*Acta Cryst.* (1965). **19**, 536

# A Neutron Diffraction Study of Uranyl Nitrate Hexahydrate

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(*Received* 28 *October* 1964 *and in revised form* 25 *January* 1965)

The crystal structure of uranyl nitrate hexahydrate has been determined by neutron diffraction. The structure is orthorhombic with $a=13\cdot197\pm0\cdot003$, $b=8\cdot035\pm0\cdot002$, $c=11\cdot467\pm0\cdot003$ Å, space group $Cmc2_1$. Intensities of 1136 independent reflections with a $2\theta<105°$ were obtained with $\lambda=1\cdot065$ Å. The structure was solved from the three-dimensional neutron Patterson and Fourier syntheses, and refined by a full-matrix least squares, using a statistical weighting scheme. The final weighted $R$ index was 3·9%.

The uranyl group is surrounded equatorially by a near-planar oxygen hexagon of four oxygen atoms from two non-equivalent bidentate nitrate groups and two equivalent water oxygens. In the nitrate groups, the N–O bonds involving coordinated oxygens are 0·03–0·05 Å longer than the N–O bonds involving the non-coordinated oxygen atoms; also the O–N–O angles differ significantly from 120°. All hydrogens are involved in hydrogen bonding and these may be divided into (*a*) O (water) – O (water) hydrogen bonds of length 2·68–2·75 Å and (*b*) weaker O (water) – O (nitrate) hydrogen bonds of length 2·93 and 2·99 Å. The water molecules associate into sheets perpendicular to the *a* axis.

## Introduction

Uranyl nitrate hexahydrate was first studied by Pauling & Dickinson (1924) by X-ray diffraction. These authors found the unit cell to be orthorhombic, 13·15 × 8·02 × 11·42 Å with four molecules per unit cell. They believed the space group to be *Cmcm*; however, Sasvári (1957) reported a positive piezoelectric effect which suggested the crystal has the alternative non-centrosymmetric space group $Cmc2_1$.

On the basis of the infrared spectrum, Gatehouse & Comyns (1958) suggested that the structure was $[UO_2(H_2O)_6]2NO_3$, and Vdovenko, Stroganov, Sokolov & Zandin (1960) proposed such a model in $Cmc2_1$ from an X-ray diffraction study. On the other hand, Allpress & Hambly (1959), also from the infrared spectrum, considered that there was covalent bonding of the nitrate groups. Fleming & Lynton (1960), in a two-dimensional X-ray study, proposed the structure $[UO_2(NO_3)_2(H_2O)_2]\,.\,4H_2O$ but did not definitely locate the non-coordinated water molecules.

One of the authors (J.C.T.) collected neutron diffraction data for the axial projections, through the courtesy of Mr T. M. Sabine, A.A.E.C.R.E., Lucas Heights, Sydney, Australia. It was hoped that the structure could be solved with neutron diffraction since the uranium atom would not have the dominant scattering power which it has with X-rays. Attempts were made to refine the model of Fleming & Lynton using these data, but were unsuccessful as difference projections gave neither the missing atoms nor the errors in the X-ray model. This approach was therefore discontinued.

The present investigation was undertaken with the Argonne three-circle neutron instrument (Mueller, Heaton & Sidhu, 1963). This technique was selected since the resolution would be considerably better than from the two-dimensional data and the hydrogen atoms could be located simultaneously.

It was brought to our attention after our work had been completed and written for publication that a report of a two-dimensional neutron diffraction study of this compound by Makarov & Melik'yan (1962) had just appeared in Chemical Abstracts (September 14, 1964). On the basis of (*hk*0) and (*h*0*l*) neutron data projections these authors accepted the coordinates for U, N and O proposed by Fleming & Lynton and from the negative areas on their maps they deduced a preliminary set of hydrogen coordinates. These coordinates were not in agreement with the ones we obtained in our three-dimensional study. Their results are discussed in the section on *Hydrogen bonding and water molecules.*

## Experimental

Large single crystals weighing approximately 0·5 g were obtained from a slightly acidified aqueous solution. $2\theta$ values of 25 reflections (6 *h*00, 13 *hk*0 and 6 00*l*) were obtained on the three-circle neutron instrument ($\lambda=1\cdot065$ Å) for use in the determination of the unit-cell dimensions. A least-squares program (Mueller & Heaton, 1961) gave the following values: $a=13\cdot197\pm0\cdot003$, $b=8\cdot035\pm0\cdot002$, $c=11\cdot467\pm0\cdot003$ Å.

Intensity data collection was then commenced, each peak being step-scanned over 6–7° $2\theta$ in 0·1° steps. Time at each step was controlled by a monitor count with a total time of approximately 15 minutes for each reflection. After the intensities of some 200 reflections had been measured, the low ambient humidity

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caused the crystal to dehydrate; therefore, these measurements were discarded. A new crystal was then grown and shaped to a sphere (weight 540 mg) with a piece of damp filter paper. This crystal was enclosed in a thin-walled vanadium can and showed no loss of intensity, even six months later. After 852 reflections had been observed, a two-month reactor shutdown occurred. The data collection was continued, after the shutdown period, to include all reflections within a $2\theta$ of 105°, beyond which the intensities were becoming very weak. A total of 1136 independent reciprocal lattice points from the second crystal were examined with only 25 of these intensities unobservably small. The observed $F^2$ and $F$ values were placed on a near absolute scale by a comparison with the intensities from a magnesium oxide crystal. Absorption corrections were applied to the observed intensities ($\mu_{\text{meas}} = 1{\cdot}7$ cm$^{-1}$, $\mu r = 0{\cdot}61$).

A more detailed description of this investigation will be published in the Argonne National Laboratory report, ANL-6943, which may be obtained later upon request.

