

water molecules form intermolecular hydrogen bonds with the COOH oxygens, and the distances O—H—O are 2.982 and 2.996 Å (Fig. 6). Other molecular contacts less than 3.2 Å are listed in Table 9. The packing of the molecules is shown in Figs. 6 and 7 along **b** and **c** respectively.

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## Structural Studies on the Actinide Carboxylates.

### I. The Crystal and Molecular Structure of Oxydiacetatodioxouranium(VI)

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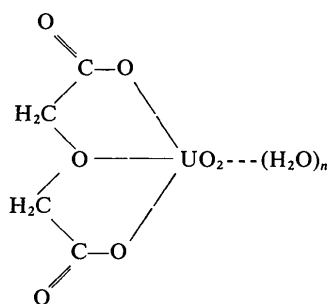
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The crystal structure of oxydiacetatodioxouranium(VI),  $\text{UO}_2$  (oxydiacetato), has been determined from three-dimensional X-ray diffractometer data. The complex crystallizes in the tetragonal space group  $P4_12_12$ ,  $Z=4$ ,  $a=8.148(3)$ ,  $c=11.051(3)$  Å. The structure was determined by the heavy-atom method and refined by full-matrix least-squares to  $R=0.038$ . The uranyl ions are equatorially surrounded by four carboxylate oxygen atoms and one ether oxygen atom, forming an irregular pentagonal bipyramid. Each ligand is shared between three uranyl units so that the structure can be described in terms of a three-dimensional network of cross-linked uranium-ligand chains.

#### Introduction

The possibility of obtaining stable complexes by reaction between the actinyl ions  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ , and  $\text{PuO}_2^{2+}$  and such ligands as oxydiacetate, iminodiacetate, thiodiacetate and glutarate has been discussed together with their probable structures in solution (Casal Di Bernardo, Portanova & Magon, 1973).

In particular the presence of monomeric species of the type:



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was proposed for the 1:1 chelate complex formed when the concentration of the oxydiacetate ligand corresponds to  $\bar{n}$  values in the range  $0 < \bar{n} < 1$  ( $\bar{n}$  = average number of ligands bound to each uranyl group). Similar structures in which the ligand behaves as tridentate through the two carboxylic groups and the central donor atom could, in principle, be postulated in the solid state also. In this case, if the water molecules are lost, the formation of polymeric species is expected.

With the aim of correlating the behaviour in solution with the coordination mode in the solid state the structure of the solid  $\text{UO}_2$ (oxydiacetate) complex has been determined by X-ray analysis.†

#### Experimental

The compound was prepared from uranyl nitrate and oxydiacetic acid as described before (Bombieri *et al.*, 1972).

*Crystal data:* –  $\text{C}_4\text{H}_4\text{O}_7\text{U}$ , F.W. 402, tetragonal,

† A preliminary account of this structure is given by Bombieri, Forsellini, Graziani, Tomat & Magon (1972).

$a = 8.148 (3)$ ,  $c = 11.051 (3)$  Å,  $U = 734$  Å<sup>3</sup>,  $D_c = 3.64$  for  $Z = 4$ . Mo  $K\alpha$  radiation  $= 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 203 \text{ cm}^{-1}$ . From the systematic absences ( $00l, l \neq 4n$ ;  $h00, h \neq 2n$ ) the possible space groups are  $P4_21_2$  and  $P4_32_1$ . The former was chosen on the basis of the structure determination.

The value of  $Z$  requires that the molecular lies on a crystallographic twofold axis.

Pale yellow c-prismatic crystals were used for the X-ray analysis. Space group and approximate cell parameters were determined initially from Weissenberg and precession photographs. After alignment of the crystal on a Siemens four-circle automatic diffractometer, the cell parameters were refined by a least-squares method using 12 high-angle reflexions measured with Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å).

A very small crystal whose approximate dimensions were  $0.10 \times 0.04 \times 0.30$  mm was mounted with the  $c$

axis parallel to the  $\phi$  axis of the goniometer, and the data were collected on a computer-controlled Siemens A.E.D. using the  $\theta = 2\theta$  scan and the five-point measuring procedure up to  $\theta_{\text{max}} = 27^\circ$ . About 4000 reflexions were collected corresponding to eight equivalent sets of data.

Owing to the very irregular dimensions of the crystal used (all attempts to obtain better crystals have been unsuccessful) we chose from two equivalent sets of reflexions, those which seemed less affected by absorption (the highest values of intensities) with the aim of reducing the large effect of absorption.

