

talline environments. In view of these similarities, it is not surprising that thioguanine can mimic guanine in biological processes and substitute for it in certain metabolic pathways. At the same time, differences in the lengths of hydrogen bonds involving these two bases might be expected to interfere with certain biological processes in which thioguanine substitutes for guanine, thus contributing to the antimetabolite activity of this base analog.

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## The Crystal Structures at 20 and 1000°C of Bismuth Uranate, $\text{Bi}_2\text{UO}_6$

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The crystal structures of two modifications of the catalyst bismuth uranate,  $\text{Bi}_2\text{UO}_6$ , have been solved by powder methods. The phase stable at 1000°C has a trigonal fluorite-like structure, space group  $P\bar{3}$ , with one molecule per cell and with lattice constants  $a = 4.045$  (5) and  $c = 9.90$  (1) Å. The final  $R$  index was 0.05. The phase stable at 20°C has a closely related monoclinic structure,  $a = 6.872$  (2),  $b = 4.009$  (1) and  $c = 9.690$  (3) Å,  $\beta = 90.16$  (1)°; the space group is  $C2$  and the cell contains two molecules. The final  $R$  index was 0.10. Both structures can be regarded as stackings of layers of interlocked  $\text{UO}_8$  polyhedra and layers of a Bi–O network.

### Introduction

The oxidative conversion of toluene to benzene has been shown by Steenhof de Jong, Guffens & Van der

Baan (1972, 1973) to be catalysed by bismuth uranate,  $\text{Bi}_2\text{UO}_6$ . A selectivity of up to 70% is obtained if toluene vapour reacts with bismuth uranate without gaseous oxygen being present; the partially reduced

catalyst is reoxidized with oxygen or air in the next step of the process. In order to understand better the mechanism of these reactions, the determination of the crystal structure of  $\text{Bi}_2\text{UO}_6$  was considered helpful. A brief investigation of this crystal structure was made by Rüdorff & Erfurth (1966) and Erfurth (1966). A hexagonal structure with 8 molecules per unit cell was proposed, based on a fluorite-type lattice. Although a fluorite-related structure is plausible, judging by the positions and intensities of the strong lines of the X-ray powder diffraction pattern, the cell chosen by Erfurth could not be correct since the weak lines did not fit.

Single crystals of  $\text{Bi}_2\text{UO}_6$  could not be grown, so the X-ray structure determination had to be carried out by powder diffractometry, both at room temperature and at elevated temperatures. The high-temperature experiments proved a considerable help,  $\text{Bi}_2\text{UO}_6$  transforming between 700 and 800°C into a modification with a closely related structure of higher symmetry.

### Experimental

Pure  $\text{Bi}_2\text{UO}_6$  was prepared by a solid-state reaction between equivalent amounts of thoroughly ground  $\alpha\text{-Bi}_2\text{O}_3$  and  $\alpha\text{-UO}_3$  at 800°C for one week. It can also be prepared by precipitation in aqueous solution and subsequent calcining, according to de Jong & Batist (1971). This product has essentially the same structure, but it is much more finely divided, as is shown by line broadening of the powder diffractograms; consequently it is more active catalytically. After recrystallization at 800°C its powder diagram is identical with that of the solid-state reaction product.

The X-ray diagrams were recorded with a normal Guinier camera and a programmed high-temperature Guinier camera, both of Nonius Delft, with a Philips PW1050 diffractometer, and with a vacuum high-temperature diffractometer constructed in our laboratory. A neutron-diffraction diagram was made at the high-flux reactor of the Reactor Centrum Nederland, Petten (Netherlands), using a wavelength of 2.57 Å and a cylindrical sample, 10 mm in diameter.

### The relation between the structures at 20 and 1000°C

From inspection of a high-temperature Guinier photograph in which the temperature is increased from 20 to 1000°C, it is evident that the multiplet character of the intense lines at room temperature is lost between 700 and 800°C. The multiplet merges together gradually, without a well defined transition temperature, and the integrated intensity remains almost constant. Upon closer examination, the same appears to apply to the weaker lines. This indicates that the structures at 20 and at 1000°C are closely related, the main difference being the symmetry of the unit cells; we may expect that the uranium and bismuth framework will remain essentially intact, and that some changes in the oxygen positions give rise to the higher symmetry at 1000°C.

