between O(1*)···C(16*) at 3·49 Å and C(20)···C(16*) at 3·68 Å. All other C···C distances are greater than 3·75 Å.

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The Crystal Structure of Bismuth (2:1) Borate, $2Bi_2O_3.B_2O_3$

BY A. HYMAN

University of Maryland, Baltimore County, Baltimore, Maryland 21228, *U.S.A.*

AND A. PERLOFF

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, *U.S.A.*

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The crystal structure of bismuth (2:1) borate ($2Bi_2O_3.B_2O_3$) was determined by single-crystal X-ray diffraction analysis. Proper classification of this compound is as an oxide-orthoborate with the formula $Bi_4O_3(BO_3)_2$. The material crystallizes in the monoclinic system, $P2_1/c$, with 4 formula units in a cell of dimensions $a=11{\cdot}107$, $b=6{\cdot}627$, $c=11{\cdot}044$ Å and $\beta=91{\cdot}04°$. Intensity data were obtained on an automated diffractometer using Nb-filtered Mo $K\alpha$ radiation ($\lambda=0{\cdot}71069$ Å). Bismuth positions were established by direct phase determining procedures and the remaining atomic positions found from a three-dimensional difference synthesis phased by the bismuth atoms. Full-matrix, least-squares, isotropic refinement of the structure yielded a residual $R=5{\cdot}1$ % for 2098 observed reflections. The structure contains discrete planar BO_3^{3-} anions held together by coordination to bismuth atoms. Additional oxygen atoms, coordinated only to bismuth, are present. The average B–O distances is 1·38 Å. The minimum Bi–O distance found is 2·14 Å. Some of the bismuth atoms do not have a clearly delineated coordination shell.

Introduction

The analysis of the structure of bismuth (2:1) borate has been undertaken as part of a general program for the study of borate compounds. In a previous study (Weir & Schroeder, 1964) the infrared spectrum of $2Bi_2O_3.B_2O_3$ was interpreted as indicative of a structure containing an anion which was a complex polymer of trigonal BO_3 groups. An X-ray structure analysis was performed to test this hypothesis.

Experimental

Single crystals of bismuth (2:1) borate were grown from a stoichiometric melt on a hot wire loop. The crystals were ground into spheres in anticipation of

severe X-ray absorption problems by blowing the crystals around a circular track lined with diamond abrasive. A suitable small (0·188 mm ± 5% diameter) and spherical crystal ($\mu R = 7{\cdot}7$ for Mo $K\alpha$) was selected for study. Intensity data were collected on a three-circle counter diffractometer using Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}710688$ Å). For each reflection, fixed time (10 sec) measurements were made of the peak height and two background intensities. The peak heights were converted to integrated intensities *via* a calibration curve of the ratio of integrated to peak-height intensities as a function of scattering angle.

The observed monoclinic symmetry and systematic extinctions of $h0l$ ($l = 2n+1$) and $0k0$ ($k = 2n+1$) confirmed the space group determination of Mighell (1967) as $P2_1/c$. The number of formula units per cell was estimated from the cell volume and confirmed by the final structure. The positions of 16 reflections were observed and subjected to a least-squares analysis yielding the following unit-cell data:

$$\begin{aligned} a &= 11{\cdot}107 \pm 0{\cdot}004 \text{ Å} \\ b &= 6{\cdot}627 \pm 0{\cdot}002 \\ c &= 11{\cdot}044 \pm 0{\cdot}002 \\ \beta &= 91{\cdot}04 \pm 0{\cdot}02^\circ \\ Z &= 4 \\ \varrho(\text{calc}) &= 8{\cdot}184 \text{ g.cm}^{-3} \end{aligned}$$

The uncertainties quoted on the cell dimensions are the standard deviations obtained from the least-squares refinement.