Of the 512 available independent reflexions, 42 with intensities  $I \leq 2\sigma(I)$  were considered unobserved and were given zero weight in the subsequent refinement.

All calculations were carried out on the CDC 6600 computer using the X-RAY System of Crystallographic Programs (Stewart, Kundell & Baldwin, 1970).

Table 1. *Final atomic parameters ( $\times 10^4$ ) with estimated standard deviations*

Thermal parameters,  $U_{ij}$  (Å<sup>2</sup> × 10<sup>4</sup>) are defined by:

$$\exp[-2\pi^2(U_{11}a^*h^2 + U_{22}b^*k^2 + U_{33}c^*l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$$

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
U	3957 (1)	6043 (1)	2500	210 (3)	210 (3)	422 (5)	-18 (4)	-5 (4)	5 (4)
O(1)	3876 (16)	1152 (17)	670 (11)	262 (63)	335 (69)	475 (70)	-112 (72)	16 (63)	-54 (67)
O(2)	3370 (17)	3522 (16)	1529 (13)	266 (81)	229 (89)	709 (91)	63 (50)	-158 (75)	-141 (72)
O(3)	6174 (15)	3826 (15)	2500	230 (58)	230 (58)	1617 (241)	-176 (89)	-379 (146)	379 (146)
O(4)	3261 (16)	5242 (17)	3918 (11)	295 (69)	373 (76)	344 (62)	4 (62)	96 (61)	16 (63)
C(1)	4350 (24)	2329 (23)	1280 (17)	424 (124)	215 (95)	309 (84)	-48 (79)	-156 (97)	-27 (78)
C(2)	5973 (25)	2330 (22)	1855 (18)	281 (93)	260 (92)	555 (113)	165 (90)	-170 (104)	-153 (90)

Table 2. *Observed and calculated structure factors*

Columns are  $h$ ,  $10F_o$  and  $10F_c$ . Unobserved reflexions are marked by \*.

$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$	$h$	$10F_o$	$10F_c$
0	0	0	10	1140	1140	20	2310	2310	30	3540	3540	40	4000	4000
2	570	580	20	2310	2310	30	3540	3540	40	4000	4000	50	4500	4500
4	2055	2001	30	3540	3540	40	4000	4000	50	4500	4500	60	5000	5000
6	1215	1215	40	4000	4000	50	4500	4500	60	5000	5000	70	5500	5500
8	801	812	50	4500	4500	60	5000	5000	70	5500	5500	80	6000	6000
10	870	850	60	5000	5000	70	5500	5500	80	6000	6000	90	6500	6500

Continuation of Table 2 (Observed and calculated structure factors). Columns are  $h$ ,  $10F_o$  and  $10F_c$ . Unobserved reflexions are marked by \*.

Atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962).

### Structure determination

The structure was solved by the heavy-atom method. The four uranium atoms lie on twofold axes [equipoint 4(a)]. Their positions were found from the Patterson map and all other atoms were located from Fourier difference syntheses phased on the heavy atom. Three cycles of full-matrix least-squares refinement with isotropic temperature factors and  $w=1$  reduced  $R$  to 9%. After correction for anomalous scattering by uranium ( $\Delta f'$  and  $\Delta f''$  were taken from Cromer, 1965), three more cycles of least-squares refinement in which the uranium atom was assigned an anisotropic temperature factor reduced the  $R$  value to 4.7%. Refinement was then continued with anisotropic thermal parameters for all atoms and convergence was reached with  $R=4.3\%$ .

The coordinates and the anisotropic temperature factors together with the scale factor were then improved in a series of least-squares refinements in which the quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , the weights  $\omega$  being calculated according to the expression

$$\omega = 1 / \left[ 1 + \left( \frac{|F_o| - b}{a} \right)^2 \right].$$

In the last cycle the values  $a=140$  and  $b=120$  were used. After a number of cycles the discrepancy indices  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $\omega R = \sum \omega (|F_o| - |F_c|)^2 / \sum \omega \times |F_o|^2$  had converged to 3.8% and 4.0% respectively. In the last cycle no parameter shift was  $>0.1\sigma$ .

A cycle of the refinement in space group  $P4_32_12$  with all the  $z$  coordinates negative gave  $R=4.1\%$  and  $R\omega=4.3\%$  and therefore  $P4_12_12$  was taken as the correct space group.

The final atomic coordinates and thermal parameters with their estimated standard deviations are listed in Table 1. Observed and calculated structure factors are listed in Table 2.

