

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.

I would like to express my appreciation to Dr Ulrich Weiss of the National Institutes of Health for providing the crystals, to Dr Jerry Donohue of the University of Pennsylvania for helpful discussions concerning hydrogen bonding, and to Dr Richard Gilardi of the Naval Research Laboratory for experimental help.

References

- BURGSTAHLER, A. W., GAWRONSKI, J., NIEMANN, T. F. & FEINBERG, B. A. (1971). *Chem. Commun.* p. 121.
- BURGSTAHLER, A. W., ZIFFER, H. & WEISS, U. (1961). *J. Amer. Chem. Soc.* **83**, 4660.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS, A Fortran Crystallographic Least-Squares Program. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- COOPER, A., NORTON, D. & HAUPTMAN, H. (1969). *Acta Cryst.* **B25**, 814.
- DAUBEN, W. G. & COATES, R. M. (1963). *J. Org. Chem.* **28**, 1698.
- DOBLLER, M. & DUNITZ, J. D. (1965). *Helv. Chim. Acta*, **48**, 1429.
- DUCHAMP, D. J. & MARSH, R. E. (1969). *Acta Cryst.* **B25**, 5.
- DUNITZ, J. D. & STRICKLER, P. (1968). In *Structural Chemistry and Molecular Biology*, p. 595. Edited by A. RICH and N. DAVIDSON. San Francisco: Freeman.
- EIJCK, B. P. VAN, KANTERS, J. A. & KROON, J. (1965). *Acta Cryst.* **19**, 435.
- HOUSTY, J. (1968). *Acta Cryst.* **B24**, 486.
- JEFFREY, G. A. & SAX, M. (1963). *Acta Cryst.* **16**, 430.
- JOHNSON, C. K. (1965). ORTEP, A Fortran Thermal-Elipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KARLE, I. L. (1970). *Acta Cryst.* **B26**, 1639.
- KARLE, J. (1968). *Acta Cryst.* **B24**, 182.
- KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
- ROELOFSEN, G., KANTERS, J. A., KROON, J. & VLIEGENTHART, J. A. (1971). *Acta Cryst.* **B27**, 702.
- SCHULLER, W. H. & LAWRENCE, R. V. (1961). *J. Amer. Chem. Soc.* **83**, 2563.
- WEISS, U., WHALLEY, W. B. & KARLE, I. L. (1971). *Chem. Commun.* p. 16.
- WEISS, U., ZIFFER, H. & CHARNEY, E. (1962). *Chem. Ind. Lond.* 1286.

Acta Cryst. (1972). **B28**, 2007

The Crystal Structure of Bismuth (2:1) Borate, $2\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$

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.

(Received 1 December 1971 and in revised form 28 January 1972)

The crystal structure of bismuth (2:1) borate ($2\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$) was determined by single-crystal X-ray diffraction analysis. Proper classification of this compound is as an oxide-orthoborate with the formula $\text{Bi}_4\text{O}_3(\text{BO}_3)_2$. The material crystallizes in the monoclinic system, $P2_1/c$, with 4 formula units in a cell of dimensions $a = 11.107$, $b = 6.627$, $c = 11.044$ Å and $\beta = 91.04^\circ$. Intensity data were obtained on an automated diffractometer using Nb-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ 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 $R = 5.1\%$ 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 $2\text{Bi}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ 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 ($0.188 \text{ mm} \pm 5\% \text{ diameter}$) and spherical crystal ($\mu R = 7.7$ 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 ($\lambda = 0.710688 \text{ \AA}$). 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:

$$\begin{aligned} a &= 11.107 \pm 0.004 \text{ \AA} \\ b &= 6.627 \pm 0.002 \\ c &= 11.044 \pm 0.002 \\ \beta &= 91.04 \pm 0.02^\circ \\ Z &= 4 \\ \rho(\text{calc}) &= 8.184 \text{ g.cm}^{-3} \end{aligned}$$

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 $E_{14\bar{4}\bar{1}}$, $E_{7\bar{1}\bar{1}3}$ and $E_{10\bar{7}\bar{1}}$. 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

