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Crystal Chemical Studies of the 5*f*-Series of Elements. XXV. The Crystal Structure of Sodium Uranyl Acetate*

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Sodium Uranyl acetate, $NaUO_2(O_2CCH_3)_3$, is cubic with space group $P2_13$ and $a = 10{\cdot}688 \pm 0{\cdot}002$ Å. The positions of all atoms were deduced from precisely measured X-ray diffraction intensities. In the collinear uranyl group U–O = 1·71±0·04 Å. Normal to the uranyl axis are six secondary bonds from uranium to acetate oxygens with U–O = 2·49±0·02 Å. Sodium is bonded to six acetate oxygens with Na–O = 2·37±0·04 Å. The bond lengths within the acetate group are C–C = 1·52±0·05 Å, C–O = 1·26±0·05 Å and 1·28±0·04 Å, and 121° is found for the carboxyl bond angle. A revised bond length *versus* bond strength curve for U^{VI}–O bonds is presented.

Introduction

Earlier crystal structure studies of uranyl salts have given some information about the crystal chemistry of these compounds. It has been shown that the uranium atom, in addition to the two strong uranyl bonds, forms four, five or six secondary bonds to oxygen or fluorine atoms. The positions of the light atoms have been determined with precision only for a small number of structures; but it was found that the lengths of the primary as well as of the secondary bonds varied considerably from compound to compound. This variation has been correlated with corresponding variation in the bond strengths (Zachariasen, 1954*a*). However, the published empirical bond length *versus* bond strength curve was based upon a small number of observations, and the present investigation was undertaken in the hope of obtaining further reliable experimental results.

The crystal structure of sodium uranyl acetate, $NaUO_2(OOCCH_3)_3$, was first studied by I. Fankuchen (1935). He reported the space group $P2_13$ and four molecules in a unit cube with $a = 10{\cdot}670 \pm 0{\cdot}001$ kX. Fankuchen described a complete structure; but only the uranium sodium and uranyl oxygen positions were deduced from the observed intensities. However, this early work gave the important result that the uranyl radical, by space group symmetry, had to be collinear.

The isostructural neptunium and plutonium compounds were identified during the war (Zachariasen, 1949). A unit cube of $a = 10{\cdot}659 \pm 0{\cdot}002$ kX. was reported for the neptunium and of $a = 10{\cdot}643 \pm 0{\cdot}002$ kX. for the plutonium compound. The analogous americium compound has since been added to the isostructural series (Ellinger, 1956).

Experimental procedure

The structure analysis of $MgUO_2O_2$ (Zachariasen, 1954*b*) and of $K_3UO_2F_5$ (Zachariasen, 1954*c*) demonstrated that it is possible by X-ray diffraction methods to locate the positions of light atoms in the presence of uranium to an accuracy of 0·03 Å. In order to reach this precision it is necessary to measure intensities with an accuracy attainable only with counters and to correct accurately for absorption and extinction effects.

Crystals were prepared by slow evaporation from a solution of uranyl nitrate and sodium acetate in molar proportions. Most of the crystals so obtained were found unsuitable for intensity measurements, as the X-ray showed a seemingly single crystal to consist of two or more individuals in slight misalignment. However, two excellent specimens were eventually found, and these were made into nearly perfect spheres in the Bond Sphere Grinder. The radii of the two spheres were 0·0116±0·0002 cm. and 0·0122±0·0003 cm., where the limits of error denote the extreme variation.

The intensity measurements were carried out with a General Electric XRD Spectrometer rebuilt for single crystal work, using filtered Cu K radiation and a proportional counter. The intensities of all possible $HK0$ reflections were measured. Because of the very high absorption ($\mu = 470$ cm.$^{-1}$) very small departures from perfect spherical shape give rise to large intensity differences for equivalent reflections. In extreme cases it was found that the intensity could vary by as much as thirty per cent from one equivalent plane to another, while intensity measurements for a given plane were reproducible to two per cent. In order to minimize this source of error measurements were made for all planes of the same crystallographic form and the average taken. As a means of further reducing the experimental errors complete $HK0$ data were ob-

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tained for both crystal spheres described above. When the intensities were reduced to structure factors, there was nearly perfect agreement between the two sets of complete data.