## Structure analysis

### *Three-dimensional Patterson map*

The analysis was commenced during the shutdown period with 852 reflections only. A three-dimensional Patterson map was calculated (Sly & Shoemaker, 1960) and the highest peaks as shown in Fig. 1 were concentrated in the section $x=0$, indicating that many of the atoms probably lie in the mirror planes (at $x=0$ and $x=\frac{1}{2}$). A large peak $A$ $(0, \frac{1}{4}, \frac{1}{2})$ (Fig. 1) was consistent with the uranium atom position $(0, \frac{1}{8}, \frac{1}{4})$, as found by Fleming & Lynton. Peak $B$, 1·77 Å from the origin, was clearly the superposition of the two U–O vectors in the (linear) uranyl group, lying in the mirror plane. There were only two peaks in the Patterson map close enough to the origin to represent N–O distances in the nitrate groups – one in the zero level at $C$, 1·23 Å from the origin, and one in the general location (0.082, 0.087, 0), 1.29Å from the orgin. The nitrate groups were located with respect to the uranyl group by means of the vector $D$ which was 2·95 Å from the origin and at right angles to the uranyl vector; this was thought to be the superposition of the two U–N vectors.

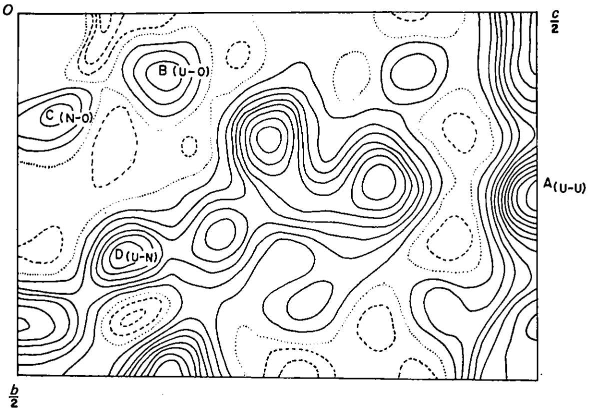

Fig. 1. Section $x=0$ of three-dimensional neutron Patterson synthesis.

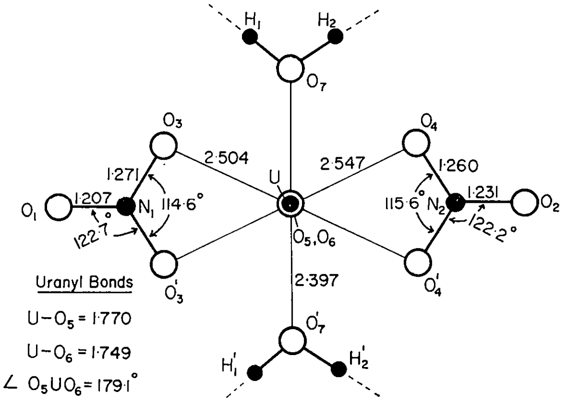

Fig. 2. Configuration of uranium atom and nitrate groups.

From the Patterson map a model for the $UO_2(NO_3)_2$ group was derived; the two nitrate groups were bidentate and bound to the uranium atom on opposite sides of the uranyl group (see Fig. 2). The Patterson map also suggested that two reflection-equivalent water oxygen atoms were coordinated to the uranium atom, completing an irregular hexagon of six oxygen atoms in the uranyl equatorial plane.

Buerger minimum functions of rank 2 and 3 were calculated (Penfold, 1960) using the U–O (uranyl), U–U and U–N vectors in Fig. 1. Although the minimum functions were somewhat smeared-out in appearance they supported the model already derived. The coordinates deduced from the Patterson and minimum functions showed fair agreement with those of Fleming & Lynton (1960). The biggest disagreement involved a shift, primarily along the $y$ direction, of 0·48 Å for the O(2) nitrate oxygen atom and a 0·28 Å shift of the O(6) uranyl oxygen atom in the same direction. At this stage the positions of the remaining two water oxygen atoms and the hydrogen atoms were not obvious.

### *Three-dimensional Fourier maps*

Structure factors were calculated for the derived model, the U, N and O atoms being given isotropic thermal parameters of 2·0, 3·0 and 3·5 Å respectively; an $R$ value of 40·7% was obtained for the 852 reflections where $R=\sqrt{\Sigma w(F_o-sF_c)^2}\,/\sqrt{\Sigma wF_o^2}$, $s$ being the scale factor and $w$ in this case being unity. A three-dimensional Fourier synthesis of the neutron scattering density was made with the calculated phase angles and the $F_o(hkl)$ values, leaving out 189 $F_o(hkl)$ terms with small $F_c(hkl)$. In this map the positions of the remaining O(8) and O(9) water oxygen atoms were apparent, and when these atoms were added to the structure factor calculations, $R$ dropped to 35%. The O(8) and O(9) coordinates found were in considerable disagreement with those proposed by Fleming & Lynton (Table 1). This fact, together with the discrepancies for O(2) and O(6), mentioned in the preceding section, may have been the cause of the inability to solve the

Table 1. *Comparison of water oxygen coordinates of Fleming & Lynton with those from the present investigation*

| Atom | $x$ | $y$ | $z$ | Comments |
|---|---|---|---|---|
| F and L O(5) | 0·183 | 0·118 | 0·250 | 0·08 Å away from present O(7) |
| Present O(7) | 0·182 | 0·121 | 0·244 | — |
| F and L O(8) (first possibility) | 0·208 | 0·457 | 0·075 | incorrect |
| F and L O(8) (second possibility) | 0·208 | 0·457 | 0·425 | 0·52 Å away from present O(8) |
| Present O(8) | 0·206 | 0·523 | 0·427 | — |
| F and L O(9) (first possibility) | 0·205 | 0·252 | 0·425 | incorrect |
| F and L O(9) (second possibility) | 0·205 | 0·252 | 0·075 | 1·19 Å away from present O(9) |
| Present O(9) | 0·295 | 0·253 | 0·070 | — |

