where the coefficients are direction cosines relative to *a*, *b*, and *c**.

The bond distances and angles involving the hydrogen atoms are listed in Table 3. The standard deviations in the coordinates of the hydrogen atoms are so large (about 0·4 Å) as to make these values of little significance. Indeed, the final least-squares position of H(4) was so ridiculous – somewhere near the center of the carbon ring – as to cause us to return it forcibly to its logical position and to remove it from the refinement.

Table 3. C–H *bond distances and angles*

| | | | |
|---|---|---|---|
| C(1)–H(1) | 0·94 Å | C(4)–H(4) | 0·98 Å |
| C(2)–H(2) | 1·12 | C(5)–H(5) | 1·10 |
| C(3)–H(3) | 1·26 | C(5)–H(6) | 0·97 |
| C(5)–C(1)–H(1) | 124° | C(5)–C(4)–H(4) | 127° |
| C(2)–C(1)–H(1) | 125 | C(4)–C(5)–H(5) | 96 |
| C(1)–C(2)–H(2) | 125 | C(4)–C(5)–H(6) | 93 |
| C(3)–C(2)–H(2) | 123 | C(1)–C(5)–H(5) | 83 |
| C(2)–C(3)–H(3) | 99 | C(1)–C(5)–H(6) | 126 |
| C(4)–C(3)–H(3) | 151 | H(5)–C(5)–H(6) | 147 |
| C(3)–C(4)–H(4) | 125 | | |

A view of the structure looking down the *b* axis is shown in Fig. 3. The shortest intermolecular C · · · C contact is 3·65 Å between C(5) atoms related by a center of symmetry.

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# The Crystal Structure of Rubidium Uranyl Nitrate: A Neutron-Diffraction Study

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The crystal structure of rubidium uranyl nitrate, $RbUO_2(NO_3)_3$, has been determined from neutron-diffraction intensities for two zones of reflexions. The light-atom positions have been defined more accurately than was possible with X-ray data. The uranium atom is surrounded by eight oxygen atoms at the corners of a distorted hexagonal bipyramid (six nitrate oxygen atoms at 2·48 Å and two uranyl oxygen atoms at 1·78 Å). Each nitrate group acts as a bidentate chelate forming a four-membered ring system. The rubidium atom has twelve oxygen atoms as its near neighbours.

## Introduction

In their X-ray study of rubidium uranyl nitrate, Hoard & Stroupe (1949) were able to locate the rubidium and uranium atoms in the unit cell but, because of the overwhelming scattering by the metal atoms, they were unable to determine directly the positions of the nitrate group atoms and the uranyl oxygen atoms. A neutron-diffraction study was undertaken by us to locate these nitrogen and oxygen atoms.

Few accurate studies of uranyl compounds have been made by X-ray diffraction; notable exceptions are the studies of Zachariasen, which are referred to in a paper on sodium uranyl acetate (Zachariasen & Plettinger, 1959). A review of the structural chemistry of uranyl compounds has been given by Evans (1963).

## Crystal data

See Hoard & Stroupe (1949).

Rubidium uranyl nitrate, $RbUO_2(NO_3)_3$, crystallizes in the rhombohedral division of the trigonal system with

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$$a = 8{\cdot}30 \pm 0{\cdot}03\ \text{Å};\quad \alpha = 68°42' \pm 20'\ .$$

There are two formula units in the rhombohedral cell. The corresponding triple hexagonal cell has dimensions

$$a' = 9{\cdot}36 \pm 0{\cdot}03,\quad c = 18{\cdot}88 \pm 0{\cdot}06\ \text{Å}\ .$$

The observed density is 3·72 g.cm$^{-3}$. The space group is $R\bar{3}C$ ($D_{3d}^{6}$, no. 167).

In the rest of this paper indices and fractional coordinates referred to the rhombohedral cell are denoted by $(h, k, l)$, $(x, y, z)$ while those referred to the hexagonal cell are denoted by $(HK\,.\,L)$, $(X, Y, Z)$.

