between  $O(1^*) \cdots C(16^*)$  at 3.49 Å and  $C(20) \cdots C(16^*)$  at 3.68 Å. All other  $C \cdots C$  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.

- DOBLER, 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.
- EUCK, 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-Ellipsoid 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. & VLIEGENT-HART, 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, 2Bi<sub>2</sub>O<sub>3</sub>.B<sub>2</sub>O<sub>3</sub>

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

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  $a = 11\cdot107$ ,  $b = 6\cdot627$ ,  $c = 11\cdot044$  Å and  $\beta = 91\cdot04^\circ$ . 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  $R = 5\cdot1\%$  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  $1\cdot38$  Å. The minimum Bi–O distance found is  $2\cdot14$  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  $\pm$  5% diameter) and spherical crystal ( $\mu R = 7.7$  for Mo K $\alpha$ ) was selected for study. Intensity data were collected on a threecircle counter diffractometer using Nb-filtered Mo  $K\alpha$ radiation ( $\lambda = 0.710688$  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 peakheight intensities as a function of scattering angle.

The observed monoclinic symmetry and systematic extinctions of hol (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:

$$a = 11 \cdot 107 \pm 0.004 \text{ Å}$$
  

$$b = 6.627 \pm 0.002$$
  

$$c = 11.044 \pm 0.002$$
  

$$\beta = 91.04 \pm 0.02^{\circ}$$
  

$$Z = 4$$
  

$$\varrho(\text{calc}) = 8.184 \text{ g.cm}^{-3}$$

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  $E_{10\ 7\ \overline{1}}$ . 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

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

The positions of the four independent bismuth atoms were revealed on an E map produced from 336 of a possible 342  $E_{hkl} > 1.5$ . Using all the data, these heavy atom positions were improved by two cycles of leastsquares 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 leastsquares analysis based on the complete set of 2098 observed and 275 unobserved reflections. Observed reflections were given unit weight if  $F_a \leq 50$  and were weighted as  $w^{1/2} = 50/F_o$  if  $F_o > 50$ . Unobserved reflections were given unit weight if  $F_c > F_o(\min)$  and zero weight if  $F_c \leq F_o(\min)$ . 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 105. Estimated standard deviations are given in parentheses and refer to the least significant digits.

	x	У	Ζ	В
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,  $10_s F_o$  and  $10 F_c$ , where s = 3.97393. An asterisk designates an unobservable reflection which has been assigned the estimated minimum observable  $F_o$  value.