Table 2. *Positional and thermal parameters*

Standard errors ( × 10⁴) appear in parentheses

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| U | 0 | 0·1292(5) | 0·2500 | 0·0030(1) | 0·0076(4) | 0·0032(2) | 0 | 0 | −0·0003(2) |
| N(1) | 0 | 0·4722(4) | 0·1581(4) | 0·0036(2) | 0·0085(5) | 0·0042(3) | 0 | 0 | 0·0014(3) |
| N(2) | ½ | 0·2919(5) | 0·3590(5) | 0·0037(2) | 0·0092(5) | 0.0050(3) | 0 | 0 | 0·0017(3) |
| O(1) | ½ | 0·1158(8) | 0·1270(7) | 0·0062(4) | 0·0106(9) | 0·0070(5) | 0 | 0 | 0·0028(7) |
| O(2) | ½ | 0·1523(8) | 0·4032(8) | 0·0048(4) | 0·0098(10) | 0·0072(5) | 0 | 0 | 0·0029(6) |
| O(3) | 0·0810(3) | 0·3913(5) | 0·1775(5) | 0·0032(2) | 0·0119(7) | 0·0076(3) | 0·0000(3) | 0·0003(2) | 0·0034(4) |
| O(4) | 0·4192(3) | 0·3678(6) | 0·3346(5) | 0·0033(2) | 0·0119(6) | 0·0084(4) | 0·0002(3) | −0·0003(2) | 0·0034(5) |
| O(5) | 0 | 0·0426(8) | 0·1080(6) | 0·0082(5) | 0·0121(11) | 0·0031(4) | 0 | 0 | −0·0014(6) |
| O(6) | 0 | 0·2114(9) | 0·3913(6) | 0·0070(5) | 0·0127(11) | 0·0033(4) | 0 | 0 | −0·0017(6) |
| O(7) | 0·1815(2) | 0·1213(8) | 0·2437(8) | 0·0030(2) | 0·0178(7) | 0·0099(4) | 0·0003(4) | 0·0012(3) | 0·0055(5) |
| O(8) | 0·2943(4) | 0·0234(8) | 0·4270(6) | 0·0047(3) | 0·0187(11) | 0·0070(4) | −0·0018(5) | −0·0008(3) | 0·0014(6) |
| O(9) | 0·2947(4) | 0·2530(9) | 0·0700(7) | 0·0040(3) | 0·0232(13) | 0·0074(4) | 0·0000(6) | 0·0005(4) | 0·0004(6) |
| H(1) | 0·2252(6) | 0·1738(13) | 0·1859(9) | 0·0039(4) | 0·0230(18) | 0·0077(7) | −0·0003(8) | 0·0006(4) | 0·0031(9) |
| H(2) | 0·2254(7) | 0·0744(12) | 0·3031(10) | 0·0044(4) | 0·0176(15) | 0·0105(8) | 0·0010(8) | −0·0017(5) | 0·0029(9) |
| H(3) | 0·3637(7) | 0·0635(14) | 0·4177(9) | 0·0061(5) | 0·0336(23) | 0·0086(8) | −0·0033(10) | 0.0010(6) | 0·0007(12) |
| H(4) | 0·2016(7) | 0·4195(14) | 0·4629(10) | 0·0052(5) | 0·0276(22) | 0·0112(9) | −0·0014(9) | −0·0001(6) | 0·0048(13) |
| H(5) | 0·3645(10) | 0·2606(18) | 0·0883(11) | 0·0081(7) | 0·0426(32) | 0·0165(16) | −0·0045(14) | −0·0049(9) | 0·0055(18) |
| H(6) | 0·2705(9) | 0·3384(15) | 0·0323(12) | 0·0076(8) | 0·0232(24) | 0·0157(13) | 0·0013(10) | −0·0005(8) | 0·0044(13) |

structure with the previous two-dimensional neutron data collected at Sydney.

In a further three-dimensional Fourier synthesis (88 reflections omitted) the six hydrogen atoms were located, and with the hydrogen atoms included ($B_H = 3{\cdot}5$ Å²), $R$ dropped to 24·2%.

### *Least-squares refinement*

The Fourier coordinates were now refined by full-matrix least squares (Busing, Martin & Levy, 1962). The scattering factors used were: $b_U = 0{\cdot}85$, $b_N = 0{\cdot}94$, $b_O = 0{\cdot}577$ and $b_H = -0{\cdot}378$ ($\times 10^{-12}$ cm). The refinement was based on $F$. The $z$ coordinate of the uranium atom was not refined as the choice of '$z$' for the first atom in $Cmc2_1$ is arbitrary. The refinement was begun using only the data with $l = 2$, 3 or 4 (268 reflections) and unit weights. Several 'isotropic' cycles with the partial data were followed with anisotropic refinement which led to an $R$ of 7·5% with the complete data.

Statistical weights were now applied by the method of Evans (1961), the function being

$$w = \frac{1}{[\sigma(F)]^2} \propto \frac{T - nb}{(T + nb)\sin 2\theta}$$

where $T$ is the total count, $n$ is the number of steps, $b$ is the background height and $\sigma(F)$ is the standard deviation of the structure factor. The final $R$ for this scheme was 3·9%, using all data except the 200 reflection which obviously suffered from extinction. During the course of this refinement use was made of $F_o$, $F_c$ and difference maps for verifying the structure.