## The model of Hoard & Stroupe (in terms of the hexagonal cell)

From refractive index measurements Hoard & Stroupe concluded that the nitrate groups lay in planes perpendicular to the hexagonal $c$ axis. The uranium and rubidium atoms were required to occupy the special positions 6($a$) and 6($b$) or *vice versa* in the hexagonal cell, while the uranyl oxygen atom was required to be in positions 12($c$) (with the variable parameter $Z$) on the hexagonal $c$ axis. The eighteen N atoms were in positions 18($e$) (point symmetry 2); the positions 18($d$) (point symmetry $\bar{1}$) were ruled out as the nitrate group has no centre of symmetry. Eighteen of the fifty-four nitrate oxygen atoms in the hexagonal cell were placed in 18($e$) and the remaining 36 in the general positions 36($f$). Assuming that the uranyl bond length was 1·58 Å and that the coordinated nitrate oxygen atoms were 2·72 Å from the uranium atom, Hoard & Stroupe deduced the parameters listed in Table 1.

To obtain the coordinates of all the atoms in the hexagonal cell, $(\frac{1}{3}, \frac{2}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ must be added to each of the above coordinates in turn (obverse orientation).

## Experimental

A crystal of rubidium uranyl nitrate (approximate volume 30 mm$^3$) was mounted on a vanadium strip on a goniometer head and lightly smeared with silicone grease to prevent deliquescence. Neutron diffraction data for the $0K\,.\,L$ and $hk0$ reflexions were collected on a single-crystal neutron diffractometer on the reactor HIFAR at Lucas Heights, N.S.W.; the neutron wavelength was 0·937 Å. Thirty-four $0K\,.\,L$ and eighty-nine $hk0$ reflexions were observed, the cutoff being at $\sin\theta/\lambda = 0{\cdot}92$.

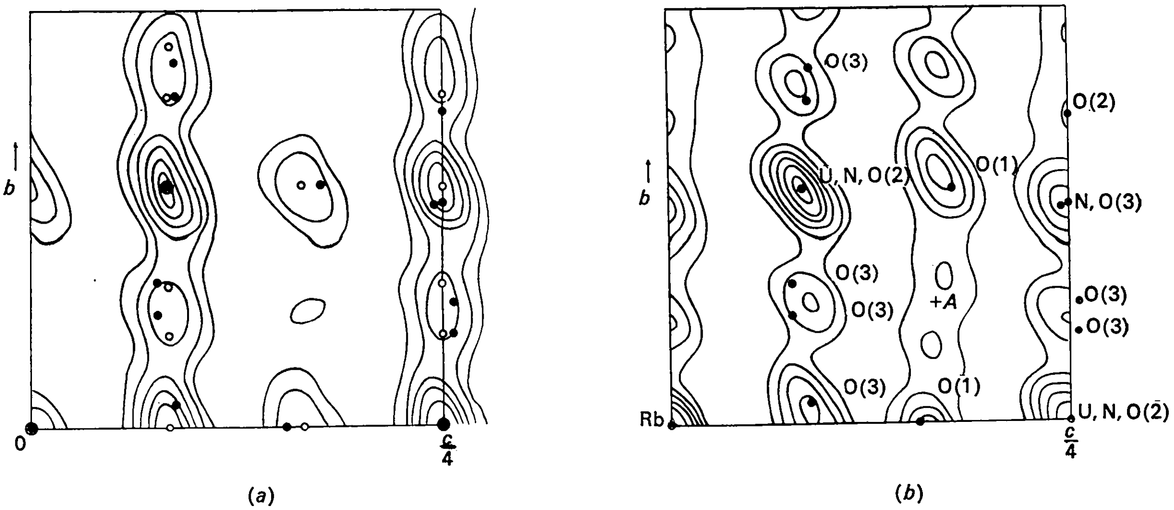
## Structure analysis

Structure factors were calculated for the observed reflexions with the use of the coordinates of Hoard & Stroupe (see Table 1), isotropic temperature factor $B$ of 3·0 Å$^2$ and scattering lengths given by Bacon (1962). Agreement between $F_o$ and $F_c$ was poor, the agreement index $R$ being 0·45 for the $OK\,.\,L$ data and 0·71 for the $hk0$ data. The coordinates proposed by Hoard & Stroupe were thus considerably in error.

