Table 4. *Bond distances, polyhedral edge lengths, and bond angles for the phosphate tetrahedron*

Numbers in parentheses are estimated standard deviations in last significant figure.

(i) Interatomic distances

P–O(1)	1·536 (2) Å	O(1)–O(2)	2·535 (3) Å
P–O(2)	1·521 (3)	O(1)–O(3)	2·445 (3)
P–O(3)	1·564 (3)	O(1)–O(4)	2·519 (3)
P–O(4)	1·537 (2)	O(2)–O(3)	2·580 (4)
		O(2)–O(4)	2·542 (3)
		O(3)–O(4)	2·445 (3)

(ii) Angles

O(1)–P–O(2)	112·0 (1)°
O(1)–P–O(3)	104·1 (1)
O(1)–P–O(4)	110·1 (1)
O(2)–P–O(3)	113·5 (1)
O(2)–P–O(4)	112·4 (1)
O(3)–P–O(4)	104·1 (1)

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The Crystal and Molecular Structure of 2-Formylpyridine Selenosemicarbazone

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The structure of 2-formylpyridine selenosemicarbazone, $SeN_4C_7H_8$, has been determined from three-dimensional X-ray photographic data. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a=9{\cdot}320$, $b=6{\cdot}524$ and $c=16{\cdot}275$ Å, $\beta=90{\cdot}53°$. There are four formula units in the cell. The structure was solved by the two-dimensional minimum Patterson function and the heavy atom method. It was refined by a full-matrix least-squares method to a final residual R value of 0·11 for 1180 observed reflexions. The Se–C bond length of 1·83 Å possesses only partial double-bond character. The molecules are linked by N–H···Se hydrogen bonds to form dimer-like units, which are held together by N–H···N hydrogen bonds.

Introduction

In recent years, several organic compounds of selenium have been investigated. The molecular structures of different selenosemicarbazones have been studied by Gingras, Suprunchuk & Bayley (1965); they described their infrared spectra with particular emphasis on the Se–C vibration and they have studied the antifugal properties of selenosemicarbazones that were found to be generally more active than the corresponding thiosemicarbazones. French & Blanz (1966) have studied various thiosemicarbazones and have found that all the tumour inhibitors are potentially capable of acting as tridentate N–N–S type ligands. Mathew & Palenik (1969) reported the crystal structure of bis-(1-formyl-isoquinolinethiosemicarbazonato)nickel(II) monohydrate and confirmed the ability of the ligand to act as a tridentate chelate. However, the compound 2-formylthiophene thiosemicarbazone (Mathew & Palenik, 1971) shows no tumour inhibition although the posibility of an N–N–S type chelate exists. On the other hand, French & Blanz (1966) reported that 4-formylpyridine thiosemicarbazone shows no carcinostatic activity, whereas they found that 2-formylpyridine thiosemicarbazone is a tumour inhibitor. Apparently the position of the thiosemicarbazone group on the pyridine nucleus dictates the biological activity of formylpyridine thiosemicarbazones. A knowledge of the conformation and bond lengths is essential for a final explanation of the requirements for biological activity in these compounds. Therefore, a crystal structure analysis of 2-formylpyridine selenosemicarbazone was carried out to correlate the molecular structure with the thiosemicarbazone analogues.

Experimental

Crystals of 2-formylpyridine selenosemicarbazone used in this work were prepared and kindly supplied by Dr J. M. Cano of this University. They are brown, needle-shaped prisms, elongated along the *b* axis and belonging to the monoclinic system.

Cell dimensions were measured from Weissenberg photographs of the three zero levels, upon which Debye–Scherrer diagrams with aluminum powder as standard were superimposed. The crystal data obtained are:

$a = 9{\cdot}320 \pm 0{\cdot}008$ Å	$D_m 1{\cdot}48 \pm 0{\cdot}02$ g.cm^{-3}
$b = 6{\cdot}524 \pm 0{\cdot}005$	$D_x = 1{\cdot}51$
$c = 16{\cdot}275 \pm 0{\cdot}014$	μ (Cu $K\alpha$) = 49 cm^{-1}
$\beta = 90{\cdot}53 \pm 0{\cdot}05°$	$F(000) = 112$
$Z = 4$.	