Structure determination

Intensities were corrected by using the appropriate Lorentz and polarization factors, for absorption based on interpolated values of the corrections for spherical crystals (*International Tables for X-ray Crystallography*, 1967), and then reduced to scaled values of normalized structure factors, *i.e.* E_{hkl} (Hauptman & Karle, 1953). Phases were assigned by a modification of Karle & Karle's (1963) symbolic addition method described in the *X-ray* 67 *System* developed at the University of Maryland Computer Science Center (1967) and the University of Washington. A set of phases was generated relative to the signs of $E_{14\,4\,1}$, $E_{7\,1\,13}$ and $E_{10\,7\,\bar{1}}$. These three phases were arbitrarily chosen positive so as to fix the origin. No $\sum_2$ relation which had a probability less than 0·97 of being correct was used in the procedure. The probability was computed from the formula

$$P\pm(E_h) = \tfrac{1}{2} \pm \tfrac{1}{2} \tanh\left[\sigma_3/\sigma_2^{3/2} \textstyle\sum |E_h| E_{h-k} E_k\right].$$

The positions of the four independent bismuth atoms were revealed on an E map produced from 336 of a possible 342 $E_{hkl} > 1{\cdot}5$. Using all the data, these heavy atom positions were improved by two cycles of least-squares refinement. A Fourier difference map, phased by the bismuth contributions of the bismuth atoms, then revealed the positions of the remaining nine oxygen and two boron atoms in the asymmetric unit. The relative peak heights clearly distinguished boron from oxygen.

The structure was refined by full-matrix least-squares analysis based on the complete set of 2098 observed and 275 unobserved reflections. Observed reflections were given unit weight if $F_o \le 50$ and were weighted as $w^{1/2} = 50/F_o$ if $F_o > 50$. Unobserved reflections were given unit weight if $F_c > F_o(\text{min})$ and zero weight if $F_c \le F_o(\text{min})$. Forty-five positional parameters, fifteen isotropic temperature factors and one scale factor were varied. The refinement was terminated

Table 1. *Atomic parameters*

Positional parameters have been multiplied by 10^5. Estimated standard deviations are given in parentheses and refer to the least significant digits.

	x	*y*	*z*	*B*
Bi(1)	99203 (6)	48234 (11)	34689 (6)	0·62 (1)
Bi(2)	80532 (6)	4765 (11)	49151 (6)	0·71 (1)
Bi(3)	50217 (6)	42316 (11)	15923 (6)	0·64 (1)
Bi(4)	34298 (6)	43779 (11)	48132 (6)	0·66 (1)
O(1)	49761 (130)	10529 (221)	10580 (128)	0·67 (20)
O(2)	38059 (129)	10545 (221)	49802 (127)	0·63 (19)
O(3)	86424 (140)	15647 (245)	28177 (138)	1·00 (22)
O(4)	92029 (143)	15278 (251)	1252 (142)	1·08 (22)
O(5)	18875 (173)	20924 (296)	14029 (170)	1·77 (28)
O(6)	67884 (128)	22915 (227)	36744 (127)	0·71 (20)
O(7)	14699 (137)	24606 (238)	35355 (136)	0·91 (21)
O(8)	34000 (133)	32045 (229)	28025 (131)	0·80 (20)
O(9)	71078 (139)	31392 (239)	15925 (137)	0·96 (22)
B(1)	75137 (180)	23521 (316)	26683 (183)	0·50 (26)
B(2)	22882 (224)	25795 (381)	25237 (218)	1·10 (32)