Table 1. *Hoard & Stroupe's positional parameters*

6 U in 6($a$): $\pm(0, 0, \frac{1}{4})$
6 Rb in 6($b$): $(0, 0, 0)$ $(0, 0, \frac{1}{2})$
12 O(1) (uranyl) in 12($c$): $\pm(0, 0, Z;\ 0, 0, \frac{1}{2}+Z)$; $Z = 0{\cdot}167$
18 N in 18($e$): $\pm(X, 0, \frac{1}{4};\ 0, X, \frac{1}{4};\ \bar{X}, \bar{X}, \frac{1}{4})$; $X = 0{\cdot}333$
18 O(2) (nitrate) in 18($e$): $\cdots$ ; $X = 0{\cdot}460$
36 O(3) (nitrate) in 36($f$); $\pm(X, Y, Z;\ \bar{Y}, X-Y, Z;\ Y-X, \bar{X}, Z;\ \bar{Y}, \bar{X}, \frac{1}{2}+Z;\ X, X-Y, \frac{1}{2}+Z;\ Y-X, Y, \frac{1}{2}+Z)$; $X = 0{\cdot}333$, $Y = 0{\cdot}130$, $Z = 0{\cdot}250$

Attempts to refine the $OK\,.\,L$ projection with the use of this model as a starting-point failed; there was considerable overlap in the projection [Fig. 1($a$)] and the corresponding difference synthesis showed deep holes at the atomic sites but there were no slopes indic-



($a$) ($b$)

Fig. 1. O$K.L$ projection of neutron scattering density. ($a$) Structure factors from Hoard & Stroupe parameters. ($b$) Terms with phases fixed by uranium and rubidium atoms. Open circles: Hoard & Stroupe model. Dots: final neutron diffraction parameters.

ating the directions in which the atoms of the nitrate group should be shifted.

A $0K.L$ projection was now constructed using only those terms whose signs were probably fixed by the metal atoms (moderately large $F$'s, with $L/4$ integral) [Fig. 1(*b*)]. On the basis of this map, the nitrate group was shifted 0·24 Å closer to the uranium atom along the twofold axis and the uranyl oxygen atom O(1) was shifted 0·17 Å away from the uranium atom. The value of $R(0K.L)$ using the revised coordinates now improved to 0·23. After two difference syntheses, $R(0K.L)$ dropped to 0·125.

At this stage, the bond distances in the nitrate group were N–O(2) = 1·32 Å and N–O(3) = 1·20 Å. The difference in these distances, together with the fact that there were negative peaks in the difference synthesis of about $\frac{1}{5}$ the height of the atomic peaks in the direct synthesis, suggested that the nitrate group coordinates were still somewhat in error.

The rhombohedral *hk*0 data were now included in the refinement. For the parameters derived from the $0K.L$ refinement, $R(hk0)$ was 0·35. In the *hk*0 difference projection the atoms of nitrate groups were clearly resolved and slopes at these sites indicated shifts of 0·12, 0·13 and 0·09 Å for N, O(3) and O(2) respectively. Only a slight shift was indicated for the uranyl oxygen atom O(1) which was well resolved in the $0K.L$ projection.

From this point, refinement of the structural parameters was made by calculating both $0K.L$ and *hk*0 difference syntheses, and the refinement proceeded smoothly in four cycles to $R(0K.L) = 0{\cdot}128$ and $R(hk0) = 0{\cdot}142$. After these cycles the difference maps were flat; peaks at the atomic positions were less than $^1/_{10}$ of the corresponding peak heights in the direct Fourier map. An inspection of the $F_o$ and $F_c$ values indicated that the data were not seriously affected by extinction.