The transformation is reversible: upon cooling, the multiplets appear again in the diffraction pattern.

### The structure at 1000°C

The strong lines at 1000°C belong to a fluorite-type pattern, corresponding to a cubic lattice with  $a = 5.72$  Å. The weak lines, however, do not fit. A related lattice of hexagonal symmetry accounts for all the lines, the constants being  $a = 4.045$  (5) and  $c = 9.90$  (1) Å. A simple operation transforms a cubic face-centred cell into a hexagonal cell:  $a_{\text{cub}} = \frac{1}{3}c_{\text{hex}}/\sqrt{3} = 5.72$  Å,  $a_{\text{cub}} = a_{\text{hex}}/\sqrt{2} = 5.72$  Å. The composition of  $\text{Bi}_2\text{UO}_6$  indicates that there are 3 heavy atoms per formula unit, so it is understandable that this compound crystallizes in the hexagonal modification of the fluorite type. The cubic cell can accommodate 4 molecules, the hexagonal cell 3 molecules of  $\text{AB}_2$ . With one molecule of  $\text{Bi}_2\text{UO}_6$  per cell the calculated density is  $8.92$  g  $\text{cm}^{-3}$ . If the f.c.c.  $\text{CaF}_2$  structure has been transformed into a hexagonal structure, the space group can be  $P\bar{6}$  or  $P\bar{3}$ : we arbitrarily chose space group  $P\bar{3}$  and shall henceforth call the  $\text{Bi}_2\text{UO}_6$  (1000°C) structure trigonal. In  $\text{CaF}_2$  (space group  $P\bar{3}$ ) the atoms occupy the following positions: Ca(1)  $1(a)$  0,0,0; Ca(2)  $2(d)$   $\frac{2}{3}, \frac{1}{3}, z$ ;  $\frac{1}{3}, \frac{2}{3}, \bar{z}$  ( $z = \frac{1}{3}$ ); F(1)  $2(d)$   $\frac{2}{3}, \frac{1}{3}, z$ ;  $\frac{1}{3}, \frac{2}{3}, \bar{z}$  ( $z = \frac{1}{12}$ ); F(2)  $2(d)$   $\frac{2}{3}, \frac{1}{3}, z$ ;  $\frac{1}{3}, \frac{2}{3}, \bar{z}$  ( $z = \frac{7}{12}$ ); F(3)  $2(c)$  0,0, $z$ ; 0,0, $\bar{z}$  ( $z = \frac{1}{4}$ ).

The Ca(1) atom and the two Ca(2) atoms have to be replaced by one U atom and two Bi atoms; arbitrarily we put U at 0,0,0 (any other choice gives the same basic arrangement of the metal atoms). The agreement between the intensities calculated for this model with  $\text{CaF}_2$  parameters and the observed intensities measured with the high-temperature diffractometer was good, and the structure was refined by means of a least-squares Algol 60 program for overlapping reflexions. Using 46 reflexions (Table 1), the 4 unknown  $z$  parameters and the thermal parameter  $B$  (supposed to be isotropic) converged well until an  $R$  value of 0.05 was reached ( $R = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$ ). Parameters are

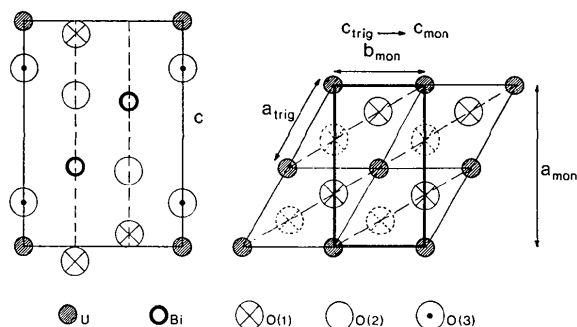


Fig. 1. Structure of  $\text{Bi}_2\text{UO}_6$  (1000°C). Left, a section parallel to (1120). Right, the projection along [0001]; for the sake of clarity, only U and O(1) atoms are indicated. The monoclinic axes of the low-temperature form are shown in relation to the trigonal axes.

given in Table 2, and some interatomic distances in Table 3.