The coordinates and anisotropic temperature factors obtained with the statistical scheme are given in Table 2 and the corresponding bond lengths and angles in Tables 3 and 4 as calculated with the program of Busing, Martin & Levy (1964). The standard errors include the effects of cell dimension errors; however,

Table 3. *Bond lengths*

Standard errors ( × 10³) are shown in parentheses

| Bond | Distance (Å)* |
|---|---|
| Uranyl bonds | |
| U–O(5) | 1·770(7) |
| U–O(6) | 1·749(7) |
| Other U–O bonds | |
| U–O(3) | 2·504(5) |
| U–O(4) | 2·547(6) |
| U–O(7) | 2·397(3) |
| Distances in nitrate groups | |
| N(1)–O(1) | 1·207(8) |
| N(1)–O(3) | 1·271(4) |
| O(1)–O(3) | 2·176(7) |
| O(3)–O(3) | 2·139(8) |
| N(2)–O(2) | 1·231(7) |
| N(2)–O(4) | 1·260(4) |
| O(4)–O(2) | 2·181(7) |
| O(4)–O(4) | 2·133(8) |
| Water molecules | |
| O(7)–H(1) | 0·974(12) |
| O(7)–H(2) | 0·970(13) |
| O(8)–H(3) | 0·977(11) |

| Bond | Distance (Å)* |
|---|---|
| Water molecules | |
| O(8)–H(4) | 0·932(15) |
| O(9)–H(5) | 0·947(15) |
| O(9)–H(6) | 0·872(17) |
| Hydrogen bonds | |
| O(7)–O(9) | 2·705(9) |
| O(9)–H(1) | 1·737(11) |
| O(7)–O(8) | 2·692(9) |
| O(8)–H(2) | 1·736(11) |
| O(8)–O(2) | 2·918(6) |
| O(2)–H(3) | 1·942(9) |
| O(8)–O(9) | 2·760(10) |
| O(9)–H(4) | 1·852(12) |
| O(9)–O(1) | 2·997(7) |
| O(1)–H(5) | 2·179(14) |
| O(8)–O(9) | 2·701(9) |
| O(8)–H(6) | 1·849(13) |

* Uncorrected for the effects of thermal motion.

Table 4. *Bond angles*

Standard errors (× 10) are shown in parentheses

| Angle | Degrees |
|---|---|
| Uranyl angle | |
| O(5)–U–O(6) | 179·1(5) |
| Other angles about uranium | |
| O(6)–U–O(7) | 92·2(2) |
| O(6)–U–O(3) | 89·4(3) |
| O(6)–U–O(4) | 87·7(3) |
| O(6)–U–N(1) | 88·7(3) |
| O(6)–U–N(2) | 87·4(3) |
| O(6)–U–O(1) | 87·6(3) |
| O(6)–U–O(2) | 87·6(3) |
| O(5)–U–O(3) | 91·5(3) |
| O(5)–U–O(4) | 91·5(3) |
| O(5)–U–N(1) | 92·2(3) |
| O(5)–U–N(2) | 91·6(3) |
| O(5)–U–O(1) | 93·3(3) |
| O(5)–U–O(2) | 91·5(3) |
| Water molecule angles | |
| H(1)–O(7)–H(2) | 106·9(5) |
| H(3)–O(8)–H(4) | 106·8(9) |
| H(5)–O(9)–H(6) | 114·6(12) |
| Hydrogen bond angles | |
| O(7)–H(1) · · · O(9) | 172·8(9) |
| O(7)–H(2) · · · O(8) | 168·2(10) |
| O(8)–H(3) · · · O(2) | 177·4(10) |
| O(8)–H(4) · · · O(9) | 164·0(10) |
| O(9)–H(5) · · · O(1) | 144·0(13) |
| O(9)–H(6) · · · O(8) | 164·9(12) |

| Angle | Degrees |
|---|---|
| Nitrate group angles | |
| O(1)–N(1)–O(3) | 122·7(2) |
| O(3)–N(1)–O(3) | 114·6(5) |
| O(4)–N(2)–O(2) | 122·2(2) |
| O(4)–N(2)–O(4) | 115·6(5) |
| O–O–O angles around water oxygen atoms | |
| O(9)–O(7)–O(8) | 112·5(2) |
| O(7)–O(8)–O(2) | 109·7(3) |
| O(7)–O(8)–O(9) | 92·2(3) |
| O(7)–O(8)–O(9) | 134·4(3) |
| O(9)–O(8)–O(2) | 103·0(3) |
| O(9)–O(8)–O(2) | 109·8(3) |
| O(9)–O(8)–O(9) | 100·2(2) |
| O(1)–O(9)–O(8) | 140·4(2) |
| O(1)–O(9)–O(8) | 80·5(2) |
| O(7)–O(9)–O(1) | 101·2(3) |
| O(8)–O(9)–O(7) | 96·9(3) |
| O(8)–O(9)–O(7) | 117·8(2) |
| O(8)–O(9)–O(8) | 100·0(2) |

Table 5. *Least-squares planes*

| Plane | Atoms | Equation of plane* |
|---|---|---|
| 1 | N(1), O(1), O(3), O(3′): $(NO_3)_{I}$ | $2{\cdot}4575Y+10{\cdot}9106Z=2{\cdot}8951$ |
| 2 | N(2), O(2), O(4), O(4′): $(NO_3)_{II}$ | $3{\cdot}3241Y+10{\cdot}4331Z=3{\cdot}0518$ |
| 3 | Oxygen Hexagon | $3{\cdot}1605Y+10{\cdot}5360Z=3{\cdot}0550$ |
| 4 | $(NO_3)_{I}$, U, O(7), O(7′) | $2{\cdot}6602Y+10{\cdot}8134Z=2{\cdot}9800$ |
| 5 | $(NO_3)_{II}$, U, O(7), O(7′) | $3{\cdot}4844Y+10{\cdot}3262Z=2{\cdot}9760$ |
| 6 | $(NO_3)_{I}$, $(NO_3)_{II}$, U, O(7), O(7′) | $3{\cdot}0941Y+10{\cdot}5760Z=3{\cdot}1006$ |

