Acta Cryst. (1964). **17**, 758

The crystal structure of uranium(IV) acetate.

By I. Jelenić, D. Grdenić and A. Bezjak, *Department of Structural and Inorganic Chemistry, Rudjer Bošković Institute, Zagreb, Yugoslavia*

(*Received* 28 *October* 1963)

The present work forms part of a research program which is being carried out in this laboratory on octacoordination in complexes and salts of heavy metals. The structures of some quadrivalent metal acetylacetonates have already been determined (Grdenić & Matković, 1958, 1959; Matković & Grdenić, 1963). Attention has also been directed to 'ato-complexes' with acetate and nitrate ions (Kamenar, 1963; Šćavničar & Prodić, 1963). These anions can function both as unidentate and as bidentate ligands, but the crystallochemical factors deciding in favour of one of these two coordinations are not known. The structure analysis of uranium(IV) as well as of other heavy metal acetates was therefore undertaken.

The inconvenient form and size of the crystal specimen of uranium(IV) acetate made collection of accurate intensity data difficult. The large diffraction effect prevented the determination of interatomic distances in the surroundings of the uranium atom with an accuracy any better than ±0·05 Å. For this reason no further work is contemplated on this compound. The results reported have been obtained from two-dimensional Fourier syntheses evaluated from $hk0$, $hk1$ and $h0l$ reflexion intensity data.

Uranium(IV) acetate (Rosenheim & Kelmy, 1932) was prepared from uranyl(VI) acetate as will be described elsewhere (Grdenić, in preparation). The crystals obtained from glacial acetic acid were mainly fine fibers along the monoclinic c axis so that suitable specimens (about $0{\cdot}02 \times 0{\cdot}04$ mm^2 in cross-section) were very rare. Any attempts to grow larger specimens failed because of the low solubility of uranium(IV) acetate and its liability to oxidize in solution.

Table 1. *Crystallographic data for* $U(OCOCH_3)_4$

Monoclinic, space group $C2/c$ (C_{2h}^6)

$a = 17{\cdot}80$ Å	$Z = 4$
$b = 8{\cdot}35$ Å	
$c = 8{\cdot}33$ Å	$d_m = 2{\cdot}75$ g.cm^{-3} (flotation method)
$\beta = 106° \, 50'$	$d_x = 2{\cdot}64$ g.cm^{-3}

The crystallographic data are summarized in Table 1. Systematically absent reflexions were $hk1$ with $h+k$ odd, $h0l$ with h odd l odd. Of two possible space groups $C2/c(C_2^6)$ and $Cc(C_s^4)$ the former was found to be correct in the course of the analysis. No pyroelectric effect could be observed. The $hk0$, $hk1$, and $h0l$ reflexions were recorded on integrating Weissenberg photographs by the multiple-film technique (filtered Cu K radiation). The relative intensities were measured by means of a microdensitometer, except for very weak reflexions which were estimated visually. The corrections for polarization and Lorentz factors as well as for the absorption in prismatic crystals were made according to formulae given in *International Tables for X-Ray Crystallography* (1959).

In the space group $C2/c$ with $Z=4$ there are two possible locations of the uranium atoms: on twofold axes (one set of positions) or on the centres of symmetry (four sets of positions). Because the known polyhedra for octacoordinated uranium (square antiprism and trigonal dodecahedron) are not centrosymmetrical, the twofold axis symmetry location of uranium atoms was expected. Consequently, the position of the uranium atom is defined only by the y parameter, which was confirmed by means of the (x, y) Patterson projection. The y_U parameter obtained from the U–U vector in the Patterson projection was only approximate, because of its small value ($y_U = 0{\cdot}032$). The accurate value was obtained from the generalized $C_1(x,y)$ projection and checked by a trial and error procedure. The (x,y) (Fig. 1) and (x,z) electron-density distribution projections, calculated neglecting light atom contributions, unambiguously proved that there

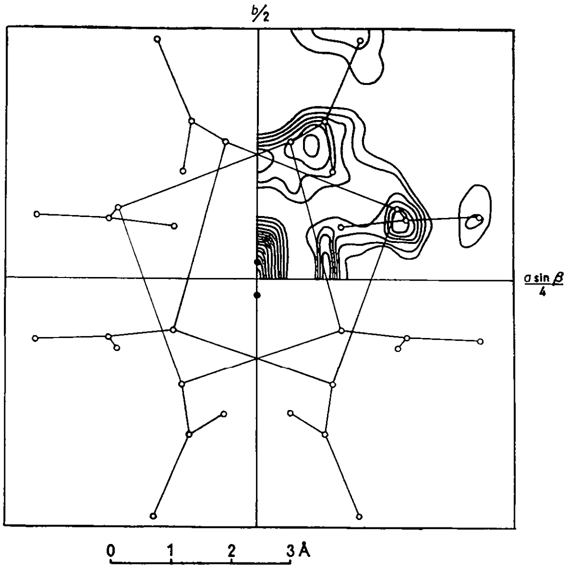

Fig. 1. The (x, y) Fourier synthesis of the electron density in a crystal of uranium(IV) acetate. Contours are drawn on an arbitrary scale.