Determination of the structure

In agreement with Fankuchen's early work it was found that $a = 10{\cdot}688 \pm 0{\cdot}002$ Å with four molecules per unit cell and space group $P2_13$. The positions of this space group are:

$$\begin{array}{ll} 4a & (x, x, x);\ (\tfrac{1}{2}+x, \tfrac{1}{2}-x, \bar{x}) \circlearrowleft; \\ 12b & (x, y, z) \circlearrowleft;\ (\tfrac{1}{2}+x, \tfrac{1}{2}-y, \bar{z}) \circlearrowleft; \\ & (\tfrac{1}{2}+y, \tfrac{1}{2}-z, \bar{x}) \circlearrowleft;\ (\tfrac{1}{2}+z, \tfrac{1}{2}-x, \bar{y}) \circlearrowleft. \end{array}$$

The uranium atoms must be in positions $4a$. The single parameter for uranium is readily determined from chance absences and from measured structure factor ratios $|F_{HK0}|/|F_{KH0}|$ for $H+K$ odd and large. As a preliminary value subject to further refinement one finds easily $x = 0{\cdot}429 \pm 0{\cdot}001$.

Since the uranium scattering predominates, and since there are inversion centers in the XY projection, the positions of the light atoms were found directly from Fourier syntheses of the type $\int_0^1 \varrho\, dz$. Difficulties due to partial superposition of non-equivalent atoms were eliminated by the use of difference syntheses. The first synthesis to be carried out, $\int_0^1 (\varrho - \varrho_u)\, dz$, gave approximate coordinates for sodium and oxygen atoms. These atoms were then removed in the second difference synthesis, and preliminary positions for the carbon atoms were obtained. Further refinements were carried out with the aid of difference syntheses in which the effect of all but one set of atoms at a time was removed. Four such successive refinements were made. The final set of parameters so obtained is shown in Table 1. The atoms U, Na, O_I and O_{II} are in the special positions $4b$ and all other atoms in general positions $12b$. Actual X-RAC photographs for two of the difference syntheses are shown in Fig. 1(a) and (b).

Table 1. *Atomic coordinates*

		Fankuchen (1935)	This study
U	x	$0{\cdot}428 \pm 0{\cdot}002$	$0{\cdot}4292 \pm 0{\cdot}0003$
Na	x	$0{\cdot}81 \pm 0{\cdot}03$	$0{\cdot}8289 \pm 0{\cdot}0006$
O_I	x	$0{\cdot}31 \pm 0{\cdot}02$	$0{\cdot}336 \pm 0{\cdot}002$
O_{II}	x	$0{\cdot}55 \pm 0{\cdot}02$	$0{\cdot}521 \pm 0{\cdot}002$
O_{III}	x	—	$0{\cdot}382 \pm 0{\cdot}002$
	y	—	$0{\cdot}291 \pm 0{\cdot}001$
	z	—	$0{\cdot}608 \pm 0{\cdot}001$
O_{IV}	x	—	$0{\cdot}551 \pm 0{\cdot}001$
	y	—	$0{\cdot}241 \pm 0{\cdot}001$
	z	—	$0{\cdot}500 \pm 0{\cdot}002$
C_I	x	—	$0{\cdot}482 \pm 0{\cdot}001$
	y	—	$0{\cdot}229 \pm 0{\cdot}002$
	z	—	$0{\cdot}598 \pm 0{\cdot}001$
C_{II}	x	—	$0{\cdot}509 \pm 0{\cdot}002$
	y	—	$0{\cdot}118 \pm 0{\cdot}002$
	z	—	$0{\cdot}683 \pm 0{\cdot}001$