* *Y* and *Z* are fractional coordinates

Deviations $\Delta$(Å)

| Atom | Plane 1 | Plane 2 | Plane 3 | Plane 4 | Plane 5 | Plane 6 |
|---|---|---|---|---|---|---|
| N(1) | −0·0101 | | | −0·0146 | | 0·0321 |
| O(1) | 0·0037 | | | 0·0313 | | 0·1478 |
| O(3) | 0·0032 | | 0·0520 | −0·0196 | | −0·0125 |
| O(3′) | 0·0032 | | 0·0520 | −0·0196 | | −0·0125 |
| N(2) | | 0·0019 | | | 0·0060 | 0·0524 |
| O(2) | | −0·0007 | | | −0·0238 | 0·0882 |
| O(4) | | −0·0006 | 0·0522 | | 0·0182 | 0·0288 |
| O(4′) | | −0·0006 | 0·0522 | | 0·0182 | 0·0288 |
| U | | | *−0·0128** | 0·0670 | 0·0556 | −0·0569 |
| O(7) | | | −0·1042 | −0·0223 | −0·0371 | −0·1481 |
| O(7′) | | | −0·1042 | −0·0223 | −0·0371 | −0·1481 |

* Not included in L.S. plane calculation.

Dihedral angles

| Planes | Angle |
|---|---|
| 1 and 2 | 6·63° |
| 4 and 5 | 6·37 |
| 1 and 3 | 5·35 |
| 2 and 3 | 1·28 |

these were quite small. A complete listing of the final $F_o$ and $F_c$ values has been deposited with the Library of Congress.*

## Discussion

### *Uranyl coordination*

The configuration about the uranium atom is shown in Fig. 2. The uranyl group is perpendicular to the paper, and is surrounded equatorially by an irregular hexagon of six oxygen atoms, four from the two crystallographically non-equivalent nitrate groups and two from symmetry related water oxygen atoms O(7).

The uranyl distances are not quite equivalent. The distance U–O(5) is 1·770 ± 0·007 Å, while U–O(6) is 1·749 ± 0·007 Å. These distances may be compared with the distance of 1·78 Å found in the linear, symmetrical uranyl group in rubidium uranyl nitrate (Barclay, Sabine & Taylor, 1965). The uranyl angle of 179·1 ± 0·5° is nearly linear. This hexagonal arrangement of oxygen atoms about the uranyl group is very similar to the arrangements found in rubidium uranyl nitrate, a neutron diffraction study (Barclay, Sabine & Taylor) and in sodium uranyl acetate, an X-ray diffraction study (Zachariasen & Plettinger, 1959).

### *Nitrate groups*

The dimensions of the nitrate groups are also shown in Fig. 2. It is noticed that in each nitrate group the N–O bonds are not equivalent; the N–O bonds involving coordinated oxygen atoms are 0·06 and 0·03 Å longer than those involving the non-coordinated oxygen atoms. The bond angles in the nitrate groups are also distorted from the ideal value of 120° by the coordination with uranium. Similar differences in the bond lengths and angles were also observed in the nitrate group in rubidium uranyl nitrate. The N–O distances may be compared with the distance of 1·218 Å found by Sass, Vidale & Donohue (1957) in sodium nitrate and the distance of 1·268 Å found by Hamilton (1957) in lead nitrate.

### *Least-squares planes*

As mentioned above, the uranium atom, the nitrate groups and the O(7) water oxygen atoms are approximately coplanar. In order to determine the deviations from the ideal planar arrangement, least-squares planes were calculated (Schomaker, Waser, Marsh & Bergman, 1959) using a computer program (Norment, 1963). The equations of the least-squares planes and the deviations of the atoms are shown in Table 5.

The $(\mathrm{NO_3})_{\mathrm{I}}$ and $(\mathrm{NO_3})_{\mathrm{II}}$ nitrate groups are very close to planar. The oxygen hexagon is slightly puckered around the uranium level as the O(3), O(3′), O(4) and O(4′) nitrate oxygen atoms have significant positive deviations (+0·05 Å) while the O(7) and O(7′) water oxygen atoms have significant negative deviations (−0·10 Å). The uranium atom deviation from the hexagon plane is slightly negative (−0·01 Å) but probably not significant; the uranium atom was not included in the calculation of this plane. The nitrate groups lie nearly in the plane of the hexagon, the dihedral angles between $(\mathrm{NO_3})_{\mathrm{I}}$ and $(\mathrm{NO_3})_{\mathrm{II}}$ and the hexagon plane being 5·35° and 1·28° respectively.

The equatorial system appears to be bent about the O(7)–O(7′) line. The plane formed by $(\mathrm{NO_3})_{\mathrm{I}}$, O(7), O(7′) and U lies at an angle of 6·37° to the plane formed by $(\mathrm{NO_3})_{\mathrm{II}}$, O(7), O(7′) and U. The nitrate group planes intersect at an angle of 6·63° to each other indicating that these planes and the respective halves of the bent system are nearly coplanar. The sixth plane shown in Table 5 was calculated for all the atoms in the equator of the uranyl group. The larger deviations shown are a result of the bending mentioned above.

### *Thermal parameters*

The r.m.s. radial thermal displacements are shown in Table 6. These vary according to the type of atom – the uranium atom has the smallest value, with the two nitrogen atoms next, followed by the oxygens and finally the hydrogens having the greatest displacements. The atoms H(1) and H(2) which are attached through their O(7)'s to the oxygen hexagon, have the smallest values of the hydrogens. The r.m.s. values were also consistent with peak heights in the Fourier syntheses.