The following deviations from the fluorite structure can be noted (*cf.* Fig. 1). The bismuth parameter is a

Table 1.  $\text{Bi}_2\text{UO}_6$  (1000°C): values of  $hkl$ ,  $I_{\text{calc}}$ , the intensity  $SI_{\text{calc}}$  of a composite peak and the intensity  $SI_{\text{obs}}$

Intensities are in arbitrary units; V-filtered Cr radiation was used.

<i>h</i>	<i>k</i>	<i>l</i>	$I_{\text{calc}}$	$SI_{\text{calc}}$	$SI_{\text{obs}}$
0	0	1	2	2	0
0	0	2	64	64	87
1	0	0	3	3	0
1	0	1	1602	2230	2268
0	1	1	64		
0	0	3	564	1024	1074
1	0	2	22		
0	1	2	1002	18	10
0	0	4	18		
1	0	3	21	62	46
0	1	3	41		
1	1	0	540	873	866
1	0	4	254		
0	1	4	79	32	40
1	1	1	0		
0	0	5	32	13	10
1	1	2	13		
2	0	0	0	0	0
2	0	1	7	831	865
0	2	1	212		
1	0	5	13	216	226
0	1	5	168		
1	1	3	431	19	10
2	0	2	166		
0	2	2	3	13	10
0	0	6	47		
1	1	4	19	47	49
2	0	3	7		
0	2	3	6	90	72
1	0	6	41		
0	1	6	6	54	59
2	0	4	20		
0	2	4	70	0	0
1	1	5	51		
0	0	7	3	277	211
2	1	0	0		
2	1	1	138	212	172
1	2	1	4		
2	0	5	54	9	0
0	2	5	4		
1	0	7	33	116	94
0	1	7	44		
2	1	2	2	94	9
1	2	2	116		
1	1	6	94	9	0
0	0	8	9		

Table 2. Coordinates and standard deviations of the atoms in  $\text{Bi}_2\text{UO}_6$  (1000°C); space group  $P\bar{3}$

	$B=2.7 \text{ \AA}^2$		
	<i>x</i>	<i>y</i>	<i>z</i>
U	0	0	0
Bi	$\frac{2}{3}$	$\frac{1}{3}$	0.357 (2)
O(1)	$\frac{2}{3}$	$\frac{1}{3}$	0.94 (2)
O(2)	$\frac{2}{3}$	$\frac{1}{3}$	0.66 (2)
O(3)	0	0	0.21 (2)

Table 3. Interatomic distances (Å) in  $\text{Bi}_2\text{UO}_6$  (1000°C)

U-O(1)	2.40 (5)	O(1)-O(1)	2.6 (1)
U-O(3)	2.1 (1)	O(1)-O(2)	2.8 (2)
Bi-O(2)	3.0 (2)	O(1)-O(3)	2.8 (2)
Bi-O(2)	2.34 (1)	O(2)-O(3)	2.7 (1)
Bi-O(3)	2.74 (10)		

little larger than  $\frac{1}{3}$ , which means that the bismuth atoms are a little closer to each other than they are in a fluorite model. The O(3) parameter is somewhat smaller than  $\frac{1}{3}$ , and the O(1) parameter has shifted considerably; thus the uranium atom is coordinated by eight oxygen atoms, of which two form collinear uranyl bonds with a bond length of 2.1 Å, and six, O(1), form a hexagon whose atoms lie alternately a little above and below the plane perpendicular to the uranyl bonds. The U-O(1) bond length in this hexagon is 2.40 Å. This type of uranium coordination is found in various U(VI) compounds, for instance in uranyl nitrate dihydrate (Kent Dalley, Mueller & Simonsen, 1971). All oxygen atoms near this plane are shared by 3 uranium atoms; thus the structure can be considered as the stacking of a layer of interlocked U-O polyhedra and a layer of a Bi-O network. The difference between the *z* parameters of Bi and O in this network is much less than it would be on the basis of an undeformed fluorite lattice. Apparently the Bi-O molecular orbitals favour a planar coordination, whilst molecular orbitals perpendicular to this plane and directed towards the uranyl layer are strongly anti-bonding, as would follow from the fact that the oxygen atom O(1) is shifted rather a long way from the position it has in the fluorite structure.