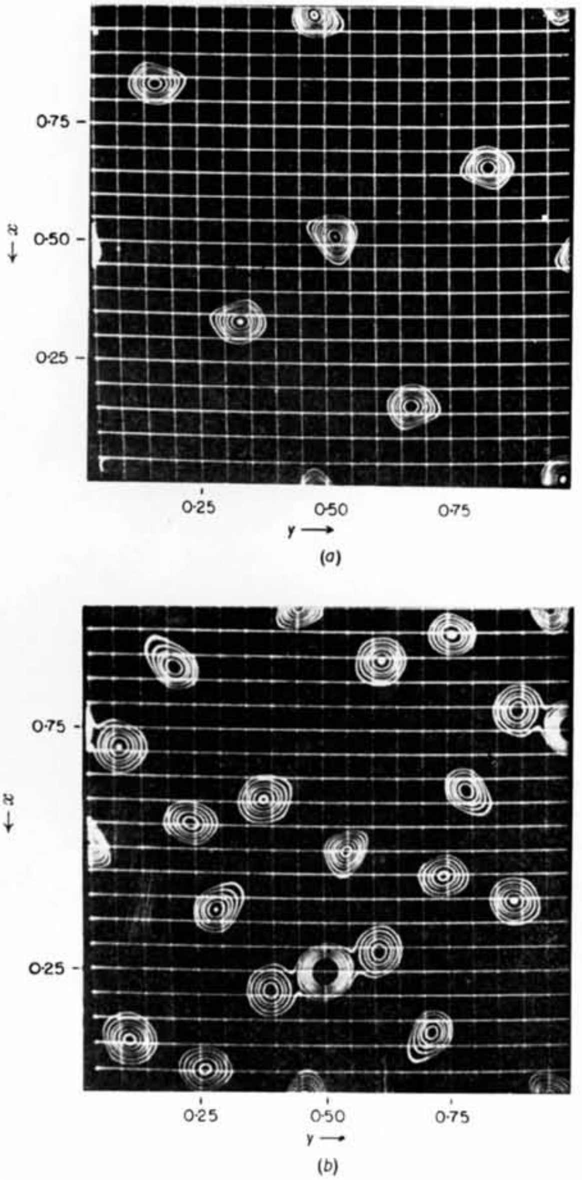

Fig. 1. (a) shows the X-RAC photograph of a Fourier difference synthesis in which all but the uranyl oxygens have been removed. The two lowest contour lines have been deleted. (b) is an X-RAC photograph of a Fourier difference synthesis with all but acetate oxygen atoms removed. The large peak at $x = \frac{1}{4}$, $y = \frac{1}{2}$ is due to the superposition of two O_{IV} atoms.

In the refinement process it was assumed that the heat motion could be represented adequately by two isotropic temperature factors, one for uranium and the other common to all light atoms. The effective scattering power of uranium was taken to be $f - 5{\cdot}0 + i14{\cdot}0$, where f is the normal f-curve without anomalous dispersion (Dauben & Templeton, 1955). The imaginary term in the anomalous dispersion was taken into account by applying a correction to the experimental structure factors. This correction is

$$F_{\text{corr.}} = (|F_{\text{obs.}}|^2 - |F'_U|^2)^{\frac{1}{2}} \tag{1}$$

where F'_U is the structure factor for the uranium atoms resulting from the imaginary dispersion term alone. This correction is small, but not constant, and hence it could not be incorporated in the scale factor.

In the course of the refinement, it was found that extinction effects were small, but not negligible. For small extinction the intensity correction is

$$I_{\text{corr.}} = I_{\text{obs.}}/(1 - 2gI_{\text{obs.}})$$

where $2gI_{\text{obs.}} \ll 1$ for the strongest reflection. Hence, extinction correction can be applied to the experimental structure factors as follows

$$F_{\text{corr.}} \approx F_{\text{obs.}}(1 + kI_{\text{obs.}}) \tag{2}$$

where k is a constant.

When the investigation was undertaken there was neither hope nor expectation that the hydrogen atoms would show up in the Fourier projections in the presence of the heavy uranium atoms. However, in several of the difference syntheses small and diffuse secondary maxima and irregularities in the lowest contour lines about oxygen and carbon peaks were observed. A difference synthesis with all but hydrogen atoms was therefore carried out. Only terms for which $\sin\theta/\lambda < 0{\cdot}3$ were included. The resulting X-RAC summation showed small peaks at the uranium positions (indicating that the scale factor was too small by a fraction of one per cent) and peaks corresponding to three sets of atoms in general positions 12*b*. The coordinates of these maxima were not consistent to better than 0·03 because of diffuseness and superposition, and there was also considerable variation in the heights of the peaks. These concentrations of residual scattering matter were at distances of 0·8–1·5 Å from the C_{II} atoms and are probably to be identified as the hydrogen atoms. In Table 2 are shown the crude hydrogen coordinates as obtained directly from the X-RAC photographs as well as a set of idealized coordinates. The latter set was deduced from the experimental values by adjustments within experimental error so as to yield more reasonable C–H bond lengths and bond angles.