The r.m.s. components along the principal axes of the vibration ellipsoids are also shown in Table 6. The direction cosines of the principal axes are given in

Table 6. *R.M.S. radial thermal displacements and the components along the principal axes $R_i$ of the vibration ellipsoids*

Standard errors (×10³) are given in parentheses

| Atom | R.M.S. radial displacement (Å) | Displacements along $R_1$(Å) | $R_2$(Å) | $R_3$(Å) |
|---|---|---|---|---|
| U | 0·270(3) | 0·144(5) | 0·159(4) | 0·164(4) |
| N(1) | 0·295(4) | 0·146(6) | 0·178(4) | 0·185(5) |
| N(2) | 0·310(4) | 0·153(6) | 0·181(5) | 0·199(5) |
| O(1) | 0·370(6) | 0·162(10) | 0·235(7) | 0·235(9) |
| O(2) | 0·349(7) | 0·156(10) | 0·206(8) | 0·235(9) |
| O(3) | 0·343(4) | 0·163(6) | 0·171(6) | 0·249(6) |
| O(4) | 0·351(4) | 0·164(6) | 0·177(6) | 0·255(6) |
| O(5) | 0·365(7) | 0·137(10) | 0·204(9) | 0·269(9) |
| O(6) | 0·354(7) | 0·138(10) | 0·210(9) | 0·249(8) |
| O(7) | 0·388(4) | 0·155(7) | 0·194(6) | 0·299(6) |
| O(8) | 0·387(5) | 0·190(7) | 0·211(7) | 0·262(7) |
| O(9) | 0·401(5) | 0·186(7) | 0·224(7) | 0·276(8) |
| H(1) | 0·402(8) | 0·181(10) | 0·216(11) | 0·286(11) |
| H(2) | 0·408(8) | 0·174(12) | 0·236(11) | 0·284(10) |
| H(3) | 0·470(8) | 0·212(12) | 0·246(11) | 0·340(12) |
| H(4) | 0·459(8) | 0·211(10) | 0·244(13) | 0·327(12) |
| H(5) | 0·567(12) | 0·219(13) | 0·319(14) | 0·414(16) |
| H(6) | 0·497(10) | 0·241(14) | 0·273(13) | 0·339(13) |

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* The table of observed and calculated structure factors was submitted with the manuscript and has been deposited as document number 8305 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting $2·50 for photoprints or $1·75 for 35-mm microfilm. Advance payment by check or money order, payable to Chief, Photoduplication Service, Library of Congress, is required.

Table 7. *Direction cosines of principal axes $R_1$, $R_2$ and $R_3$ of vibration ellipsoids*

The *direction cosines* for $R_1$ are $p_i$, for $R_2$ are $q_i$ and for $R_3$ are $r_i$

| Atom | $p_1$ | $p_2$ | $p_3$ | $q_1$ | $q_2$ | $q_3$ | $r_1$ | $r_2$ | $r_3$ |
|---|---|---|---|---|---|---|---|---|---|
| U | 0 | −0·326 | −0·945 | 0 | 0·945 | −0·326 | 1 | 0 | 0 |
| N(1) | 0 | 0·711 | −0·703 | 1 | 0 | 0 | 0 | −0·703 | −0·711 |
| N(2) | 0 | 0·773 | −0·634 | 1 | 0 | 0 | 0 | −0·634 | −0·773 |
| O(1) | 0 | −0·841 | 0·541 | 1 | 0 | 0 | 0 | −0·541 | −0·841 |
| O(2) | 0 | −0·868 | 0·497 | 1 | 0 | 0 | 0 | −0·497 | −0·868 |
| O(3) | 0·668 | −0·589 | 0·455 | −0·742 | −0·573 | 0·348 | 0·056 | −0·570 | −0·820 |
| O(4) | 0·736 | 0·566 | −0·371 | −0·676 | 0·646 | −0·355 | −0·039 | −0·512 | −0·858 |
| O(5) | 0 | −0·297 | −0·955 | 0 | 0·955 | −0·297 | 1 | 0 | 0 |
| O(6) | 0 | −0·334 | −0·943 | 0 | 0·943 | −0·334 | 1 | 0 | 0 |
| O(7) | 0·928 | −0·194 | 0·320 | −0·352 | −0·745 | 0·568 | 0·128 | −0·639 | −0·759 |
| O(8) | 0·894 | −0·249 | −0·372 | 0·225 | −0·468 | 0·854 | −0·387 | −0·848 | −0·363 |
| O(9) | 0·968 | −0·011 | 0·250 | −0·250 | −0·070 | 0·966 | 0·007 | −0·998 | −0·071 |
| H(1) | 0·927 | −0·151 | 0·343 | −0·375 | −0·399 | 0·837 | 0·011 | −0·905 | −0·426 |
| H(2) | 0·841 | 0·364 | −0·401 | −0·499 | 0·808 | −0·312 | −0·211 | −0·463 | −0·861 |
| H(3) | 0·851 | −0·208 | −0·483 | 0·442 | −0·215 | 0·871 | −0·285 | −0·954 | −0·091 |
| H(4) | 0·963 | −0·227 | 0·144 | −0·246 | −0·531 | 0·811 | −0·108 | −0·816 | −0·568 |
| H(5) | 0·868 | −0·093 | −0·488 | 0·311 | −0·665 | 0·679 | −0·387 | −0·741 | −0·548 |
| H(6) | 0·664 | 0·662 | −0·348 | −0·748 | 0·590 | −0·305 | −0·004 | −0·463 | −0·887 |

Table 7. Table 8 lists the r.m.s. displacements along the bond directions and it may be noted, that the magnitudes are nearly the same as the displacements along the shortest principal axes, indicating that the maximum vibration directions are more or less perpendicular to the bonds. Table 8 also lists the angles between the shortest principal axes $R_1$ (and in some cases $R_2$) and the bond directions. It is seen that the angles are small for the U–O and N–O bonds while for the O–H bonds they are somewhat larger.