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

The positions of the four independent bismuth atoms were revealed on an E map produced from 336 of a possible 342 $E_{hkl} > 1.5$. 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 $F_o \leq 50$ 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 $F_c \leq F_o(\text{min})$. 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.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
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)

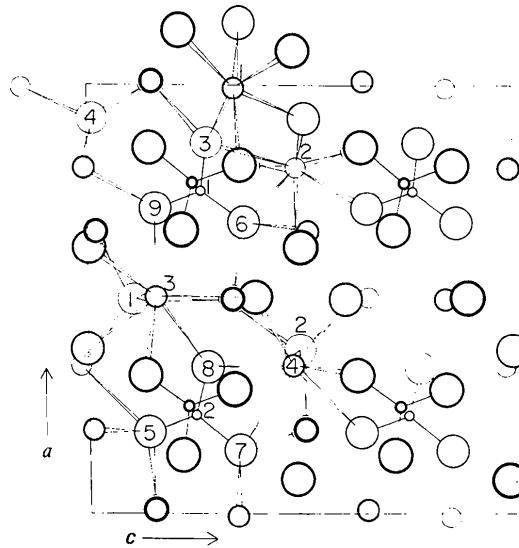


Fig. 1. Projection of bismuth (2:1) borate structure on (010). The largest circles represent oxygen atoms, intermediate size ones are bismuth atoms, and the smallest circles are boron atoms. The thickness of circles indicates the relative height. The numbers indicate the atoms as given in Table 1. For 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 I , $10sF_0$ and $10F_c$, where $s=3.97393$. An asterisk designates an unobservable reflection which has been assigned the estimated minimum observable F_0 value.

	$0+L$	$0+L$	$+5$	955	122	$7+L$	0	$185*$	-68	-9	65	-70	-13	521	-309	-2	866	852	5	$207*$	-20	11	$177*$	35	-12	$174*$	177	-7	$184*$	-86	$0+5-L$								
2	3030	327	-12	1919	-1875	-3	1912	127	$1398*$	-12	1165	1172	1	180	180	-1	209	209	-11	1289	1372	1	1641	1677	7	663	732	$10+3-L$	-13	808	-1775	-5	2231	-2366	1	766	883		
$*+1154$	1255	-10	1042	-94	-2	2072	2592	-12	1165	1172	3	1037	1987	-6	362	362	-7	1289	1372	1	2161	2691	8	3496	-3510	-9	1132	-1266	-4	2193	-2244	2	539	600					
6	7695	8615	-8	301	293	-1	2047	198	-11	1783	-191	4	412	412	-5	1792	-189	-9	473	-67	2	119	-100	9	1624	-1657	-11	1405	-1555	-5	189	-1867	3	370	-3586				
10	573	5865	$+5$	335	-217	0	1558	1630	-10	2958	-2820	0	345	323	-10	2958	-2820	-1	1641	1651	11	680	-1685	-9	1132	-1126	-5	1627	-1508	-1	170	-1296	5	315	-349				
10	603	605	-4	248	-21	1	2047	198	-11	1783	-191	2	412	412	-5	1792	-189	-9	473	-67	2	119	-100	9	1624	-1657	-11	1405	-1555	-5	189	-1867	3	370	-3586				
12	3094	3427	-2	1579	153	-2	425	454	-9	348	-217	7	1031	1952	-2	242	-97	-6	1201	1228	5	466	400	$12+2-L$	-8	723	752	-5	2675	-2492	0	1787	-1990	1	769	883			
14	1756	1898	0	1143	1352	3	380	146	-1	2005	1907	8	1734	-101	1	1330	1554	-1	2923	2936	14	1887	-1910	-1	1520	-1555	-5	189	-1867	3	370	-3586							
$1+0+L$	-2	2325	2525	5	125	9	-5	1109	-1171	2	510	-527	-2	1249	-1249	-1	360	-282	5	51	-281	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703			
6	1569	511	-6	483	-107	1	2047	198	-11	1783	-191	7	102	73	-6	1000	1000	-1	1641	1651	1	624	531	$14+0-L$	-1	1560	-1570	-5	1801	-1955	-1	1560	-1560	-1	1560	-1560	-1	1560	-1560
10	603	605	-10	1042	-94	-1	2047	198	-11	1783	-191	2	412	412	-5	1792	-189	-9	473	-67	2	119	-100	9	1624	-1657	-11	1405	-1555	-5	189	-1867	3	370	-3586				
12	607	605	-8	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
14	607	605	-6	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
16	605	605	-4	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
18	605	605	-2	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
20	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
22	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
24	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
26	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
28	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
30	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
32	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
34	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
36	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
38	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	212	-2146	-1	2062	-2059	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703	-1	1703	-1703				
40	605	605	-1	1769	171	7	542	675	-3	1455	-1670	1	185	-1170	-1	2																							