Further refinement was carried out with Busing & Levy's full-matrix least-squares program. The rhombohedral data were re-indexed according to the hexagonal setting and equal weights were given to each reflexion; anisotropic thermal parameters were not included in the refinement because of the relatively small number of reflexions available. Convergence was obtained after three cycles ($R$=0·12). Recent work by Sidhu (1964) suggested that the neutron scattering length for rubidium should be 0·85 and not 0·55 ($10^{-12}$ cm) as had been used up to this point. Three further cycles were carried out with the changed value; $R$ remained un-

Table 2. *Neutron diffraction atomic parameters*

| Atom | Difference synthesis refinement | | | | Least-squares refinement | | | |
|---|---|---|---|---|---|---|---|---|
| | $X$ | $Y$ | $Z$ | $B$ | $X$ | $Y$ | $Z$ | $B$ |
| O(3) | 0·3045 | 0·1303 | 0·2555 | 3·52 | 0·3044<br>(±0·0013) | 0·1328<br>(±0·0012) | 0·2549<br>(±0·0005) | 3·02<br>(±0·16) |
| O(2) | 0·4395 | 0 | ¼ | 3·82 | 0·4377<br>(±0·0017) | 0 | ¼ | 3·74<br>(±0·30) |
| N | 0·3095 | 0 | ¼ | 3·39 | 0·3080<br>(±0·0009) | 0 | ¼ | 2·65<br>(±0·14) |
| O(1) | 0 | 0 | 0·1550 | 3·45 | 0 | 0 | 0·1557<br>(±0·0009) | 2·96<br>(±0·28) |
| Rb | 0 | 0 | 0 | 2·36 | 0 | 0 | 0 | 3·42<br>(±0·25) |
| U | 0 | 0 | ¼ | 2·12 | 0 | 0 | ¼ | 2·09<br>(±0·21) |

Table 3. *Bond lengths, bond angles and contact distances in rubidium uranyl nitrate*

| | Difference synthesis refinement | Least-squares refinement | |
|---|---|---|---|
| Bond | Distance | Distance | E.s.d. |
| U–O(1) | 1·79 Å | 1·78 Å | 0·01$_7$ Å |
| U–O(3) | 2·48 | 2·48 | 0·01$_1$ |
| N–O(3) | 1·25 | 1·26 | 0·01$_3$ |
| N–O(2) | 1·22 | 1·21 | 0·01$_7$ |
| O(3)–O(3) | 2·12; 2·83 | 2·16; 2·79 | 0·01$_5$ |
| O(3)–O(2) | 2·15 | 2·16 | 0·01$_9$ |
| O(1)–O(3) | 3·12; 3·00; 3·28 | 3·10; 3·00; 3·28 | 0·02$_0$ |
| O(1)–O(2) | 3·07 | 3·08 | 0·02$_3$ |
| Rb–O(1) | 2·93 | 2·94 | 0·01$_7$ |
| Rb–O(2) | 3·18 | 3·18 | 0·01$_5$ |
| Rb–O(3) | 3·29 | 3·29 | 0·01$_1$ |
| Bond angle | Angle | Angle | E.s.d. |
| O(1)–U–O(3) | 92·4; 87·6° | 92·2; 87·8° | 0·6° |
| O(3)–N–O(2) | 121·8 | 121·2 | 1·1 |
| O(3)–N–O(3) | 116·5 | 117·5 | 0·9 |

changed at 0·12 and there were only small changes in the parameters of the other atoms but the temperature factor of the rubidium atom changed from $B=1{\cdot}78$ Å$^2$ to $B=3{\cdot}42$ Å$^2$.

The atomic parameters obtained from difference syntheses and least-squares are listed in Table 2; the errors listed are the least-squares errors to which must be added uncertainties in unit-cell dimensions. Bond lengths, bond angles and contact distances are listed in Table 3 and a list of the observed structure amplitudes and final calculated structure factors is given in Table 4.

## Discussion

It is interesting to note that the atomic parameters (with the exception of the *B* values), contact distances, and angles which were obtained by difference synthesis refinement did not differ significantly from those obtained with full-matrix least-squares refinement even when a vastly different neutron-scattering length for rubidium was used.