## *Hydrogen bonding and water molecules*

The uranyl coordination group is tied into the structure by means of the shorter hydrogen bonds O(7)–H(1) · · · O(9) and O(7)–H(2) · · · O(8) and the longer hydrogen bonds O(1) · · · H(5)–O(9) and O(2) · · · H(3)–O(8), the latter bonds involving the nitrate oxygen atoms (Fig. 3). The water molecules form an infinite sheet which is held together by hydrogen bonds as shown in Fig. 4; the 'up' and 'down' weaker hydrogen bonds with the nitrate oxygens are also shown in this figure.

The H(1)–O(7)–H(2) water molecule forms two hydrogen bonds with the O(8) and O(9) water oxygen atoms and is coordinated to the uranium atom; it thus has a different environment to the other two water molecules [H(3)–O(8)–H(4) and H(5)–O(9)–H(6)] which are surrounded by a roughly tetrahedral arrangement of hydrogen-bonded oxygens (see Table 4 for a listing of the O–O–O angles). The H(1)–O(7)–H(2) water molecule has a lower thermal displacement than either of the other two water molecules.

Table 8. *R.M.S. components of thermal displacement along bond directions and angles between bonds and shortest principal axes*

Standard errors (× 10³) are given in parentheses

| Atom | Bond | R.M.S. component along bond | Angle $R_1$ | $R_2$ |
|---|---|---|---|---|
| O(5) | O(5)–U | 0·138(10) Å | 6° | |
| O(6) | O(6)–U | 0·138(10) | 2 | |
| O(1) | O(1)–N(1) | 0·169(9) | 16 | |
| O(3) | O(3)–N(1) | 0·171(6) | 20 | |
| O(2) | O(2)–N(2) | 0·157(10) | 5 | |
| O(4) | O(4)–N(2) | 0·166(6) | 75 | 16° |
| H(1) | H(1)–O(7) | 0·193(12) | 76 | 15 |
| H(2) | H(2)–O(7) | 0·190(12) | 86 | 34 |
| H(3) | H(3)–O(8) | 0·225(11) | 39 | 76 |
| H(4) | H(4)–O(8) | 0·262(13) | 78 | 32 |
| H(5) | H(5)–O(9) | 0·235(13) | 43 | 66 |
| H(6) | H(6)–O(9) | 0·245(14) | 63 | 27 |

The distances and angles in the water molecules and hydrogen bonds are shown in Tables 3 and 4. The thermal corrections to the apparent O–H distances are large; when corrected for 'riding' motion (Busing & Levy, 1964), the O–H distances lie between 0·92 and 1·02 Å. The water angles are 106·9, 106·8 and 114·6°.

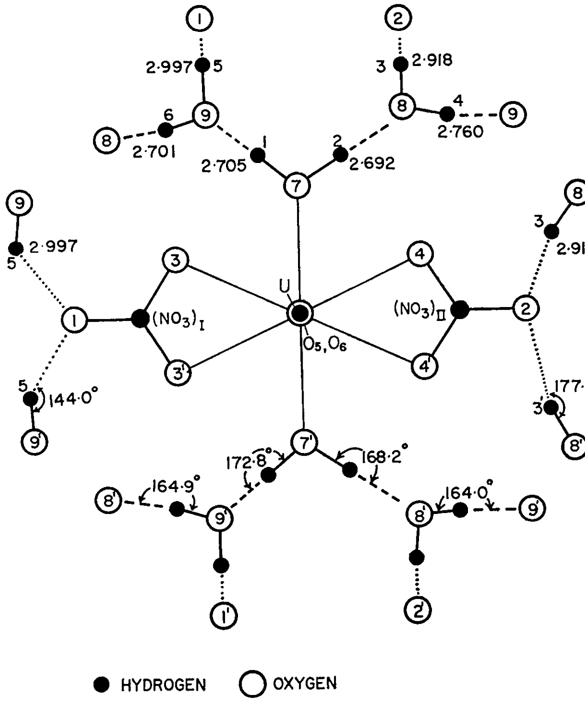

Fig. 3. Hydrogen bonding.

The O–H · · · O angles are in the range of 164–178° except for O(9)–H(5) · · · O(1) (144·0°), which is bent considerably in order to accommodate the two O(1)–O(9)–O(8) angles of 80·5° and 140·4°. Bent hydrogen bonds in hydrates are not unusual and have been reported previously for $MgSO_4 . 4H_2O$–140° (Baur, 1964) and $Li_2SO_4 . H_2O$–two bonds bent by 30° (Smith, Peterson & Levy, 1961).

The distances between the hydrogen positions of Makarov & Melik'yan (1962) and the nearest hydrogen atoms as found by us are given in Table 9. These distances are very large, indicating a lack of correlation between the two sets of hydrogen atoms. Makarov & Melik'yan did not state which of the alternative water oxygen locations suggested by Fleming & Lynton they used; however we deduced these by calculation of O–H distances. We found on comparison with our coordinates that two of the three water oxygen positions they assumed were incorrect, and thus it was not surprising that their hydrogen positions were different. More details of the comparison of the hydrogen positions are given in ANL-6943, mentioned above.

The inelastic neutron scattering experiments of Rush (1964) on uranyl nitrate gave a broad peak, due to the torsional oscillation of the water molecules, centered at about 450 wave numbers. The width of this peak, combined with an indication of splitting, suggested several different water molecule environments. The comparatively low frequency indicates that the hydrogen bonding is relatively weak.

### (0*kl*) *Fourier synthesis*

Although two-dimensional projections were not used in the solution of the crystal structure it was thought worthwhile to calculate such a projection after completing the determination. The result is shown in Fig. 5 as an (0*kl*) Fourier synthesis which has some overlap but well illustrates the structure. Since this is a view in the plane of the oxygen hexagon, one can see a number of structural features such as: the relative orientation of the oxygen hexagon and uranyl group within the unit cell; the slight twist of the nitrate group planes; the relative positions of the hydrogens; and the twist of H(1) and H(2), attached to the O(7)'s of the hexagon, out of the plane of the hexagon.