Table 2. *Hydrogen coordinates*

		Experimental values		Idealized
H_I	*x*	0·43	0·46	0·43
	y	0·06	0·08	0·06
	z	0·67	0·69	0·67
H_{II}	*x*	0·56	0·57	0·52
	y	0·17	0·20	0·15
	z	0·77	0·81	0·77
H_{III}	*x*	0·58	0·59	0·58
	y	0·04	0·06	0·07
	z	0·66	0·67	0·65

Table 3. *Observed and calculated structure factors**

*HK*0	F_o	F_c	*HK*0	F_o	F_c
110	45·0	−45·6	660	30·3	31·1
200	54·2	55·1	830	10·8	−10·1
210	26·7	27·1	380	1·8	−2·1
120	51·3	50·2	750	3·3	5·1
220	23·3	24·2	570	25·6	25·9
310	45·1	−46·1	840	8·0	6·9
130	13·3	14·1	480	9·5	9·8
320	2·1	0·9	910	22·2	20·4
230	40·5	43·4	190	9·4	10·4
400	7·8	−7·7	920	14·2	−13·6
410	27·1	28·3	290	21·1	−19·4
140	48·7	48·1	760	15·6	−15·5
330	6·4	−4·2	670	0	1·1
420	8·4	7·2	850	7·7	−8·8
240	2·8	1·6	580	5·4	7·3
430	60·9	59·9	930	4·2	3·6
340	9·1	9·4	390	23·0	20·5
510	42·5	−42·2	940	22·6	−20·7
150	8·2	9·6	490	22·4	−22·2
520	42·3	−44·0	770	0	−0·7
250	34·9	35·8	10,0,0	6·1	−3·5
440	9·3	10·1	860	21·2	20·6
530	18·9	−18·9	680	18·6	18·1
350	24·5	25·7	10,1,0	7·5	−8·0
600	37·6	−38·0	1,10,0	25·2	−24·6
610	3·7	3·2	10,2,0	2·8	−2·9
160	16·0	16·5	2,10,0	8·2	−7·4
620	31·2	−30·2	950	13·4	−12·7
260	32·4	−35·9	590	9·7	7·9
540	26·4	29·2	10,3,0	25·1	−24·1
450	32·0	34·2	3,10,0	8·2	−8·4
630	26·3	26·2	870	0	−0·4
360	0	−0·5	780	8·2	8·6
710	0	−0·4	10,4,0	0	0
170	17·3	19·1	4,10,0	0	0·7
550	25·6	26·6	960	7·5	−5·7
640	5·3	3·9	690	7·1	−6·3
460	3·2	1·5	11,1,0	23·5	21·4
720	35·1	−34·5	1,11,0	4·3	−4·2
270	4·4	6·1	11,2,0	1·7	1·1
730	7·4	7·8	2,11,0	16·2	−15·7
370	43·8	44·7	10,5,0	16·3	−15·1
650	15·0	15·3	5,10,0	9·6	9·4
560	13·9	−14·3	880	18·0	16·7
800	33·2	−29·9	11,3,0	5·2	5·6
810	7·1	−7·4	3,11,0	1·4	−1·9
180	15·5	−15·5	970	16·2	−16·4
740	41·3	−40·2	790	3·2	2·5
470	4·4	4·6	10,6,0	4·3	4·1
820	17·5	−17·6	6,10,0	2·1	1·8
280	20·5	−20·7			

* Values are given per stoichiometric molecule. When *H* is odd, the structure factor is purely imaginary.