Systematic absences were consistent with space group $P2_1/c$. Two series of equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation about the *a* axis up to the third layer, and about the *b* axis up to the fourth layer. The multiple-film technique was used and 1180 independent reflexions were collected. The intensities were estimated visually with a standard film strip and were converted to $F_o(hkl)$ by applying the usual Lorentz, polarization and spot-shape corrections. No correction was made for either absorption or extinction. One of the crystals used for the *a* axis rotation had a cross section of $0{\cdot}10 \times 0{\cdot}11$ mm, and that for the *b* axis rotation a cross section of $0{\cdot}07 \times 0{\cdot}06$ mm. The two series of intensity data were correlated and reduced to a common scale by a least-squares method. The data were brought to the absolute scale by comparison with the calculated values at a later stage.

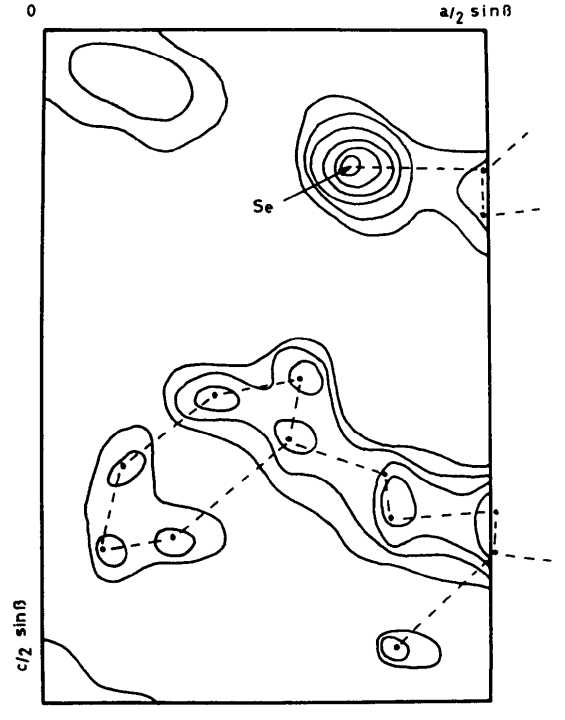


Fig. 1. The minimum function $M_2(x,z)$.

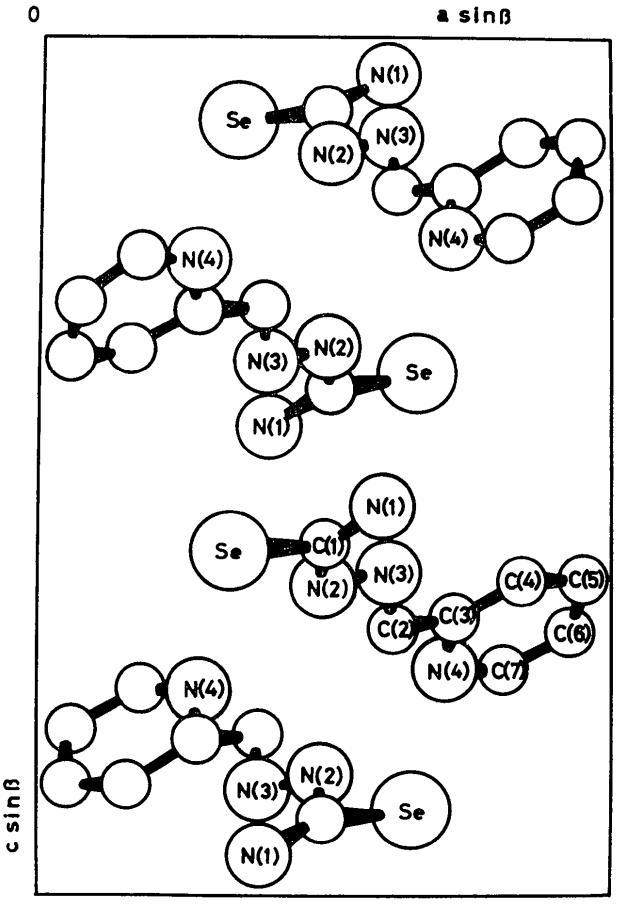


Fig. 2. A projection of the structure along the *b* axis.

Structure determination and refinement

The structure was solved by combining two-dimensional Patterson superposition methods and three-dimensional Fourier syntheses. The two-dimensional Patterson syntheses $P(v, w)$ and $P(u, w)$ showed outstanding maxima which were attributed to selenium–selenium vectors. The minimum functions $M_2(y, z)$ and $M_2(x, z)$ (Buerger, 1951) were then calculated using the vectors Se–Se through the symmetry centre. The $M_2(x, z)$ function (Fig. 1) shows good resolution and led to the location of the possible positions for all the light atoms. However, the relative position of the molecule makes the interpretation of the other projection difficult. It proved necessary to use three-dimensional methods to obtain the *y* coordinates for the light atoms.