Bond lengths and bond angles are listed in Table 3 (see Fig. 1 for labelling of the atoms). In Table 4 are reported the equations of some selected atomic planes of the molecule.

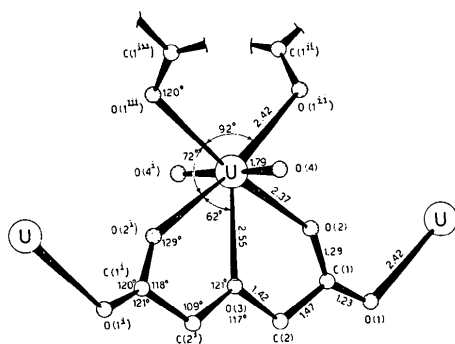


Fig. 1. Bond lengths and valency angles in  $UO_2(\text{oxydiacetato})$ .

Table 3. *Intramolecular bond lengths (Å) and bond angles (°)*

The e.s.d.'s (in parentheses) are in units in the last figure.

U-O(1 <sup>ii</sup> )	2.42 (1)	C(1)-O(1)	1.23 (2)
U-O(2)	2.37 (1)	C(1)-O(2)	1.29 (2)
U-O(3)	2.55 (1)	C(1)-C(2)	1.47 (3)
U-O(4)	1.79 (1)	O(3)-C(2)	1.42 (2)
O(4)-U-O(4')	176.1 (5)		
O(1 <sup>ii</sup> )-U-O(1 <sup>iii</sup> )	91.3 (5)		
O(1 <sup>ii</sup> )-U-O(2)	72.6 (5)		
O(2)-U-O(3)	62.0 (4)		
U-O(1 <sup>ii</sup> )-C(1 <sup>ii</sup> )	120 (1)		
U-O(2)-C(1)	129 (1)		
O(2)-C(1)-O(1)	120 (2)		
O(1)-C(1)-C(2)	121 (2)		
O(2)-C(1)-C(2)	118 (2)		
U-O(3)-C(2)	121 (1)		
C(2)-O(3)-C(2')	117 (2)		
O(3)-C(2)-C(1)	109 (1)		
Non-bonded intramolecular distances (Å)			
O(1)···O(2)	2.19 (2)		
O(2)···O(3)	2.54 (2)		
O(2)···O(1 <sup>ii</sup> )	2.84 (2)		
O(1 <sup>ii</sup> )···O(1 <sup>iii</sup> )	3.33 (2)		

Table 4. *Least-squares planes*

Coordinates refer to the directions of the crystallographic axes.

- (1)  $-0.3076x - 0.3013y + 0.9025z = 0.0180$   
[U-O(1<sup>ii</sup>)-O(1<sup>iii</sup>)]
- (2)  $-0.3635x - 0.3635y + 0.8578z = -0.5917$   
[U-O(2)-O(3)]
- (3)  $-0.3469x - 0.4652y + 0.8145z = -0.9294$   
[O(2)-O(3)-C(1)-C(2)]

[Deviations: O(2) 0.018 Å; O(3) -0.015 Å; C(1) -0.031 Å; C(2) 0.028 Å]

Dihedral angles: Planes 1 and 2, 5.4°; 2 and 3, 6.4°

The codes for symmetry-related atoms are as follows:

Symbol	Symmetry code		
	$x$	$y$	$z$
i	$\bar{y}$	$\bar{x}$	$\frac{1}{2} - z$
ii	$\frac{1}{2} - x$	$\frac{1}{2} + y$	$\frac{3}{4} - z$
iii	$\frac{1}{2} - y$	$\frac{1}{2} + x$	$\frac{3}{4} + z$

### Description of the structure

In the uranyl oxydiacetato complex the uranyl ions are equatorially surrounded by four carboxylate oxygen atoms and one ether oxygen atom forming an irregular pentagonal bipyramid.

The ligand molecule is shared between three uranium atoms and shows nearly  $C_{2v}$  symmetry.

Two carboxylate oxygens [O(2) and O(2')] and the ether oxygen of each ligand form two identical five-membered rings with the central atom, while the carboxylate oxygens O(1) and O(1') are linked to two contiguous uranium atoms. The two other coordination sites are occupied by the oxygen atoms O(1<sup>ii</sup>) and O(1<sup>iii</sup>) of two different ligands. The linear uranyl

group, [U–O=1.79 (2) Å] is perpendicular to the equatorial plane. The structure is polymeric and can be described in terms of a three-dimensional network of cross-linked uranium–ligand chains, as shown in Fig. 2 in which the unit-cell content is projected along the *a* axis.