Table 3 shows the observed and calculated structure factors. The observed values have been corrected for extinction (equation (2)) and for the imaginary part of the anomalous dispersion in uranium (equation (1)). The *f*-curve of Thomas–Fermi as given in *Internationale Tabellen* was used for uranium, of McWeeny (1951) for hydrogen, and of Berghuis *et al.* (1955) for the other atoms. The following temperature factors were obtained: $B = 2{\cdot}9$ Å^2 for uranium, and $B = 3{\cdot}6$ Å^2 for the light atoms. The agreement between experimental and calculated structure factors corresponds to

$$R = \Sigma||F_o| - |F_c|| \div \Sigma|F_c| = 0{\cdot}055\,.$$

Bond lengths

The lengths of the bonds formed by the various atoms in the structure are:

$\text{U}-1\,\text{O}_{\text{I}} = 1\cdot72\pm0\cdot04$ Å
$-1\,\text{O}_{\text{II}} = 1\cdot70\pm0\cdot04$ Å
$-3\,\text{O}_{\text{III}} = 2\cdot47\pm0\cdot02$ Å
$-3\,\text{O}_{\text{IV}} = 2\cdot51\pm0\cdot02$ Å

$\text{Na}-3\,\text{O}_{\text{III}} = 2\cdot39\pm0\cdot04$ Å
$-3\,\text{O}_{\text{IV}} = 2\cdot36\pm0\cdot04$ Å

$\text{C}_{\text{I}}-1\,\text{C}_{\text{II}} = 1\cdot52\pm0\cdot05$ Å
$-1\,\text{O}_{\text{III}} = 1\cdot26\pm0\cdot05$ Å
$-1\,\text{O}_{\text{IV}} = 1\cdot28\pm0\cdot04$ Å
$\text{O}_{\text{III}}-\text{C}_{\text{I}}-\text{O}_{\text{IV}} \approx 121°$

$\text{C}_{\text{II}}-1\,\text{C}_{\text{I}} = 1\cdot52\pm0\cdot05$ Å
$-1\,\text{H}_{\text{I}} = 1\cdot1\ (0\cdot8)$ Å
$-1\,\text{H}_{\text{II}} = 1\cdot0\ (1\cdot5)$ Å
$-1\,\text{H}_{\text{III}} = 1\cdot0\ (1\cdot1)$ Å

$\text{O}_{\text{I}}-1\,\text{U} = 1\cdot74\pm0\cdot04$ Å

$\text{O}_{\text{II}}-1\,\text{U} = 1\cdot70\pm0\cdot04$ Å

$\text{O}_{\text{III}}-1\,\text{U} = 2\cdot47\pm0\cdot02$ Å
$-1\,\text{Na} = 2\cdot39\pm0\cdot03$ Å
$-1\,\text{C}_{\text{I}} = 1\cdot26\pm0\cdot05$ Å

$\text{O}_{\text{IV}}-1\,\text{U} = 2\cdot51\pm0\cdot02$ Å
$-1\,\text{Na} = 2\cdot36\pm0\cdot04$ Å
$-1\,\text{C}_{\text{I}} = 1\cdot28\pm0\cdot04$ Å

The bond lengths given in parentheses for the C_{II}–H bonds correspond to the crude experimental values for the hydrogen coordinates.

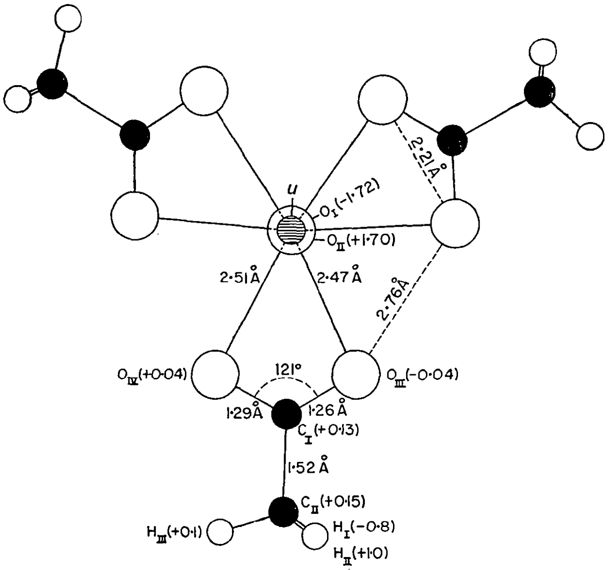

Fig. 2 shows the configuration about a uranium atom and within the acetate group, as seen along a three fold axis. The uranium atom lies in the projection plane. Numbers in parentheses give the height in Å above this plane.