THE CRYSTAL STRUCTURE OF BISMUTH (2:1) BORATE

Table 2 (cont.)

S+5·L	B+5·L	S 1072	1112	1·6·L	-4 2400 -281*	6 2544	2745	-1 613	501	3 2725 -2900	-7 1100 -1217	6·7·L	0 445 -413	3·8·L	* 1191 -1359
6 721 732	-10 317 222	7 1123 1181	-11 178* 16	-3 355	-155*	8 178*	553	-140	4 353 -346	-6 179* -177	4 1259 -1250	5 761 -841			
7 691 701	-9 1386 -1424	9 994 -1033	-10 114* -1258	-1 192*	-83	9 263	181	2 365	3·1	-5 1343 -1349	6 61 -114*	4 1259 -1250	-7 586 -500		
9 407 230	-7 1630 182	11 1532	-10 114* -1258	0 208*	2215	10 1059 -108	3 1493 160	7 148* 1625	-2 1242 -1379	-7 779 455	4 1465 -1532	-5 1643 -1778			7·8·L
10 181* -216	6 1018 1159	-7 1247 -1482	2 2012 -2367	6·6·L	5 428	303	9 1461 -1482	-1 1188 -1268	-1 182* -149	13·7·L					1·77* -168
11 181* -115	5 324* -275	-7 178* -100	-6 2693 3022	3 67*	502	10 530	572	0 563	-3 2364 -2599	-2 1915 -208	-2 538 -524	-2 142* -1553	-1 1072 -1074	-1 1441 -1528	
12 399* -354	3 1941 -2059	-7 178* -100	-6 2693 3022	3 67*	502	10 530	572	0 563	-3 2364 -2599	-2 1915 -208	-2 538 -524	-2 142* -1553	-1 1072 -1074	-1 1441 -1528	
6·5·L	2 1198 1271	-2 2143 2215	-3 1730 -2210	6 1672 1775	-8 181	85	1 2003 -2111	8 1672 1812	3 1490 -1557	0 934 -1052	-1 2003 -2111	-2 271 -154	1 1533 -1174	2 412 363	
7 1946 2005	-5 259 -214	-2 323	7 1798 1926	-7 1766 -1856	9·6·L	-10 577	630	1 1042 -1088	1 184* -64	1 1751 -1920	2 1133 -1174	3 605 -665	3 471 -533		
-11 810 -755	7 1946 2005	-5 259 -214	-2 323	7 1798 1926	-7 1766 -1856	9·6·L	-10 577	630	1 1042 -1088	1 184* -64	1 1751 -1920	2 1133 -1174	3 605 -665	3 471 -533	
-10 817 -935	1 821 894	-3 485 389	0 5239 3704	9 1856 1988	-7 1766 -1856	9·6·L	-10 577	630	1 1042 -1088	1 184* -64	1 1751 -1920	2 1133 -1174	3 605 -665	3 471 -533	
-9 1512 -1553	2 546 894	0 2489 2524	1 2019 -2348	10 2052 -2173	-8 673	-659	-6 1267 1338	-7 1255 1404	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L			
-8 1492 1494	3 181* -141	2 453* -141	2 511 -729	11 1062	1079	-3 2158 -2330	-5 658 658	-5 1150 1221	8 276 149	2 2125 -2246	6 933 -1365				
-7 1492 1649	5 1499 1470	3 183* -50	4 1535 -1422	4·6·L	-1 2501 -2643	3 184* -67	-1 1058 1121	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L				
-6 159* 241	5 1499 1470	3 183* -50	4 1535 -1422	4·6·L	-1 2501 -2643	3 184* -67	-1 1058 1121	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L				
-5 368 -331	6 333 113	8 829 751	5 2832 -3215	4 1624 -1656	4·7·L	-1 1942 -1497	-2 692 -752	-3 1759 1888	4·7·L	8 1913 2042	2 142* -1494	4·8·L	0·9·L		
-4 2080 -2234	8 348 -358	6 1921 1969	7 2026 -2228	-11 1945 2124	1 155	-370	4 1694 1592	2 268 1611	3 184* -67	3 288 97					
-3 2710 -2919	8 348 -358	6 1921 1969	7 2026 -2228	-11 1945 2124	1 155	-370	4 1694 1592	2 268 1611	3 184* -67	3 288 97					
-2 1499 1514	9 1389 -1358	7 301 251	5 555 -326	-9 476	537	3 1399 -1443	1 1308 1394	0 768 848	8 1819 -2019	-7 726 759	6 1685 -1667	4 1023 1072	3 939 -1036		
-1 1092 1170	10 192* -319	12·5·L	3 1498 -1637	-8 1195	1368	4 626 -693	2 2185 -2305	1 615 660	7 269 2616	-2 1511 1504	7 411 -147	-3 565 566	4 1512 -1450		
1 336 308	9 1356 9·5·L	11 1847 -1973	-5 2301 2305	-6 713	768	5 200 -1233	4 1804 -1804	2 1216 1280	-6 182* -223	-2 1511 1504	7 411 -147	-3 565 566	4 1512 -1450		
2 975 1335	-9 365 -402	-5 404 -223	2·6·L	-4 053	921	8 733 -688	6 1143 1157	5 182* -216	3 1260 -1076	-3 1166 1179	0 562 5·3				1·9·L