Atoms coordinated to uranium are not exactly coplanar. Plane [U, O(1<sup>ii</sup>), O(1<sup>iii</sup>)] forms a dihedral angle of 5.4° with plane [U, O(2), O(3), O(2<sup>i</sup>)], and this plane forms a dihedral angle of 6.4° with plane [O(2), O(3), C(1), C(2)], so that the only symmetry the chemical units possess is the crystallographic twofold axis along the U–O(3) bond direction. The U–O distances are not equivalent. As expected, the distance between uranium and the ether oxygen O(3) is significantly greater (by 0.15 Å) than the average of the two independent U–O(1)

and U–O(2) bond distances. This difference compares favourably with the values of 0.10 and 0.09 Å found in the isomorphous pair Na<sub>3</sub>[Nd(ODA)<sub>3</sub>].NaClO<sub>4</sub> and Na<sub>3</sub>[Yb(ODA)<sub>3</sub>].2NaClO<sub>4</sub>.6H<sub>2</sub>O (Albertsson, 1968, 1970) (ODA = oxydiacetato). The value of the U–O(2) bond [2.37 (1) Å] is normal for uranyl complexes with five oxygens coordinated in the equatorial plane (Panattoni, Graziani, Bandoli, Zarli & Bombieri, 1969; Dalley, Mueller & Simonsen, 1971). The difference of about 0.05 Å from the U–O(1) bond length [2.42 (1) Å] seems to suggest that the negative charges are mainly located on the two O(2), O(2<sup>i</sup>) oxygen atoms (crystallographically equivalent). The difference of 10° between the U–O(2)–C(1) angle [129 (1)°] and the U–O(1)–C(1) angle [120 (1)°] is probably related to small strains due to bridging. The ether oxygen–carbon bond length