The configuration about a uranium atom is shown in Fig. 2. As Fankuchen first pointed out, the space group requires the uranyl group to be collinear. It is seen that the two uranyl bonds, $\text{U}-\text{O}_{\text{I}}$ and $\text{U}-\text{O}_{\text{II}}$, are equal within experimental error, and so are the secondary bond lengths, $\text{U}-\text{O}_{\text{III}}$ and $\text{U}-\text{O}_{\text{IV}}$. The secondary bonds are very nearly at right angles (89°) to the uranyl axis. Every other edge of the hexagon formed by the O_{III} and O_{IV} atoms is an edge of a carboxyl group. In this manner the hexagon can be planar without causing unreasonably small oxygen–oxygen separations. The same configuration of oxygen atoms about the heavy atom as observed in this structure has previously been found in $\text{RbUO}_2(\text{NO}_3)_3$ (Hoard & Stroupe, 1949), KPuO_2CO_3 (Ellinger & Zachariasen, 1954) and UO_2CO_3 (Christ, Clark & Evans, 1955; Cromer & Harper, 1955). In other structures with six secondary bonds where the hexagon does not share edges with radicals such as nitrate, carbonate or carboxyl, the hexagon becomes puckered so as to yield larger O–O or F–F separations. Such puckered hexagons have been found in CaUO_2O_2 (Zachariasen, 1948*a*), UO_2F_2 (Zachariasen, 1948*b*), KAmO_2F_2 (Asprey, Ellinger & Zachariasen, 1954). When uranium forms five or four secondary bonds to fluorine or oxygen atoms as in $\text{K}_3\text{UO}_2\text{F}_5$ and MgUO_2O_2, there is no steric problem and the polygons are found to be planar. In other words, whenever sterically possible the secondary bonds lie in the plane normal to the $X\text{O}_2$ axis.

Since the O_{I} and O_{II} atoms are bonded only to uranium, detailed valence balance requires that a bond strength of $s = 2\cdot00$ be assigned to each uranyl bond and of $s = \frac{1}{3}$ to each secondary bond. The bond length *versus* bond strength curve previously published predicts $\text{U}-\text{O}_{\text{I}} = \text{U}-\text{O}_{\text{II}} = 1\cdot60$ Å and $\text{U}-\text{O}_{\text{III}} = \text{U}-\text{O}_{\text{IV}} = 2\cdot6$ Å, as against the observed values of $1\cdot71\pm0\cdot04$ Å and $2\cdot49\pm0\cdot02$ Å. There is a similar discrepancy between predicted and observed values in the UO_2CO_3 structure where the bond strengths are the same as in the present case. In that structure the values are $1\cdot67\pm0\cdot09$ Å and $2\cdot49\pm0\cdot05$ Å for the two bond lengths.

These observations show that the bond length *versus* bond strength curve needs revision. The revised curve is shown in Fig. 3, and in analytical form in Table 4.

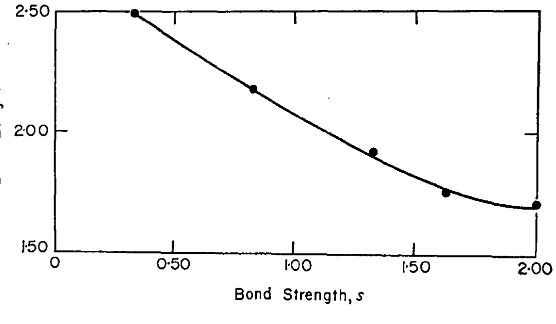

Fig. 3 shows the variation of bond length with bond strength. The experimental points shown are the results obtained from the structural studies of $\text{K}_3\text{UO}_2\text{F}_5$, MgUO_2O_2 and $\text{NaUO}_2(\text{O}_2\text{CCH}_3)_3$.