Using only the phases the selenium atom, all the light atoms excepting hydrogen were located after one cycle of structure-factor calculations and a three-dimensional electron-density synthesis. A structure-factor calculation with the set of coordinates obtained gave an R index of 0·21. A Fourier synthesis was calculated and the R value dropped to 0·17 for all observed reflexions. Isotropic temperature factors, $\exp(-2{\cdot}5\ \sin^2\theta/\lambda^2)$, were used in calculating structure factors.

The refinement by means of six least-squares cycles, of which the last three were with anisotropic thermal factors, were sufficient to reduce the discrepancy index to 0·11. A full-matrix program written by Busing, Martin & Levy (1962) was used, in which the weighting scheme was that of Hughes (1941). In the anisotropic refinement complex scattering factors were introduced for the correction of the anomalous dispersion, which was expected to be significant for the Se atom ($\Delta f' = -1{\cdot}0$, $\Delta f'' = 1{\cdot}1$).

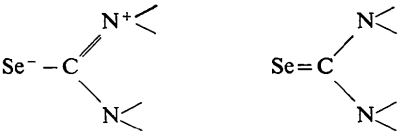
With the above calculations, inter- and intramolecular distances and bond angles were obtained as a test of the improvement in the structure.

The F_o and final F_c values are given in Table 1, and the final atomic parameters and their corresponding standard deviations in Tables 2 and 3.

Description of the structure

A projection of the structure along the [010] direction is shown in Fig. 2. Bond distances and angles in the 2-formylpyridine selenosemicarbazone molecule are listed in Table 4 and shown in Fig. 3.

The observed value of 1·83 Å for the Se–C distance is intermediate between the Se–C single-bond distance of 1·92 Å and the Se–C double-bond value of 1·71 Å. Thus, the Se–C bond in this selenosemicarbazone possesses only partial double-bond character in agreement with the canonical forms:



The C(2)–N(3) bond of 1·29 Å should be a double bond. The corresponding C(1)–N(1) bond distance of 1·37 Å and the C(1)–N(2) bond distance of 1·35 Å are

Table 1. *Observed and calculated structure factors*

The columns are in the order h, k, l, F_o and F_c.

Table 1 (*cont.*)

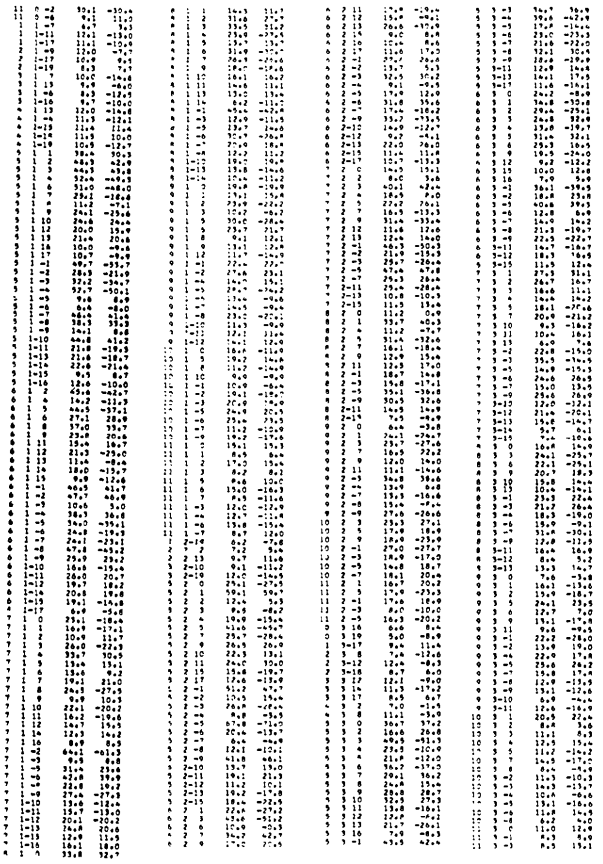


Table 2. *Fractional coordinates* ($\times 10^4$) *with standard deviations* ($\times 10^4$)