The structure is conveniently discussed in terms of the hexagonal cell. The atoms are stacked in layers perpendicular to *C*, the layers being spaced *C*/12 apart. The layers $Z=11/12, 0, \frac{1}{12}, \frac{1}{6}, \frac{1}{4}$ and $\frac{1}{3}$ are shown in Fig. 2(*a*)–(*f*). The U, Rb, N and O(2) atoms lie exactly at the specified levels, while the nitrate oxygen atoms, O(3), and the uranyl oxygen atoms, O(1), deviate slightly by 0·09 and 0·21 Å respectively. The layers are alternately (rubidium ions + uranyl oxygen atoms) and (uranium atoms + nitrate groups).

The configuration of oxygen atoms about the uranium atom is shown in Fig. 3. The uranyl ion is seen end-on; the uranium atom lies in the plane of the paper

Table 4. *Observed structure amplitudes and calculated structure factors*

Reflexions too weak to be recorded are listed with $|F_o|=0$.

(a) Rhombohedral hk0 data - hexagonal indices

0 K.L

| | | | |
|---|---|---|---|
| 1 | 2 | 7.94 | -6.32 |
| 2 | 4 | 1.87 | -1.06 |
| 3 | 6 | 3.29 | -2.51 |
| 4 | 8 | 11.20 | 11.89 |
| 5 | 10 | 2.35 | -2.88 |
| 6 | 12 | 16.74 | 18.33 |
| 7 | 14 | 12.38 | -12.06 |
| 8 | 16 | 3.49 | -2.86 |
| 9 | 18 | 1.86 | -1.44 |
| 10 | 20 | 3.63 | 5.38 |
| 11 | 22 | 0 | -1.22 |

1 K.L

| | | | |
|---|---|---|---|
| -2 | -3 | 21.92 | -20.87 |
| -3 | -5 | 1.83 | 1.93 |
| -4 | -7 | 1.24 | -0.94 |
| -5 | -9 | 1.22 | 0.87 |
| -6 | -11 | 5.20 | -5.52 |
| -7 | -13 | 2.23 | -1.64 |
| -8 | -15 | 7.26 | -7.03 |
| -9 | -17 | 4.36 | 5.75 |
| -10 | -19 | 1.82 | 1.39 |
| -11 | -21 | 1.31 | -0.36 |

2 K.L

| | | | |
|---|---|---|---|
| 0 | 2 | 0 | 0.54 |
| -1 | 0 | 2.64 | -1.44 |
| -3 | -4 | 1.60 | 1.78 |
| -4 | -6 | 8.16 | -6.37 |
| -5 | -8 | 13.56 | 12.39 |
| -6 | -10 | 1.50 | 1.62 |
| -7 | -12 | 2.13 | 2.53 |
| -8 | -14 | 3.36 | 3.64 |
| -9 | -16 | 2.11 | 2.25 |
| -10 | -18 | 1.64 | 0.80 |
| -11 | -20 | 2.39 | 2.96 |

3 K. L

| | | | |
|---|---|---|---|
| -2 | -1 | 2.10 | -2.36 |
| -4 | -5 | 3.84 | 2.78 |
| -5 | -7 | 4.16 | 4.85 |
| -6 | -9 | 9.51 | 8.99 |
| -7 | -11 | 2.05 | -1.42 |
| -8 | -13 | 2.94 | -2.48 |
| -9 | -15 | 3.01 | 3.14 |
| -10 | -17 | 0 | -0.83 |
| -11 | -19 | 0 | -0.37 |

4 K.L

| | | | |
|---|---|---|---|
| 0 | 4 | 4.94 | 4.70 |
| -3 | -2 | 7.50 | -5.63 |
| -5 | -6 | 15.47 | 14.53 |
| -6 | -8 | 3.21 | 4.02 |
| -7 | -10 | 8.18 | -8.07 |
| -8 | -12 | 7.28 | 7.14 |
| -9 | -14 | 4.29 | -3.26 |
| -10 | -16 | 1.29 | 1.83 |
| -11 | -18 | 0 | 0.57 |
| -12 | -20 | 1.04 | 1.16 |