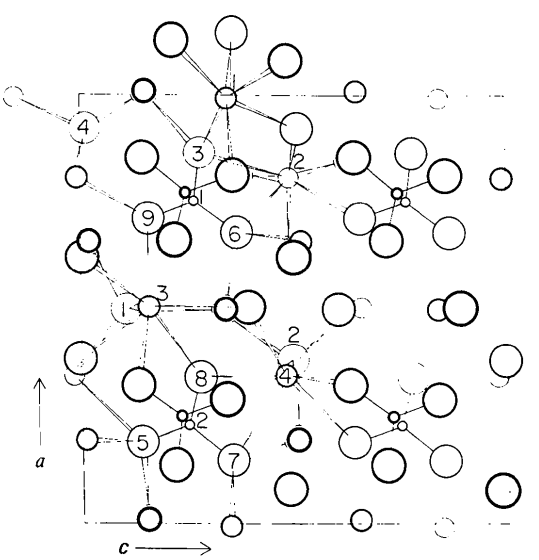
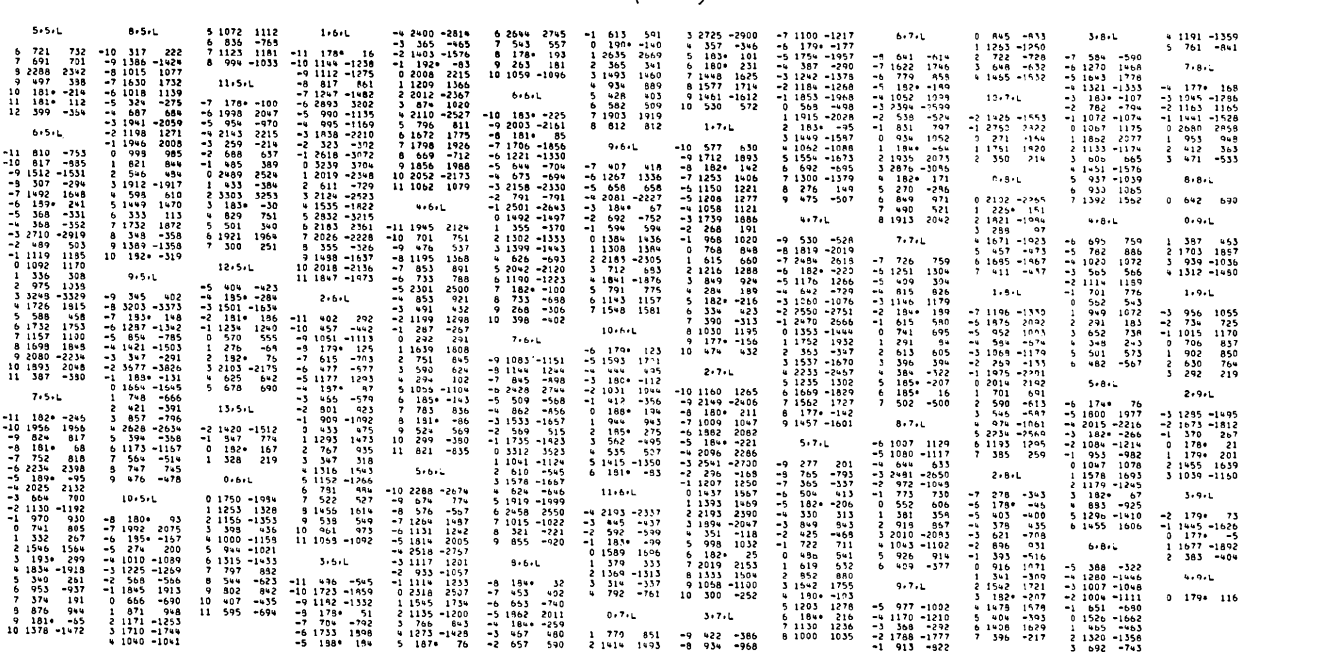


Fig. 1. Projection of bismuth (2:1) borate structure on (010). The largest circles represent oxygen atoms, intermediate size ones are bismuth atoms, and the smallest circles are boron atoms. The thickness of circles indicates the relative height. The numbers indicate the atoms as given in Table 1. For simplicity only the numbered oxygen and bismuth atoms have their complete coordination shown. The bismuth coordination has been arbitrarily limited to a maximum Bi–O distance of 2·87 Å.

Table 2. *Observed and calculated structure factors*

The columns are respectively l, $10sF_o$ and $10F_c$, where s = 3·97393. An asterisk designates an unobservable reflection which has been assigned the estimated minimum observable F_o value.

Table 2 *(cont.)*



after three cycles, at which point both $\sum w(F_o-F_c)^2$ and R had stopped changing significantly. The final R value was 0·051 and the final weighted $R'\{=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}\}$ was 0·066 based on the observed reflections only. In the last cycle the maximum shift per standard deviation was 0·0485 and the average for this quantity was 0·0082. The standard deviation of an observation of unit weight was 2·2420. The final values of the parameters are listed in Table 1. The rather large standard deviations for the boron and oxygen parameters are attributed to the virtual domination of the intensity distribution by the bismuth atoms. Observed and calculated structure factors are listed in Table 2. The atomic scattering factors used were those for neutral Bi, B and O (*International Tables for X-ray Crystallography*, 1962).