The six O_{III} and O_{IV} atoms about sodium form a slightly distorted octahedron, and the observed bond lengths are close to the usual value for six coordination.

In the acetate group the carbon and oxygen atoms are coplanar within experimental error, and this plane

Table 4. U–O *bond lengths as function of bond strengths*

Uranyl bond		Six secondary bonds		Four secondary bonds	
s	Bond length	*s*	Bond length	*s*	Bond length
2·00	1·70 Å	0·33	2·49 Å	0·50	2·38 Å
1·75	1·74	0·42	2·43	0·63	2·30
1·50	1·83	0·50	2·38	0·75	2·23
1·25	1·95	0·58	2·33	0·88	2·15
1·00	2·08	0·67	2·28	—	—

is nearly normal (86°) to the associated uranyl axis. The distances and bond angles within the group agree well with those observed in other acetates.

The crude experimental determination of the hydrogen coordinates places the H_{III} atom in the same plane as the carbon and oxygen atoms, and this feature was retained in modifying the experimental coordinates for the hydrogen atoms so as to give more reasonable C–H distances and bond angles. H–O distances outside a given acetate group are all greater than 2·7 Å, showing that there is no real bonding.

The O_{III}–O_{IV} distances are 2·21±0·05 Å within and 2·76±0·05 Å between acetate groups. These are alternating edges of the nearly plane hexagon of oxygen atoms about the uranium atom shown in Fig. 2.

The Fourier syntheses were carried out on X-RAC, while all other calculations were made by hand. The authors are deeply grateful to Prof. Raymond Pepinsky for the generous and hospitable manner in which he made X-RAC available to us, and to the X-RAC personnel for their valuable help.

References

ASPREY, L. B., ELLINGER, F. H. & ZACHARIASEN, W. H. (1954). *J. Amer. Chem. Soc.* **76**, 5235.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

CHRIST, C. L., CLARK, J. R. & EVANS, H. T. (1955). *Science*, **121**, 472.

CROMER, DON T. & HARPER, PAUL E. (1955). *Acta Cryst.* **8**, 847.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.

ELLINGER, F. H. (1956). Private communication.

ELLINGER, F. H. & ZACHARIASEN, W. H. (1954). *J. Phys. Chem.* **58**, 405.

FANKUCHEN, I. (1935). *Z. Kristallogr.* **91**, 473.

HOARD, J. L. & STROUPE, J. D. (1949). *National Nuclear Energy Series*, Division III, vol. 2, chap. 2, p. 15.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

ZACHARIASEN, W. H. (1948*a*). *Acta Cryst.* **1**, 281.

ZACHARIASEN, W. H. (1948*b*). *Acta Cryst.* **1**, 277.

ZACHARIASEN, W. H. (1949). *Acta Cryst.* **2**, 388.

ZACHARIASEN, W. H. (1954*a*). *Acta Cryst.* **7**, 795.

ZACHARIASEN, W. H. (1954*b*). *Acta Cryst.* **7**, 788.

ZACHARIASEN, W. H. (1954*c*). *Acta Cryst.* **7**, 783.

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An Account of some Computing Experiences

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Experience is summarized in the use of fractional shifts of scale, temperature and distance parameters, values of $r = \Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w|F_o|^4$, the behavior of temperature factors and a three-dimensional Patterson superposition program in the determination of a number of structures.

The increasing availability of high-speed digital computers in crystallography makes it desirable that general accounts of procedures and experience be available. Certain changes and developments in known methods, especially greater emphasis on three-dimensional methods, as well as the development of new methods, are taking place in a number of different laboratories. The variety of computers now available renders an account of programs for some particular computer of only special interest, but we feel that a more general statement of computer experience and techniques is of interest to crystallographers.

The Remington Rand 1103 UNIVAC SCIENTIFIC high-speed digital computer, in use for crystallographic computations in this laboratory for over three years, has a larger memory than computers for which similar computations have been described (Bennet & Kendrew, 1952; Ahmed & Cruickshank, 1953; Mayer & Trueblood, 1953; Thompson, Caminer, Fantl, Wright & King, 1954; Cochran & Douglas, 1955; Friedlander,