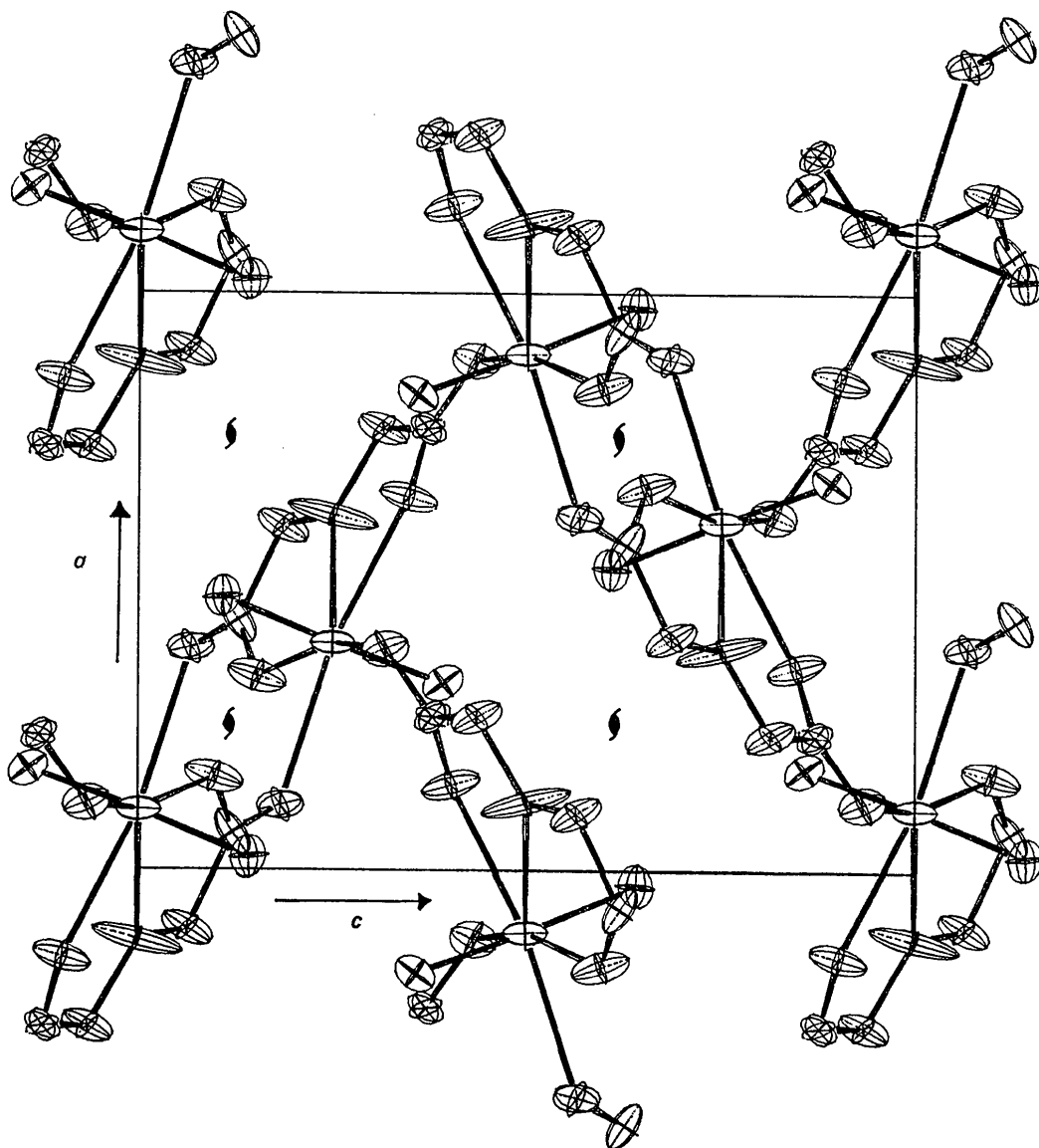


Fig. 2. Projection of the structure along the *a* axis. Thermal motion ellipsoids of 50% probability. The projection was drawn using *ORTEP* (Johnson, 1965).

[1.42 (2) Å] has the usual single-bond value (André, Fourme & Zechmeister, 1972; Jeffrey & Park, 1972), and the C(2)–O(3)–C(2<sup>1</sup>) angle of 117 (2)° is consistent with the observations reported for other ethers and is close to the value of 115° found in Na<sub>3</sub>[Yb(ODA)<sub>3</sub>]·2NaClO<sub>4</sub>·6H<sub>2</sub>O.

The C(1)–C(2)–O(3) angle has the expected tetrahedral value while the three angles subtended at C(1) are very close to 120°.

The oxygen–oxygen contact distances along the edges of the uranium coordination polyhedron are reported in Table 3.

Apart from the O(1<sup>ii</sup>)–O(1<sup>iii</sup>) contact of 3.33 Å, all distances between the coordinated oxygen atoms, except those belonging to the same ligand are in the range 2.83–2.99 Å, *i. e.* larger than twice the van der Waals radius of oxygen (1.4 Å).

However, the relatively small hindrance of the organic ligand, as well as the fact that each chemical unit is linked to four others, causes the structure to be very compact, so that there are relatively short U–U contacts of 5.46 and 6.03 Å.

Finally we point out that from the solution a three-dimensional polymeric covalent crystal has been obtained.

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## An Improved Structure of *trans*-Stilbene\*

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The structure of *trans*-stilbene has been reinvestigated and an improved set of structure parameters determined. Cell constants of  $a=15.710$  (4),  $b=5.723$  (1),  $c=12.381$  (3) Å and  $\beta=111.89$  (4)° were measured and the space group  $P2_1/c$  with  $Z=4$  was confirmed. Least-squares refinement of all atoms including the hydrogen atoms converged to an  $R$  of 0.072. The molecule was found to be almost planar with the phenyl rings only slightly twisted from the general plane of the molecule. A disorder similar to that found for the isostructural compound, azobenzene, has been observed. Various parameters have been compared with those found in the earlier work.

### Introduction

There appeared in the literature (Robertson & Woodward, 1937) some time ago an X-ray structure determination of *trans*-stilbene (I). The analysis suffers from many of the problems which early crystallographers faced: comparatively inaccurate data collection methods, solution of structure in projection, poor e.s.d.'s, and limited computational facilities. However, this

structure has been used by numerous authors in the last few years as the basis for MO calculations (Ljunggren & Wettermark, 1970; Bromberg & Muszkat, 1972; Beringhelli, Gavezzotti & Simonetta, 1972), conclusions about u.v. geometries (Bernstein, 1972; Bürgi & Dunitz, 1971; Momicchioli, Baraldi & Bruni, 1972), and other results (Baughman, 1971; Frank, Myasnikova & Kitaigorodskii, 1971). We were in need of a better determination of the geometry of (I) for molecular mechanics work that is in progress (Allinger & Sprague, 1973) and consequently recollected the 3-D X-ray data and refined the structure of (I). We now report the findings of this study.

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