	x/a	*y/b*	*z/c*
Se	6610 (2)	−3630 (3)	4013 (1)
N(1)	3950 (15)	−2280 (25)	4614 (9)
N(2)	5008 (14)	− 192 (24)	3634 (9)
N(3)	3788 (15)	1067 (23)	3692 (9)
N(4)	2835 (16)	5649 (25)	2649 (9)
C(1)	5053 (17)	−1942 (26)	4081 (10)
C(2)	3856 (18)	2626 (30)	3208 (11)
C(3)	2697 (16)	4169 (32)	3199 (11)
C(4)	1523 (20)	4045 (38)	3750 (11)
C(5)	519 (20)	5564 (38)	3716 (12)
C(6)	631 (21)	7103 (37)	3142 (14)
C(7)	1847 (22)	7049 (41)	2618 (13)

indicative of some double-bond character, in agreement with the above resonance forms. The N(2)–N(3) bond distance of 1·41 Å agrees well with the single N–N bond and with the value reported by Andreetti, Domiano, Gasparri, Nardelli & Sgarabotto (1970) in thiosemicarbazide. In this paper, the most striking evidence for the single-bond character of N(2)–N(3) is the tetrahedral configuration for N(2). On the other hand, in the structure of 4-formylpyridine thiosemicarbazone, the N–N bond is 1·375 Å, which suggests that other canonical forms may be important (Restivo & Palenik, 1970). However, there is no evidence for the existence of these forms in this structure. A slight shortening of the C(4)–C(5) and C(5)–C(6) bond lengths, is noted, which may indicate the presence of resonance forms involving the pyridine ring. Regarding the bond angles, one finds that the angle N(2)–N(3)–C(2) is 112·1° and the C(2)–C(3)–N(4) is 115·4°, which are below the corresponding values observed in 4-formylpyridine thiosemicarbazone. These significant deformations occur in the part of the molecule that is engaged in the shortest intermolecular contact. A comparison with other structural studies of similar thio- and selenosemicarbazones may help to explain some of the observed values. The complete molecule is nearly planar, as illustrated in Table 5. The maximum deviations from the mean plane are for N(1) at 0·064, N(2) at 0·054 and C(5) at 0·049 Å; the first below and the other two above the plane. The pyridine ring is planar as expected, the maximum deviation from the ring plane involving C(5) at 0·012 Å above the plane.

In Table 6 the shorter intermolecular contacts are listed. The structure includes three intermolecular hydrogen bonds which link the molecules. There are dimer-like molecules formed by two N–H···Se hydrogen bonds across a centre of symmetry; these N–H···Se hydrogen bonds are rather weak since the N···Se distance is 3·52 Å. The dimer-like units are linked into a three-dimensional network by a strong N–H···N hydrogen bond. The N···N distance of 2·96 Å is shorter than most of the $-NH_2\cdots$ring–N distances reported by Fuller (1959), which average 3·06 Å. The molecular packing is analogous to that found in the structural analysis of 4-formylpyridine thiosemicarbazone.

Table 3. *Anisotropic thermal parameters* ($\times 10^4$) *with estimated standard deviations* ($\times 10^4$)

The form of the temperature factor is: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Se	71 (2)	151 (5)	31 (1)	−39 (4)	7 (1)	−16 (2)
N(1)	85 (18)	167 (40)	37 (6)	11 (26)	20 (8)	20 (14)
N(2)	62 (15)	157 (42)	30 (6)	23 (25)	1 (7)	2 (13)
N(3)	80 (17)	103 (41)	31 (6)	24 (26)	−3 (8)	0 (13)
N(4)	80 (18)	144 (37)	30 (6)	24 (27)	5 (8)	17 (13)
C(1)	77 (18)	85 (40)	23 (6)	18 (27)	−1 (8)	− 8 (13)
C(2)	74 (19)	157 (49)	32 (7)	44 (30)	−5 (9)	− 4 (16)
C(3)	46 (17)	227 (60)	33 (7)	15 (31)	−4 (9)	− 4 (17)
C(4)	95 (23)	349 (81)	30 (7)	− 1 (40)	10 (10)	12 (19)
C(5)	88 (22)	277 (65)	39 (8)	59 (38)	−3 (11)	0 (20)
C(6)	91 (24)	262 (63)	51 (11)	80 (38)	1 (12)	−17 (22)
C(7)	121 (25)	302 (75)	42 (9)	58 (41)	16 (13)	1 (22)

Table 4. *Bond lengths and angles with e.s.d.'s in parentheses*

(*a*) Bond lengths (Å)

Se—C(1)	1·83 (2)	C(3)–C(4)	1·42 (3)
C(1)–N(1)	1·37 (2)	C(4)–C(5)	1·36 (3)
C(1)–N(2)	1·35 (2)	C(5)–C(6)	1·38 (3)
N(2)–N(3)	1·41 (2)	C(6)–C(7)	1·42 (3)
N(3)–C(2)	1·29 (2)	C(7)–N(4)	1·32 (3)
C(2)–C(3)	1·48 (3)	N(4)–C(3)	1·32 (3)