Discussion of the structure

The results of this investigation reveal that the bismuth (2:1) borate compound is actually an oxide-orthoborate with the formula $Bi_4O_3(BO_3)_2$. A projection of the structure onto (010) is shown in Fig. 1. We can consider the basic structural unit to be the planar (within 0·007 Å) anion BO_3^{3-}. There are two such anions in the asymmetric unit. Looking down the b axis one finds stacks of these ions, the planes of which are inclined somewhat (8·2°) toward each other and rotated so as to maximize oxygen–oxygen distances between adjacent ions. Bismuth atoms are distributed between the stacks of anions in such a manner that each bismuth atom is coordinated to oxygen atoms from several different BO_3^{3-} groups. The bismuth atoms thus serve to bind the anions into a three-dimensional

Table 3. *Bond lengths and angles*

Standard deviations referred to least significant digits are given in parentheses. Superscripted atoms have had their positional parameters transformed by: (i) $2-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1+x, y, z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $1-x, -y, 1-z$; (vi) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (viii) $1-x$,i$1-y$, $1-z$.

(*a*) Boron–oxygen

Distances		Angles	
B(1)–O(3)	1·365 (25) Å	O(3)–B(1)–O(6)	115·99 (1·68)
B(1)–O(6)	1·385 (25)	O(3)–B(1)–O(9)	122·60 (1·75)
B(1)–O(9)	1·367 (25)	O(6)–B(1)–O(9)	121·40 (1·70)
B(2)–O(5)	1·347 (31)	O(5)–B(2)–O(7)	119·48 (2·03)
B(2)–O(7)	1·455 (29)	O(5)–B(2)–O(8)	125·17 (2·14)
B(2)–O(8)	1·333 (29)	O(7)–B(2)–O(8)	115·35 (1·89)
Average	1·376		120·00

(*b*) Bismuth–neighbor distances < 3·3 A (dashed lines indicate end of coordination sphere assumed for Fig. 1)

Bi(1)–O(4^{i})	2·140 (16) Å	Bi(3)–O(1)	2·188 (15) Å
Bi(1)–O(4^{ii})	2·199 (16)	Bi(3)–O(2^{vii})	2·223 (14)
Bi(1)–O(7^{iii})	2·327 (15)	Bi(3)–O(8)	2·362 (15)
Bi(1)–O(3^{i})	2·446 (16)	Bi(3)–O(9)	2·428 (15)
Bi(1)–O(5^{iv})	2·525 (19)	Bi(3)–O(2^{iv})	2·501 (14)
Bi(1)–O(3)	2·766 (16)	Bi(3)–O(1^{iv})	2·862 (14)
		Bi(3)–O(6^{iv})	2·867 (15)
Bi(1)–O(7^{iv})	3·196 (16)		
Bi(1)–B(2^{iii})	3·212 (25)	Bi(3)–O(8^{iv})	3·226 (15)
Bi(1)–B(2^{iv})	3·234 (25)	Bi(3)–B(1)	3·241 (20)
Bi(1)–B(1)	3·244 (20)	Bi(3)–O(6)	3·260 (14)
Bi(2)–O(6)	2·287 (14)	Bi(4)–O(1^{ii})	2·199 (14)
Bi(2)–O(2^{v})	2·306 (14)	Bi(4)–O(2)	2·249 (15)
Bi(2)–O(9^{ii})	2·334 (15)	Bi(4)–O(1^{iv})	2·314 (15)
Bi(2)–O(4^{ii})	2·370 (16)	Bi(4)–O(8)	2·353 (15)
Bi(2)–O(3)	2·524 (15)	Bi(4)–O(5^{ii})	2·660 (19)
Bi(2)–O(7^{v})	2·639 (15)	Bi(4)–O(6^{viii})	2·781 (15)
Bi(2)–O(5^{vi})	2·675 (19)	Bi(4)–O(7)	2·869 (15)
Bi(2)–B(1)	2·830 (20)	Bi(4)–O(9)	2·991 (16)
		Bi(4)–B(2)	3·051 (24)
		Bi(4)–O(4^{iv})	3·255 (16)

structure. The structure does not contain a complex polymer of borate groups.