5 K.L

| | | | |
|---|---|---|---|
| -3 | -1 | 6.61 | 5.92 |
| -4 | -3 | 1.86 | 1.47 |
| -6 | -7 | 3.83 | -4.55 |
| -7 | -9 | 7.12 | -7.80 |
| -9 | -13 | 4.51 | 4.26 |
| -10 | -15 | 0 | -0.93 |
| -11 | -17 | 0.74 | -0.01 |
| -12 | -19 | 0 | -0.93 |

6 K.L

| | | | |
|---|---|---|---|
| 0 | 6 | 11.62 | -10.93 |
| -3 | 0 | 14.90 | 16.25 |
| -4 | -2 | 2.35 | 2.30 |
| -5 | -4 | 2.39 | -2.67 |
| -7 | -8 | 12.91 | 11.37 |
| -9 | -12 | 8.12 | 7.14 |
| -10 | -14 | 1.64 | -1.57 |
| -12 | -18 | 1.54 | -0.83 |

7 K.L

| | | | |
|---|---|---|---|
| -4 | -1 | 3.20 | -2.65 |
| -5 | -3 | 8.28 | -8.71 |
| -6 | -5 | 6.50 | 5.28 |
| -8 | -9 | 7.18 | 7.88 |
| -9 | -11 | 3.29 | -3.95 |
| -10 | -13 | 2.29 | -2.31 |
| -11 | -15 | 0.79 | -0.25 |
| -12 | -17 | 2.28 | 2.12 |

8 K.L

| | | | |
|---|---|---|---|
| 0 | 8 | 0 | -0.33 |
| -4 | 0 | 10.65 | 11.06 |
| -5 | -2 | 1.96 | 1.63 |
| -6 | -4 | 5.39 | -4.42 |
| -7 | -6 | 8.40 | 6.81 |
| -9 | -10 | 1.00 | 2.12 |
| -10 | -12 | 2.38 | 3.38 |
| -11 | -14 | 0 | -0.43 |
| -12 | -16 | 0.92 | -0.57 |

9 K.L

| | | | |
|---|---|---|---|
| -5 | -1 | 4.71 | -4.42 |
| -6 | -3 | 4.13 | -3.16 |
| -7 | -5 | 6.64 | -4.92 |
| -8 | -7 | 10.00 | 10.59 |
| -10 | -11 | 1.14 | -0.46 |
| -11 | -13 | 2.70 | -3.31 |
| -12 | -15 | 0 | 0.34 |

10 K.L

| | | | |
|---|---|---|---|
| 0 | 10 | 5.67 | -7.09 |
| -5 | 0 | 4.12 | 4.80 |
| -6 | -2 | 3.13 | -3.21 |
| -7 | -4 | 6.85 | 6.73 |
| -8 | -6 | 2.43 | 2.84 |
| -9 | -8 | 4.51 | 5.82 |
| -11 | -12 | 0 | 2.41 |
| -12 | -14 | 0 | 0.42 |

11 K.L

| | | | |
|---|---|---|---|
| -6 | -1 | 2.60 | -1.24 |
| -7 | -3 | 1.14 | 0.87 |
| -8 | -5 | 1.68 | 2.46 |
| -9 | -7 | 2.97 | -4.36 |
| -10 | -9 | 0 | -1.30 |
| -12 | -13 | 0 | 0.43 |

12 K.L

| | | | |
|---|---|---|---|
| 0 | 12 | 2.52 | 2.90 |
| -6 | 0 | 4.51 | 5.82 |
| -7 | -2 | 1.71 | -1.29 |
| -8 | -4 | 0 | -0.51 |
| -9 | -6 | 2.14 | -1.08 |
| -10 | -8 | 1.22 | 1.71 |
| -11 | -10 | 0 | 0.99 |

13 K.L

| | | | |
|---|---|---|---|
| -7 | -1 | 1.39 | 0.63 |
| -8 | -3 | 0 | -0.52 |
| -9 | -5 | 1.12 | -1.23 |
| -10 | -7 | 3.48 | 3.60 |
| -11 | -9 | 0 | 0.75 |
| -12 | -11 | 0 | -0.87 |