(*b*) Bond angles (°)

Se—C(1)–N(1)	122·9 (2·4)	C(2)–C(3)–N(4)	115·4 (3·0)
Se—C(1)–N(2)	119·8 (2·3)	C(3)–C(4)–C(5)	121·4 (3·4)
N(1)–C(1)–N(2)	117·2 (2·8)	C(4)–C(5)–C(6)	120·1 (4·3)
C(1)–N(2)–N(3)	118·5 (2·8)	C(5)–C(6)–C(7)	118·0 (3·8)
N(2)–N(3)–C(2)	112·1 (2·7)	C(6)–C(7)–N(4)	122·6 (4·0)
N(3)–C(2)–C(3)	120·3 (3·3)	C(7)–N(4)–C(3)	118·4 (3·9)
C(2)–C(3)–C(4)	121·4 (3·4)	N(4)–C(3)–C(4)	123·2 (3·5)

Table 5. *Deviations of the atoms from least-squares planes*

The planes are expressed as $AX+BY+CZ+D=0$, where X, Y and Z are referred to orthogonal axes. The atoms indicated with asterisks were omitted from the calculations of the least-squares planes.

Plane	Description	*A*	*B*	*C*	*D*
I	Through all atoms	0·497	0·528	0·688	6·245
II	Through pyridine ring atoms	0·513	0·541	0·666	6·204

	I	II
Se	0·034	−0·005*
N(1)	−0·064	−0·152*
N(2)	0·054	0·035*
N(3)	−0·013	−0·040*
N(4)	−0·037	−0·001
C(1)	−0·030	−0·080*
C(2)	0·017	0·021*
C(3)	0·002	0·003
C(4)	0·028	−0·008
C(5)	0·049	0·012
C(6)	−0·008	−0·009
C(7)	−0·031	0·004

Table 6. *Interatomic distances less than* 4 Å

Symmetry code

i	$1-x$	$-1-y$	$1-z$	v	$1-x$	$-y$	$1-z$
ii	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	vi	x	$1+y$	z
iii	x	$-1+y$	z	vii	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	$1+x$	$-1+y$	z	viii	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

Distances

Se—N(1^{i})	3·52 Å	N(2)–C(2^{ii})	3·49 Å
Se—N(4^{ii})	3·92	N(2)–C(3^{ii})	3·70
Se—C(2^{iii})	3·77	N(2)–C(7^{iii})	3·80
Se—C(2^{ii})	3·73	N(2)–C(7^{ii})	3·88
Se—C(5^{iv})	3·72	N(3)–C(1^{v})	3·86
N(1)–N(1^{v})	3·77	N(3)–N(4^{ii})	3·82
N(1)–N(2^{v})	3·41	N(3)–C(7^{iii})	3·60
N(1)–N(3^{v})	3·55	N(4)–C(1^{vi})	3·55
N(1)–N(4^{iii})	3·62	N(4)–C(1^{vii})	3·64
N(1)–C(1^{v})	3·60	N(4)–C(2^{vii})	3·63
N(1)–C(3^{iii})	3·46	C(1)–C(1^{v})	3·97
N(1)–C(4^{iii})	3·58	C(1)–C(2^{iii})	3·97
N(1)–C(5^{iii})	3·78	C(1)–C(2^{ii})	3·82
N(1)–C(6^{iii})	3·92	C(1)–C(3^{iii})	3·64
N(1)–C(7^{iii})	3·80	C(1)–C(7^{iii})	3·86
N(2)–N(4^{iii})	3·74	C(4)–C(6^{viii})	3·87
N(2)–N(4^{ii})	2·96	C(5)–C(6^{viii})	3·92
N(2)–C(1^{v})	3·97	C(5)–C(7^{viii})	3·82

