].2C_6H_6$, $M_r = 1010{\cdot}22$, triclinic, $P\bar{1}$, $a = 9{\cdot}794$ (4), $b = 11{\cdot}633$ (6), $c = 12{\cdot}038$ (5) Å, $\alpha = 103{\cdot}92$ (6), $\beta = 111{\cdot}53$ (3), $\gamma = 94{\cdot}40$ (6)°, $V = 1217{\cdot}5$ Å^3, $Z = 1$, $D_x = 1{\cdot}378$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 3·256 mm^{-1}, $F(000) = 504$, $T = 295$ K, final $R = 0{\cdot}065$ for 2787 observed independent reflexions. The U atom lies at the inversion center and is hexacoordinated by two triphenylphosphine oxide ligands in *trans* positions [U—O = 2·27 (1) Å] and four tetrahydroborate ions; the two significantly different U—B distances [2·55 (3) and 2·75 (3) Å] seem to indicate tridentate and bidentate bonding for the BH_4^- ions. The benzene molecules are not in the immediate environment of the metal atom and lead to the formulation of the compound as a solvate.

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