14 K.L

| | | | |
|---|---|---|---|
| -7 | 0 | 4.17 | 5.88 |
| -8 | -2 | 0 | -0.06 |
| -9 | -4 | 1.26 | 0.19 |
| -10 | -6 | 1.38 | 0.15 |
| -11 | -8 | 0 | 1.95 |

15 K.L

| | | | |
|---|---|---|---|
| -8 | -1 | 2.66 | -3.69 |
| -9 | -3 | 0 | -2.14 |
| -10 | -5 | 0 | -0.26 |
| -12 | -9 | 0 | 0.27 |

16 K.L

| | | | |
|---|---|---|---|
| -8 | 0 | 0 | 0.46 |
| -9 | -2 | 1.29 | -2.74 |
| -10 | -4 | 2.09 | 3.14 |

17 K.L

| | | | |
|---|---|---|---|
| -9 | -1 | 1.45 | 1.50 |
| -10 | -3 | 0 | -0.10 |

(b) Hexagonal 0 K.L data.

0 K.L

| | | | |
|---|---|---|---|
| 0 | 6 | 35.22 | -38.19 |
| 0 | 12 | 45.15 | 45.21 |
| 0 | 18 | 22.49 | -22.12 |
| 0 | 24 | 15.39 | 15.79 |
| 1 | 2 | 7.98 | -6.46 |
| 1 | 8 | 12.06 | 11.68 |
| 1 | 14 | 0 | -0.10 |
| 1 | 20 | 12.49 | 7.47 |
| 1 | 26 | 1.62 | 0.64 |
| 2 | 4 | 2.22 | -1.08 |
| 2 | 10 | 1.83 | 1.88 |
| 2 | 16 | 5.20 | -4.75 |
| 2 | 22 | 0 | 2.06 |
| 2 | 28 | 0 | -1.62 |
| 3 | 0 | 21.91 | 24.46 |
| 3 | 6 | 3.03 | -2.57 |
| 3 | 12 | 19.05 | 15.74 |
| 3 | 18 | 5.33 | -3.74 |
| 3 | 24 | 8.91 | 5.48 |
| 4 | 2 | 5.46 | -5.16 |
| 4 | 8 | 11.76 | 12.17 |
| 4 | 14 | 5.19 | -4.16 |
| 4 | 20 | 11.60 | 10.34 |
| 5 | 4 | 0 | 0.65 |
| 5 | 10 | 2.91 | -2.94 |
| 5 | 22 | 2.45 | -2.60 |
| 6 | 0 | 25.99 | 27.01 |
| 6 | 6 | 12.06 | -11.01 |
| 6 | 12 | 19.63 | 18.76 |
| 6 | 18 | 7.07 | -7.64 |
| 7 | 2 | 22.38 | -21.56 |
| 7 | 8 | 23.33 | 22.46 |
| 7 | 14 | 12.23 | -12.34 |
| 7 | 20 | 12.96 | 12.16 |
| 7 | 26 | 2.27 | -4.06 |
| 9 | 0 | 10.34 | 11.60 |

with the uranyl oxygen atoms above and below it at a distance of 1·78 Å. The uranyl ion is symmetrical and linear. A hexagon of six O(3) atoms from three bidentate nitrate groups surrounds the uranyl ion equatorially, U–O(3) being 2·48 Å. The hexagon is slightly puckered as the O(3) atoms are alternately 0·09 Å above and below the plane. The configuration around U(VI) is thus an irregular hexagonal bipyramid. The U–O distances agree well with those found by Zachariasen & Plettinger (1959) in sodium uranyl acetate.