### The structure at 20°C

Since the similarity of the diffraction patterns indicates but small differences in crystal structure, the results at 1000°C were used to derive the structure at room temperature. To resolve the multiplets in diffractometer recordings of the pattern, slits of minimal width were necessary and for an accurate intensity measurement both Ni-filtered Cu radiation and V-filtered Cr radiation were used.

First, the trigonal cell was transformed into an orthorhombic cell, in which the *a* axis coincided with  $[10\bar{1}0]_{\text{trig}}$ , the *b* axis with the trigonal *a* axis and the *c* axis with the trigonal *c* axis. Powder line positions could be explained fairly well using  $a=6.875$ ,  $b=4.008$ ,  $c=9.69$  Å. However, if the atoms are inserted into this cell in the positions suggested by the 1000°C determination, as would be required in view of the smooth transition of the one form into the other, they do not fit any of the orthorhombic space groups. The cell constants found should be nearly correct, but the crystal system must be monoclinic, the orthorhombic *b* axis changing into a monoclinic *b* axis with  $\beta$  almost equal to 90° (*cf.* Fig. 1). A least-squares calculation

produced the following cell:  $a=6.872$  (2),  $b=4.009$  (1),  $c=9.690$  (3) Å,  $\beta=90.16$  (1)°. The X-ray density is  $9.36$  g cm<sup>-3</sup>, a little higher than the experimental value  $9.20$  g cm<sup>-3</sup>. This may indicate a small number of vacancies; these were found by Greaves & Fender (1972) in rather great number in the related  $\alpha$ -UO<sub>3</sub> structure.

The reflexions obey the condition  $h+k=2n$ . Given the atomic parameters in the trigonal phase, two space groups remain:  $C2$  and  $C2/m$ . In the refinement with 70 X-ray intensities, the initial parameters were the transformed trigonal parameters. The refinement in the space group  $C2/m$  proceeded unsatisfactorily: the oxygen atoms shifted to unlikely positions and convergence was poor. The space group  $C2$  refined much better, but still the standard deviations of the oxygen atoms were too large for an unambiguous assessment of the structure.

To increase the accuracy of the oxygen parameters, a neutron diffraction diagram was made (Table 4), and the refinement in space group  $C2$  was continued. The scattering lengths were, for U  $0.85$ , for Bi  $0.86$  and for O  $0.58 \times 10^{-12}$  cm. A program was used which is especially helpful if overlap of reflexion peaks is severe, as in our case, by taking into account the profiles of the diffraction maxima.

Table 4. Bi<sub>2</sub>UO<sub>6</sub> (20°C): values of  $hkl$ ,  $I_{\text{calc}}$  and  $I_{\text{obs}}$ ; neutron radiation,  $\lambda=2.57$  Å