4 1726 1815	8 3203 -3203	-3 501 -184	2 511 -729	2 1198 1200	10 598 -492	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L						
5 588 -58	7 193* -148	1 181* -186	-11 202	2 1198 1200	10 598 -492	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L						
6 1522 1753	-6 1287 -132	-1 2353 1290	-10 451 -451	-4 182* -264	-2 287	-267	6 1804 -1804	5 182* -216	3 1260 -1076	-3 1166 1179	0 562 5·3				1·9·L
7 1159 1200	4 1421 -1503	1 276 -59	-3 179* -125	16 1639	1751	4 624 -693	2 2185 -2305	1 615 660	7 269 2616	-6 182* -223	-2 1511 1504	7 411 -147	-3 565 566	4 1512 -1450	
8 1699 1843	3 347 -291	2 192* -192	7 615 -703	7 151	645	-9 1083 -1151	-5 1593 1711	6 1709 1723	10 476 -432	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L		
9 2080 -2234	3 347 -291	2 192* -192	7 615 -703	7 151	645	-9 1083 -1151	-5 1593 1711	6 1709 1723	10 476 -432	7 1300 -1379	4 182* -171	5 937 -1039	8·8·L		
10 1387 -330	1 189* -186	2 2026 -2175	-6 477 -577	3 590	592	-9 1144 1244	4 184* -184	5 184* -184	2 273 -2567	3 184* -184	2 273 -2567	3 184* -184	2 273 -2567	3 292 219	
11 1654 -1545	5 670 690	-4 197* -197	12 178* -178	6 1597 -1667	3 1570 -1667	1 1207 1250	-7 365 -537	-3 972 -1049	1 1207 1250	-7 365 -537	-3 972 -1049	1 1207 1250	-7 365 -537	3 184* -184	
12 2025 2132	6 751 784	-4 197* -197	12 178* -178	6 1597 -1667	3 1570 -1667	1 1207 1250	-7 365 -537	-3 972 -1049	1 1207 1250	-7 365 -537	-3 972 -1049	1 1207 1250	-7 365 -537	3 184* -184	
13 664 700	10 15·5	10 15·5	15·5·L	-5 456 -579	5 185* -185	-5 509 -568	-1 412 -356	9 2149 -2405	7 1562 1727	5 502 -500	2 500 -613	-6 174* -176			2·9·L
14 970 1192	8 180* -93	1 1253 1328	8 1455 1614	8 576 -597	6 2458 -2550	-4 2103 -2337	2 2193 2390	-6 330 313	1 381 -358	-5 403 -400	5 1296 -1410	-2 179* -73			
0 791 805	7 1992 2075	3 393 -356	10 163 -163	-6 151 -151	9 529 -549	5 185 -275	6 1852 -2082	-6 330 313	1 381 -358	-5 403 -400	5 1296 -1410	-2 179* -73			
1 332 267	2 155* -157	4 1000 -1159	11 1059 -1092	-5 1014 -1014	2 095 -855	-9 185 -202	-1 183 -183	5 998 1032	1 722 711	-5 1043 -1102	8 896 -931	6·8·L			
2 153 267	3 155* -157	4 1000 -1159	11 1059 -1092	-5 1014 -1014	2 095 -855	-9 185 -202	-1 183 -183	5 998 1032	1 722 711	-5 1043 -1102	8 896 -931	6·8·L			
3 193* -299	4 1010 -1039	9 1315 -1333	5·9·L	-3 1111 -1111	5 184* -184	5 184* -184	1 1809 -1809	6 182* -25	0 498 -541	9 261 914	-5 191 -1071	-5 388 -322			
1834 -1919	3 125 -1255	7 797 882	-2 233 -1057	2 1369 -1313	9·6·L	1 1809 -1809	6 182* -25	0 498 -541	9 261 914	-5 191 -1071	-5 388 -322				
5 340 -281	-5 565 -566	8 594 -623	-11 1111	1 1111	1233	-8 184	32	3 314 -337	9 1058 -1100	3 1524 -1755	9·7·L				
6 374 191	0 666 -690	10 497 -835	-9 1112 -1112	3 1321 2318	-7 453 -492	4 792 -761	10 300 -300	-5 192 -192	7 1562 1727	5 1296 -1410	-2 1007 -1048	4·9·L			
9 876 94	1 871 -868	11 595 -694	-9 178* -51	2 1135 -1200	-5 192	2011	0 47·L	3 184* -207	5 1296 -1410	-2 1007 -1048	4·9·L				
9 181* -55	2 137* -1253	-7 704 -702	3 766 843	-4 184* -259	4 1273 -1249	-3 457 -480	1 770 851	-9 422 -386	8 1000 1035	-2 1768 -1777	7 396 -217	2 1320 -1358			
10 1378 -1742	-4 1040 -10·1	-5 198* -198	5 187* -187	2 1414 1493	-8 934 -934	-9 394 -398	1 770 -770	-1 913 -922	3 692 -743						