The arrangement of oxygen atoms around the rubidium ion can be seen by comparing Figs. 2(*c*), (*d*) and (*e*). The $Rb^+$ ion at ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{6}$) has twelve nitrate oxygen atoms as near neighbours – three O(2) and three O(3) atoms at the level $C/4$ and three O(2) and three O(3) atoms at the level $C/12$. The Rb–O separations are 3·18 Å for Rb–O(2) and 3·29 Å for Rb–O(3). There are also two O(1) atoms on the threefold inversion axis ($\frac{1}{3}$, $\frac{2}{3}$, $Z$) distant 2·94 Å from the $Rb^+$ ion. The rubidium ion thus has the rather large coordination number of 14. The irregular hexagons of nitrate oxygen atoms around $Rb^+$ at $C/4$ and $C/12$ are not superposable; the N–O(2) bonds in the two layers are inclined at 60° [*cf.* Fig. 2(*c*), (*e*)].

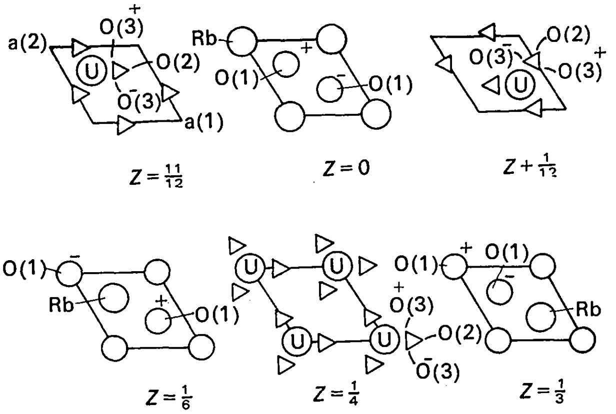


Fig. 2. The structure of rubidium uranyl nitrate illustrating the alternating layers of rubidium ions plus uranyl oxygen atoms and uranium atoms plus nitrate groups.

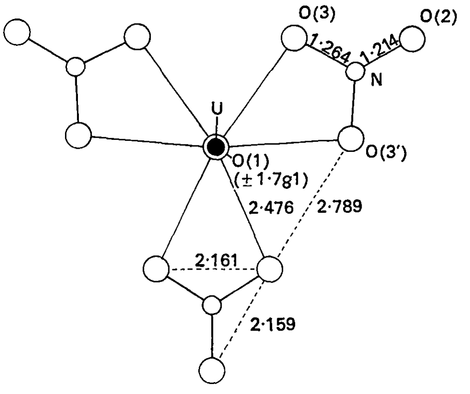


Fig. 3. Configuration of oxygen atoms about the uranium atom and bond distances (Å) in the nitrate group.

The uranyl oxygen atom has twelve nitrate oxygen atoms and one $Rb^+$ ion as nearest neighbours (*cf.* Fig. 2(*a*), (*b*), (*c*)]. The O(1) atom at ($\frac{1}{3}$, $\frac{2}{3}$, 0·0110) is distant 3·00 Å from three O(3) atoms and 3·10 Å from the other three O(3) atoms in the layer $11C/12$. O(1) is distant 3·28 Å from three O(3) atoms and 3·08 Å from three O(2) atoms in the layer $C/12$. The O(1)–$Rb^+$ distance is 2·94 Å.

The environments of the uranyl oxygen atom and the rubidium ion are thus very similar, which might be expected in view of their similar size and charge. The contact distances are close to the sum of the relevant ionic or atomic radii.

The nitrate group is planar but its symmetry is affected by interaction with the uranium atom. The bond lengths N–O(2) (1·21 Å) and N–O(3) (1·26 Å) are probably significantly different. Also, the angle O(3)–N–O(3) (117·5°) differs significantly from 120°. Sass, Vidale & Donohue (1957) found an N–O distance of 1·21 Å in sodium nitrate by neutron diffraction.

The curve of Zachariasen & Plettinger (1959), relating 'bond-strength' with bond-lengths in uranyl compounds, would predict U–O(1) = 1·70 Å and U–O(3) = 2·49 Å in rubidium uranyl nitrate. The small differences between these values and the values found in the present study are not significant – Zachariasen & Plettinger's curve is based on a few X-ray studies only and is simply intended as a rough guide in predicting U–O distances in uranyl compounds.

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