$h$	$k$	$l$	$I_{\text{calc}}$	$I_{\text{obs}}$	$h$	$k$	$l$	$I_{\text{calc}}$	$I_{\text{obs}}$
0	0	1	61	21	2	2	1	69	80
0	0	2	280	402	0	2	3	351	390
1	1	0	31	64	3	1	-3	409	396
2	0	0	2	3	4	0	-1	29	28
1	1	-1	204	200	1	1	-5	318	308
1	1	1	1061	1028	3	1	3	389	377
2	0	-1	476	442	4	0	1	214	208
2	0	1	46	41	1	1	5	64	62
0	0	3	544	483	2	0	-5	27	26
1	1	-2	5	10	2	0	5	182	179
1	1	2	191	179	2	2	-2	94	121
2	0	-2	75	74	2	2	2	21	26
2	0	2	0	0	4	0	-2	4	5
0	0	4	1	46	4	0	2	47	58
1	1	-3	211	264	0	0	6	143	183
1	1	3	173	237	0	2	4	25	0
2	0	-3	78	111	3	1	-4	24	6
2	0	3	74	90	3	1	4	3	1
0	2	0	1028	1182	2	2	-3	59	32
3	1	0	2213	2153	2	2	3	126	68
1	1	-4	11	11	4	0	-3	80	42
1	1	4	824	842	4	0	3	40	20
2	0	-4	387	399	1	1	-6	76	71
2	0	4	0	0	2	0	-6	167	164
0	2	1	14	19	1	1	6	307	303
3	1	-1	3	13	2	0	6	38	22
3	1	1	4	12	2	2	-4	661	629
0	0	5	567	658	2	2	4	27	27
0	2	2	48	0	4	0	-4	5	5
3	1	-2	74	23	4	0	4	375	389
3	1	2	63	12	0	2	5	759	776
2	2	0	29	23	3	1	-5	940	941
4	0	0	6	28	3	1	5	776	777
2	2	-1	407	485	0	0	7	5	7

The parameters of Table 5 were obtained with good convergence. The final  $R$  index was  $0.10$ . Table 6 lists a number of interatomic distances; they have acceptable values (*cf.* Kent Dalley *et al.*, 1971; Kovba, 1971; Meunier & Galy, 1973).

Table 5. Parameters of Bi<sub>2</sub>UO<sub>6</sub> (20°C); space group  $C2$

	$x$	$y$	$z$
U	0	0	0
Bi	0.663 (2)	-0.032 (6)	0.358 (1)
O(1)	0.664 (3)	-0.085 (9)	0.013 (1)
O(2)	0.659 (4)	0.00 (1)	0.584 (1)
O(3)	0.000 (5)	0.00 (1)	0.197 (1)

Table 6. Interatomic distances (Å) in Bi<sub>2</sub>UO<sub>6</sub> (20°C)

U—O(1)	2.34 (2)	Bi—O(3)	2.81 (3)
U—O(1)	2.01 (3)	O(1)—O(1)	2.26 (4)
U—O(3)	1.91 (1)	O(1)—O(1)	2.34 (2)
Bi—O(1)	3.35 (1)	O(1)—O(3)	2.72 (4)
Bi—O(2)	2.19 (1)	O(2)—O(2)	2.72 (4)
Bi—O(2)	2.28 (2)	O(2)—O(2)	2.88 (3)
Bi—O(2)	2.35 (5)	O(2)—O(3)	3.15 (3)
Bi—O(3)	2.72 (4)	O(2)—O(3)	3.11 (5)

## Discussion

Broadly speaking we can say that both structures consist of a succession of layers of interlocked UO<sub>8</sub> polyhedra and (BiO)<sub>2</sub> layers.

Comparison between the structures at 1000 and 20°C shows that the differences are small and that the structures can transform into each other smoothly. The main difference is the coordination of uranium, which in the high-temperature phase is surrounded by a regular hexagon in chair form, perpendicular to the O(3)—U—O(3) axis. In the 20°C phase four oxygen atoms are closer to the uranium atom than the other two; furthermore these six oxygen atoms lie more closely in one plane. It seems that by the shortening of the uranyl bond [U—O(3)] at lower temperature the O(1) oxygen atoms are forced into one plane, and since there is no room for all of them (the distance between adjoining O(1) atoms being already about 2.3 Å) two are displaced somewhat.

The shortening of the uranyl bond is plausible since in many uranyl complexes the U—O distance is as small as 1.7 Å (Bullock, 1969). The Bi atoms have moved in the same direction as the oxygen atoms of the now distorted hexagon, because they have some bonding with them, but they are stopped by the O(2) atoms which form bonds with uranium; consequently their displacement with respect to the uranium lattice is slight (0.1 Å).