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 $\text{Bi}_4\text{O}_3(\text{BO}_3)_2$. 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) $1-x, 1-y, 1-z$.	
(a) Boron-oxygen Distances	Angles
B(1)-O(3)	1·365 (25) Å
B(1)-O(6)	1·385 (25)
B(1)-O(9)	1·367 (25)
B(2)-O(5)	1·347 (31)
B(2)-O(7)	1·455 (29)
B(2)-O(8)	1·333 (29)
Average	1·376
(b) Bismuth–neighbor distances < 3.3 Å (dashed lines indicate end of coordination sphere assumed for Fig. 1)	
Bi(1)-O(4 ⁱ)	2·140 (16) Å
Bi(1)-O(4 ⁱⁱ)	2·199 (16)
Bi(1)-O(7 ⁱⁱⁱ)	2·327 (15)
Bi(1)-O(3 ^{iv})	2·446 (16)
Bi(1)-O(5 ^v)	2·525 (19)
Bi(1)-O(3)	2·766 (16)
Bi(1)-O(7 ^{vi})	3·196 (16)
Bi(1)-B(2 ⁱⁱⁱ)	3·212 (25)
Bi(1)-B(2 ^{iv})	3·234 (25)
Bi(1)-B(1)	3·244 (20)
Bi(2)-O(6)	2·287 (14)
Bi(2)-O(2 ^v)	2·306 (14)
Bi(2)-O(9 ⁱⁱ)	2·334 (15)
Bi(2)-O(4 ⁱⁱ)	2·370 (16)
Bi(2)-O(3)	2·524 (15)
Bi(2)-O(7 ^v)	2·639 (15)
Bi(2)-O(5 ^v)	2·675 (19)
Bi(2)-B(1)	2·830 (20)
Bi(4)-O(1)	2·188 (15) Å
Bi(3)-O(2 ^{vi})	2·223 (14)
Bi(3)-O(8)	2·362 (15)
Bi(3)-O(9)	2·428 (15)
Bi(3)-O(2 ^{iv})	2·501 (14)
Bi(3)-O(6 ^v)	2·862 (14)
Bi(3)-O(6 ^{vi})	2·867 (15)
Bi(2)-O(8 ^v)	3·226 (15)
Bi(3)-B(1)	3·241 (20)
Bi(3)-O(6)	3·260 (14)
Bi(2)-O(6)	2·287 (14)
Bi(2)-O(2 ^v)	2·306 (14)
Bi(2)-O(9 ⁱⁱ)	2·334 (15)
Bi(2)-O(4 ⁱⁱ)	2·370 (16)
Bi(2	