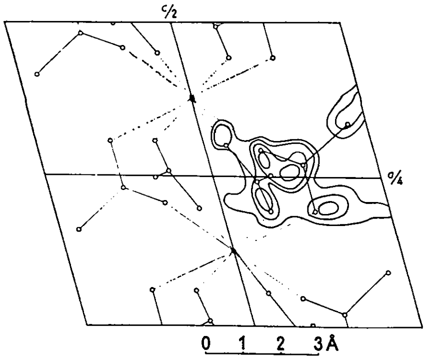

Fig. 2. The (x, z) Fourier difference synthesis with $(F_o - F_U)$. Contours are drawn on an arbitrary scale.

were no discrete $U(OCOCH_3)_4$ molecules in the structure. With the help of an (x,z) difference synthesis (Fig. 2) final coordinates were quite satisfactorily determined (Table 2). The temperature factor and the scale factor, calculated by Wilson's method, were $B(hk0) = 2{\cdot}2$ and $B(h0l) = 2{\cdot}6$ Å^2. The reliability indices are $R(hk0) = 0{\cdot}11$ and $R(h0l) = 0{\cdot}15$. The less reliable $F(h0l)$ values are explained by the inconvenient crystal form (b axis across the crystal needle) which greatly influenced the accuracy of recording $h0l$ intensity data. The secondary extinction correction for some low Bragg-angle reflexions was made according to Pinnock & Taylor (1956).

Table 2. *Atomic coordinates*

	x	y	z
U	0	0·032	1/4
O(1)	0·033	0·267	0·100
O(2)	0·075	0·208	−0·117
O(3)	0·083	−0·100	0·083
O(4)	0·135	−0·136	−0·120
C(1)	0·067	0·309	−0·010
C(2)	0·100	0·473	0·007
C(3)	0·145	−0·117	0·038
C(4)	0·222	−0·124	0·173

The structure is built up of infinite columns parallel to the c-axis direction in which each acetate ion belongs to two uranium ions (Fig. 3). Acetate-ion bridges are situated obliquely to the c-axis direction. Their oxygen atoms form square faces of the adjoining Archimedean antiprisms in the same way as already suggested for uranium(IV) dioctylpyrophosphate (Grdenić & Korpar, 1959). Because of the fixed O · · · O distance in the acetate ion, the antiprism is distorted. The amount of the distortion is best understood from the interatomic distances listed in Table 3. The U–O distances within one antiprism amount to 2·52 Å. But, owing to the fact that each following antiprism is displaced by about a half of its square face edge, two oxygen atoms (0(3) and 0(3′)) of two neighbouring polyhedra are considerably nearer to the uranium ion, at a distance of 2·80 Å instead of an average U · · · O distance of 3·58 Å, which proves the tendency of the acetate ion to act as a chelating ligand. The result is a coordination number of ten, which is accomplished in an antiprism with centred square faces. The actual coordination around the uranium ion is: two acetate ions with both their oxygen atoms near to uranium (2·52 and 2·80 Å) and six acetate ions with only one oxygen atom near to the same uranium ion (at 2·52 Å). In other words, the square face centred antiprisms of decacoordinated uranium ions form infinite $U(OCOCH_3)_4$ columns by sharing two opposite edges. The uranium–oxygen distances and the interatomic distances within the acetate ion tally well with the values obtained by previous authors for sodium uranyl acetate (Zachariasen & Plettinger, 1959).

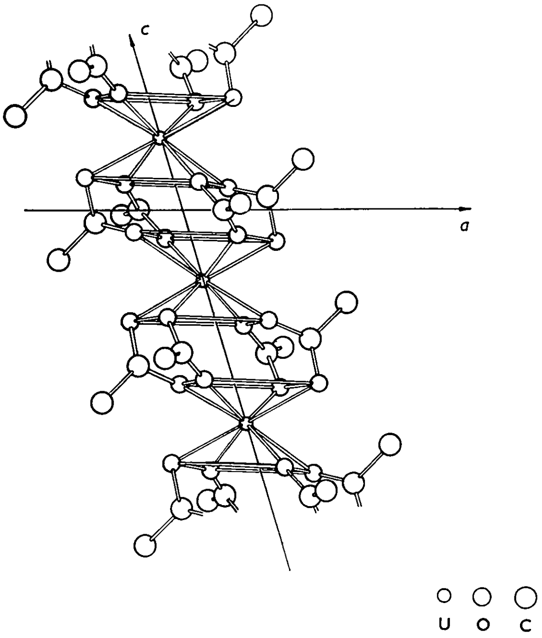

Fig. 3. Model of the polymer of uranium(IV) acetate.

Table 3. *Interatomic distances within a coordination polyhedron*

A single prime denotes a centre-of-symmetry relation to the atom defined by coordinates in Table 2

U–O(1)	2·49 Å	U–O(4′)	2·54 Å
U–O(2′)	2·55	U–O(3′)	2·80
U–O(3)	2·50 Å		

The polymeric structure explains the form of the crystals, their fibrous appearance, and the cleavage in the planes parallel to the c axis, as well as their low solubility in all common solvents. These properties are just opposite to those observed for the analogous lead(IV) acetate, the crystal structure of which is built up of discrete $Pb(OCOCH_3)_4$ molecules (Kamenar, 1963).

References

GRDENIĆ, D. & KORPAR, B. (1959). *J. Inorg. Nucl. Chem.* **12**, 149.

GRDENIĆ, D. & MATKOVIĆ, B. (1958). *Nature, Lond.* **182**, 465.

GRDENIĆ, D. & MATKOVIĆ, B. (1959). *Acta Cryst.* **12**, 817.

International Tables for X-ray Crystallography (1959). Vol. II. Birmingham: Kynoch Press.

KAMENAR, B. (1963). *Acta Cryst.* Supplement, A 34.

MATKOVIĆ, B. & GRDENIĆ, D. (1963). *Acta Cryst.* **16**, 456.

PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173.

ROSENHEIM, A. & KELMY, M. (1932). *Z. anorg. Chem.* **206**, 33.

ŠĆAVNIČAR, S. & PRODIĆ, B. (1963). *Acta Cryst.* Supplement, A 33.

ZACHARIASEN, N. H. & PLETTINGER, H. A. (1959). *Acta Cryst.* **12**, 526.