Table 9. *Deviations between the hydrogen positions of Makarov & Melik'yan and the nearest hydrogen atoms of the present investigation*

| Makarov & Melik'yan hydrogen | $\Delta$ (Å) |
|---|---|
| H(1) [O(5)]* | 1·65 |
| H(2) [O(5)] | 1·83 |
| H(3) [O(8)] | † |
| H(6) [O(8)] | 1·97 |
| H(4) [O(9)] | 0·73 |
| H(5) [O(9)] | 0·59 |

* Fleming & Lynton oxygen positions used by Makarov & Melik'yan shown in square brackets.

† Makarov & Melik'yan did not supply complete coordinates for their H(3).

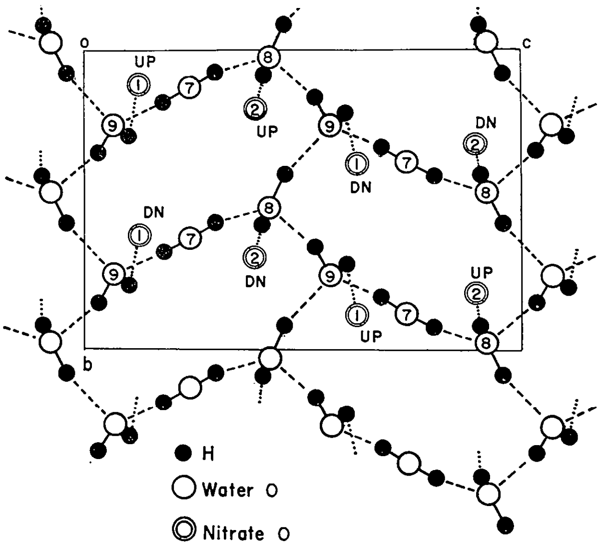

Fig. 4. Water molecule sheets.

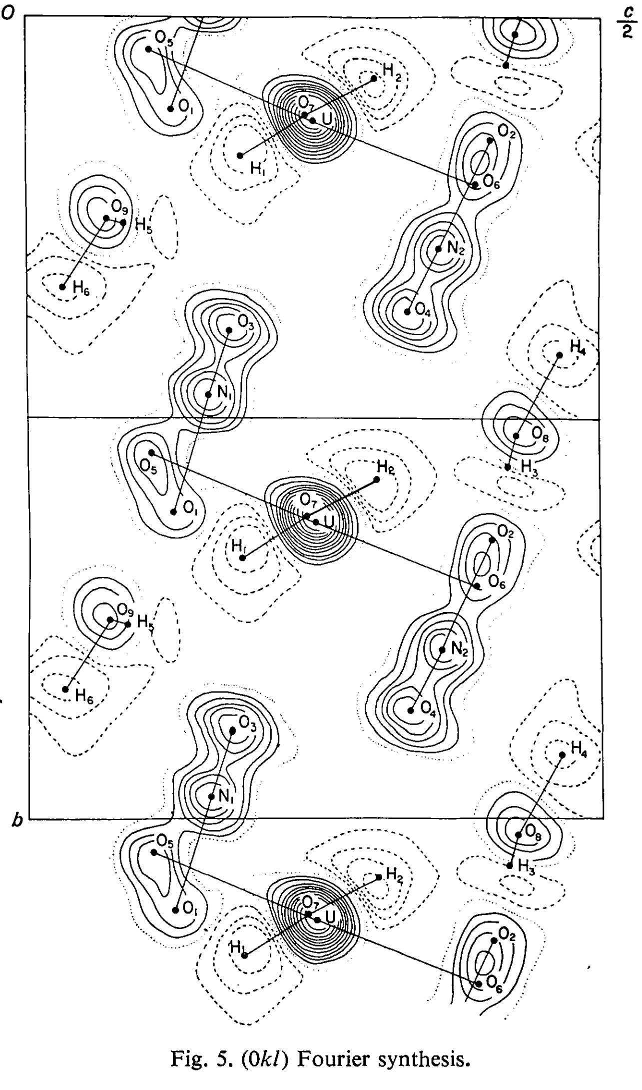

Fig. 5. (0*kl*) Fourier synthesis.

We wish to acknowledge the assistance of R. L. Hitterman and H. W. Knott in the collection of the three-dimensional data; and of J. Gvildys in the computer calculations. One of us (J.C.T.) appreciates the help of T. M. Sabine and Professor G. A. Barclay of Sydney, Australia, in the earlier two-dimensional study. We appreciate the interest shown by Alan E. Comyns and Professor H. Lynton in the present investigation and the encouragement offered by F. G. Foote and S. S. Sidhu. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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# The Crystal Structure of Lautite, CuAsS

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Lautite crystallizes in space group $Pna2_1$ of the orthorhombic system in a cell of dimensions $a=11\cdot35$, $b=5\cdot456$, $c=3\cdot749$ Å. There are four formula units in the cell. The $hk0$ and $h0l$ data were collected with Mo $K\alpha$ radiation by film methods and were estimated photometrically. The structure was solved by Patterson methods and refined by both Fourier and least-squares techniques.

Lautite has a sphalerite derivative structure. The tetrahedral environment of each atom is as follows: Cu-3S, 1As: As–2As, 1Cu, 1S: S–3Cu, 1As. Bond distances and angles are normal and one interesting feature of the structure is the existence of infinite, planar, zigzag chains of arsenic atoms extending along a direction parallel to [001].

## Introduction

Lautite (CuAsS) is a mineral found in very few occurrences, and derives its name from the type locality of Lauta, Saxony, where it occurs associated with native arsenic, tennantite, proustite, chalcopyrite, galena and barite (Palache, Berman & Frondel, 1944). The same authors give the point group as $2/m\ 2/m\ 2/m$, which is not consistent with the space group $P2_12_12_1$ reported by Berry & Thompson (1962). No previous structure