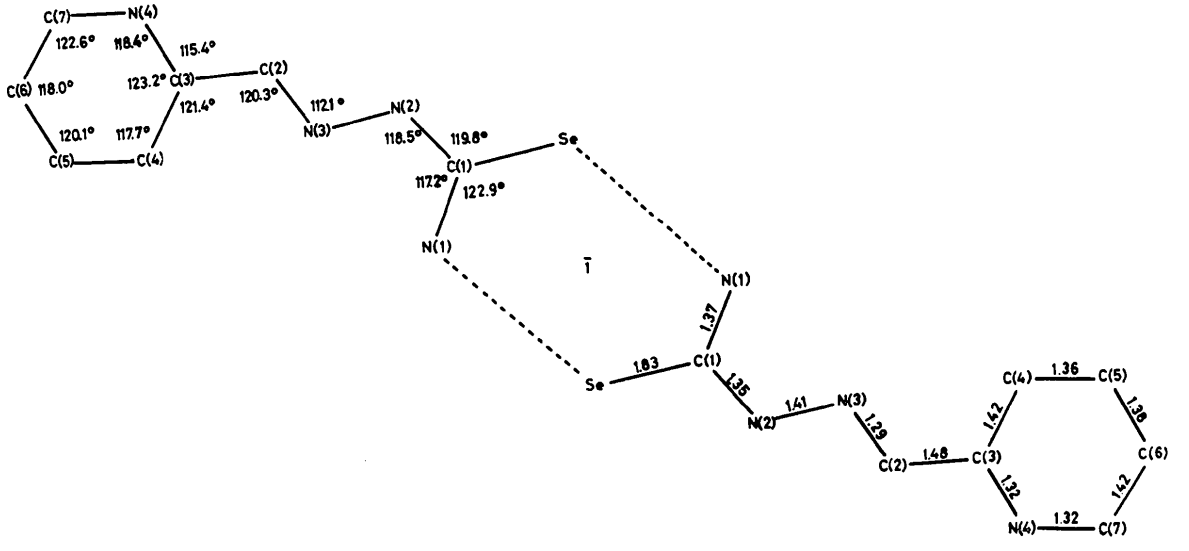


Fig. 3. Arrangement of a dimer-like unit. Bond distances and angles.

Apart from the hydrogen bonds there are some intermolecular distances shorter than the van der Waals contacts. At Se there are two carbon contacts close to 3·72 Å, which is only slightly below the sum of the van der Waals radii, 3·85 Å. There is also a carbon–carbon intermolecular contact of 3·64 Å, which is slightly below the sum of the van der Waals radii for carbon (3·70 Å).

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The Structure of γ-Uranyl Dihydroxide, $UO_2(OH)_2$*

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γ-Uranyl dihydroxide, $UO_2(OH)_2$, is monoclinic, space group $P2_1/c$ with $a=5{\cdot}560$ (3), $b=5{\cdot}522$ (3), $c=6{\cdot}416$ (3) Å, and $\beta=112{\cdot}71$ (9)°. The observed density is 5·55 g.cm^{-3} and the computed value is 5·56 g.cm^{-3} for two formula weights. The structure was solved with 317 independent reflections recorded with an automatic diffractometer utilizing both double filter and $\theta/2\theta$ scan techniques. A least-squares refinement based on F gave an R value of 6·1 %. The configuration about a uranium atom is a distorted octahedron composed of two O(1) (uranyl) and four O(2) (secondary) oxygen atoms. Each O(2) atom is shared between two octahedra leading to puckered sheets of secondary oxygen atoms distributed within the *bc* plane. Each O(1) oxygen atom is associated with only one octahedron within a layer but is hydrogen-bonded to an O(2) oxygen atom in an adjacent layer. The structure is very similar to the orthorhombic β-$UO_2(OH)_2$. Postulated coordinates for the β modification at 280 °C indicate that the β and γ forms can be related by a shear involving one-half of the hydrogen atoms. Grinding experiments demonstrate the existence of a shear effect.

Introduction

Three crystallographic modifications of uranyl dihydroxide, $UO_2(OH)_2$, have been prepared from the uranium trioxide–water system. The crystal structure of the α form was reported by Taylor (1971). Roof, Cromer & Larson (1964) published the structure of the β modification and subsequently, Bannister & Taylor (1970) reported on the results of a study of the structure and anisotropic thermal expansion of β-$UO_2(OH)_2$. A neutron powder diffraction study by Taylor & Hurst (1971) confirmed the hydrogen locations proposed in the β form by Roof *et al.* and in the α modification by Taylor. The preparation of a third form of uranyl dihydroxide and the identification of its symmetry and cell dimensions from an X-ray powder pattern has been described by Cordfunke & Debets (1964) who referred to this phase as the ε modification. As the existence of only three forms of uranyl dihydrate has been confirmed, the present phase will be regarded as γ-$UO_2(OH)_2$. The structure of γ-$UO_2(OH)_2$ and its relation to β-$UO_2(OH)_2$ will be presented here.

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