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## The Crystal and Molecular Structure of Ethylenebis(biguanide)silver(III) Sulphate Hydrogen Sulphate Monohydrate [Ag(C<sub>6</sub>H<sub>16</sub>N<sub>10</sub>)]SO<sub>4</sub>HSO<sub>4</sub>·H<sub>2</sub>O

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Crystals of the title compound are triclinic (*P* $\bar{1}$ ) with unit-cell dimensions  $a=8.645$ ,  $b=9.177$ ,  $c=13.363$  Å,  $\alpha=104.2$ ,  $\beta=117.5$ ,  $\gamma=99.4^\circ$ ,  $Z=2$ . The X-ray analysis carried out with diffractometer data (Mo  $K\alpha$  radiation; final  $R=4.0\%$  for 2875 independent reflexions) shows that the organic molecule behaves as a tetradentate ligand. It chelates to metal in a nearly planar arrangement giving rise to complex cations in which silver is in the oxidation state III. In a *trans* arrangement with respect to the coordination plane there are SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> ions, each of which directs an oxygen atom towards the metal. These two Ag–O interactions are rather long (2.932, 2.944 Å) so the complete coordination polyhedron is an elongated square bipyramid. The water molecule is involved in a system of hydrogen bonds involving sulphate oxygen and ethylenebis(biguanide) nitrogen atoms. A strong hydrogen bond (2.51 Å) is also observed between the HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions.

### Introduction

Ethylenebis(biguanide) is an interesting coordinating ligand containing nitrogens as donor atoms, which is able to stabilize the oxidation state III in silver (Rây & Chakravarty, 1944).

From the crystal structures of metal complexes with ethylenebis(biguanide) (hereinafter called EBG) studied so far [Cu(EBG)Cl<sub>2</sub>·H<sub>2</sub>O (Kunchur & Mathew, 1966; Mathew & Kunchur, 1970); Ni(EBG)Cl<sub>2</sub>·H<sub>2</sub>O (Coghi, Mangia, Nardelli & Pelizzi, 1969; Holian & Marsh, 1970; Ward, Caughlan & Smith, 1971); Ag(EBG)(NO<sub>3</sub>)<sub>3</sub> (Kunchur, 1968)] it was deduced that the ligand chelates to metal in a planar fashion through four nitrogen atoms: coordination is perfectly planar for the Cu and Ni derivatives and slightly distorted for the Ag derivative. This distortion is also observed in the title compound, which is particularly interesting because it contains both SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> ions.

### Experimental

A solution of silver sulphate (0.3 g) in water was added to a solution of ethylenebis(biguanidinium) hydrogen

sulphate (1 g) prepared as described by Chakravarty & Rây (1944). The resulting mixture, cooled to 10°C, was oxidized by an aqueous solution of potassium peroxodisulphate (1 g) and kept at 10°C for 12 h until red-orange silky diamagnetic crystals separated. These crystals were recrystallized from hot dilute sulphuric acid.

Analysis for C<sub>6</sub>H<sub>19</sub>AgN<sub>10</sub>O<sub>9</sub>S<sub>2</sub>: calculated C=13.2, H=3.5, Ag=19.8, N=25.7%; found C=12.9, H=4.2, Ag=19.6, N=25.3%.

The lattice parameters were first determined from rotation and Weissenberg photographs and then refined from a least-squares fit of  $(\theta, \chi, \varphi)_{hkl}$  angles measured by single-crystal diffractometry for 20 reflexions. The most significant crystal data are quoted in Table 1. All the diffraction measurements were made at room-temperature on a prismatic crystal with a mean diameter of 0.064 mm, using an automated on-line Siemens AED single-crystal diffractometer with Mo  $K\alpha$  radiation ( $\lambda=0.7107$  Å). Of the 3948 independent reflexions which were examined within the range  $0 < 2\theta < 55^\circ$ , 2875 had an intensity greater than twice the standard deviation of the intensity; the remaining 1073 reflexions were coded as unobserved and