The structure, also, contains non-boron coordinated oxygen atoms [O(1), O(2) and O(4)]. This is unusual for borates, being known only in the zinc (4:3) borate (Smith, Garcia-Blanco & Rivoir, 1964). These additional oxygen atoms are bound to bismuth atoms. The spread in Bi–O distances (Table 3) is large and no unambiguous coordination number can be assigned to some of the bismuth atoms. Bi(1) is six-coordinated and Bi(2) is seven-coordinated. Both have a clear-cut maximum coordination distance about 2·67 Å. The Bi(3) atom could be considered to be either five-coordinated or seven-coordinated depending on whether one chooses 2·50 Å or 2·87 Å as a cut-off point. Bi(4) has the most poorly defined coordination sphere in terms of having a marked gap between coordinated and noncoordinated atoms. For the purposes of drawing Fig. 1, a maximum Bi–O distance of 2·87 Å was arbitrarily chosen to define the Bi coordination sphere.

Table 3 lists boron–oxygen bond distances and angles as well as bismuth–oxygen distances. The mean B–O distance is 1·376 Å, which is in accord with bond lengths found in other borates for triangularly coordinated boron. One distance [1·455 Å for B(2)–O(7)] is somewhat large. There seems to be nothing in the immediate environment of these atoms to which this may be attributed. Instead, this somewhat long bond length is probably a reflection of the relatively large errors associated with the boron and oxygen coordinates. The O–B–O angles are narrowly distributed about a mean of 120·00° in agreement with similar angles in other known borates.

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Structure Cristalline de $Cs_2UO_2F_4.H_2O$

PAR NGUYEN QUY DAO

Institut de Chimie, Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, 92-Chatenay-Malabry, France

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$Cs_2UO_2F_4.H_2O$ crystallizes in the monoclinic system, space group $P2_1/c$: $a=8{\cdot}06$, $b=12{\cdot}18$, $c=9{\cdot}29$ Å, $\beta=109°12'$. The structure is composed of Cs^+ ions, of water molecules and of dimers with the formula $U_2O_4F_8^{4-}$. The dimer is formed by two $UO_2F_5^{3-}$ pentagonal bipyramids sharing a common edge of the pentagonal base. The U–F bridging bond is 2·4 Å, the U–F terminal bond 2·2 Å. The distance between the two uranium atoms inside the dimers is 4·04 Å while the shortest distance between two uranium atoms of two different dimers is 6·19 Å. The water molecule forms a bridge between two dimers. The hydrogen bonding is of medium strength. The caesium atoms are situated within the cavities and tunnel left by the chains of dimers and water molecules.

Introduction

Dans le cadre d'une étude systématique de mise en évidence des ions complexes formés par l'ion uranyle avec les ions halogénures, nous avons étudié la structure cristalline de $Cs_2UO_2F_4.H_2O$ (I) au moyen de la diffraction des rayons X par un monocristal. Ce composé (I) a été mis en évidence comme l'un des composés définis du système ternaire UO_2F_2–CsF–H_2O (Zaitseva, Lipis, Fomin & Chebotarev, 1962). Quelques raies importantes du diagramme de diffraction des rayons X de (I) à l'état de poudre ont été données par les auteurs précédents. Le diagramme complet, avec son indiçage, a été donné dans nos résultats préliminaires (Brusset & Nguyen Quy Dao, 1970).

Partie expérimentale

En portant à ébullition, pendant quelques minutes, une solution contenant une mole de UO_2F_2 pour deux moles de CsF, puis filtrant la solution et la laissant évaporer à l'air, il se forme de très beaux cristaux transparents, jaunes et fluorescents. (I) a été identifié par comparaison du diagramme de diffraction des