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 co-

ordinated 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.

References

- HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal*. A.C.A. Monograph No. 3.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1967). Vol. II. Birmingham: Kynoch Press.
KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.
MIGHELL, A. (1967). Private communication.
SMITH, P., GARCIA-BLANCO, S. & RIVOIR, L. (1964). *Z. Kristallogr.* **119**, 375.
X-ray 67 System (1967). Technical Report 67-58, Computer Science Center, Univ. of Maryland.
WEIR, C. E. & SCHROEDER, R. A. (1964). *J. Res. Nat. Bur. Std.* **68A**, 465.

Acta Cryst. (1972). **B28**, 2011

Structure Cristalline de $\text{Cs}_2\text{UO}_2\text{F}_4 \cdot \text{H}_2\text{O}$

PAR NGUYEN QUY DAO

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

(Reçu le 16 décembre 1971, revu le 27 janvier 1972)

$\text{Cs}_2\text{UO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ cristallise dans le système monoclinique, groupe d'espace $P2_1/c$: $a = 8.06$, $b = 12.18$, $c = 9.29$ Å, $\beta = 109^{\circ}12'$. La structure est composée d'ions Cs^+ , de molécules d'eau et de dimères avec la formule $\text{U}_2\text{O}_4\text{F}_8^{4-}$. Le dimère est formé par deux $\text{UO}_2\text{F}_5^{3-}$ pentagonal bipyrâmides partageant une arête commune de la base pentagonale. La liaison U–F est de 2.4 Å, la liaison U–F terminale de 2.2 Å. La distance entre les deux atomes d'uranium à l'intérieur des dimères est de 4.04 Å alors que la distance la plus courte entre deux atomes d'uranium de deux dimères différents est de 6.19 Å. Une molécule d'eau forme un pont entre deux dimères. La liaison hydrogène est de force moyenne. Les atomes de caesium sont situés dans les cavités et tunnels laissés par les chaînes de dimères et de molécules d'eau.

Introduction

Dans le cadre d'une étude systématique de mise en évidence des ions complexes formés par l'ion uranyl avec les ions halogénures, nous avons étudié la structure cristalline de $\text{Cs}_2\text{UO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ (I) au moyen de la diffraction des rayons X par un monocrystal. Ce composé (I) a été mis en évidence comme l'un des composés définis du système ternaire $\text{UO}_2\text{F}_2\text{--CsF--H}_2\text{O}$ (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 indiquage, 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