0.0.1	9.0.L	-5 935 1024 -6 1912 1967	7.1.L	0 193• -68 1 1489 1467	-9 652 -704 -8 339 -243	-13 521 -309 -12 380 497	-2 56% 452 -1 770 71%	5 207 -204 6 2862 -2958	11 177• 35	-12 179+ 107	-7 185* -86 -6 1161 1246	0.5.1
2 3030 3274 * 1154 1258 5 7968 8815	-12 1919 -1875 -10 1042 -944 -8 301 293	-3 1308 1398 -2 2872 2992 -1 2047 1992	-13 1394 1179 -12 1165 1172 -11 1780 -1914	2 321 -300 3 1837 1987	-7 209+ 308 -6 362 -225 -5 1782 -1895	-11 1289 13'2 -10 2129 -2164 -9 473 -467	9 1641 1677 1 2619 2691 2 1° 9 -1400	7 663 732 8 3496 -3618 9 1624 -1667	10.3.L -11 1405 -1455	-13 909 -1775 -9 1132 -1266 -9 188* 4	-5 2231 -2366 -4 2193 -2284 -3 1840 -1867	1 766 883 2 530 600 3 300 -3586
8 3759 3685 10 953 -1355 12 3095 3527	-5 536 -500 -4 202+ 317 -2 1579 1538	0 1558 1630	-10 944 891 -9 2955 -2990 -9 349 -237	5 2335 2500 6 335 306 7 1831 1952	-4 1472 -1555 -3 339 44 -2 2424 -97	-8 559 573 -7 1850 -140 -6 1201 1228	3 1303 1281 4 561 +565 5 466 400	10 1201 -1315 11 680 -708 12 1241 -1305	-10 56% -549 -9 1132 -1126 -8 702 752	-7 1101 -1342 -5 620 508 -5 2475 2492	-2 435 -309 -1 1470 -1296 0 1757 1590	4 1241 1489 5 315 57 6 1050 1237
14 1756 1898 1+0+L	0 1343 1352 2 1436 1477 4 2325 2525	3 390 144 4 2615 2609 5 2254 9	-7 2005 1997 -6 1201 1178 -5 1199 -1171	8 1734 -101 9 1561 1748	-1 1330 1358 0 1057 1037 1 435 322	-5 2932 2934 -4 3641 -3629 -3 842 785	15.2.L	13 758 810 14 1887 -1918	-7 180• 5 -6 523 -519 -5 18+7 -19+3	-4 1094 -1270 -3 215• 32 -2 772 -910	1 2971 -2997 2 1727 -1711 3 2751 -2743	7 1337 1639 8 1480 1730 9 1841 -2140
-14 680 687	6 1569 1722 8 1769 1971	6 511 583 7 542 605	-4 1037 994	13+1+L	2 510 -527 3 1171 1222 # 525 -512	-2 1249 -1217 -1 312 301	-3 360 -282 -2 1722 1695 -1 178* 235	5+3+L -13 1128 1208	-4 1203 -1192 -3 2384 -2371 -2 1854 121	-1 1769 -1995 0 223+ 131 1 2966 3122	+ 1628 -1629 5 1469 -1453 6 1580 1643	10 1867 2175 11 511 -601 12 1388 1580
-10 +78 -638 -8 205+ -132 -5 1025 -1377	12 1055 1141	9 304 144 10 658 592	-1 2336 2329 0 320 AL	-7 2206 2124 -5 702 734	5 2899 2980 6 1000 1040 7 939 1015	1 3420 3428 2 3523 -3601 3 1668 1735	0 1417 1349 1 824 -897 2 642 651	-12 878 859 -11 783 -864 -10 720 701	-1 306 -99 0 978 -977 1 1553 -1547	2 869 -946 3 739 727 4 1505 -1570	7 2585 -2581 8 740 -750 9 1907 -1956	13 1451 1621
-4 983 -1019 -2 306+ -640	-12 997 914	12 184• 115	2 1220 1190	-4 459 488 -3 1767 -1854	8 343 319 9 1421 1443	4 3080 -3364 5 1894 -185	0.3.	-9 1027 -1062 -8 1626 -1649 -7 1258 1262	2 2064 -2081 3 2484 -2500 4 402 -385	5 2155 -2335 6 310 247 7 1499 1625	10 1598 +1647 11 746 -767 12 789 782	-13 451 413
2 309+ -361 4 263+ -68	-5 800 701 -5 2101 2057	15 577 497	5 2122 2353 6 562 -5°4	+1 1963 2019 0 178+ 10	11 2629 2700 12 181+ 175	7 2274 2523 8 2154 -2356	1 532 526 2 1074 -1104 3 2566 -2725	-6 1920 2075 -5 1035 -1024	5 462 - 378 6 909 - 949 7 267 - 286	8 634 -625 9 757 767 10 1119 -1243	8.4	-11 181 -198 -10 1382 1672 -9 545 575
6 1142 1197 10 192• 125	-2 199+ -76 0 3535 3332	-15 391 -299	8 469 535 9 1154 -1279	2 375 393 3 19+4 -2155	14 183+ 353	10 2866 -3058	4 2482 2595 5 428 -439 6 1925 2127	-3 2480 +2630 -2 1174 -1260	8 1592 -1735 9 1592 -1732	11 2018 -2163 12 321 -271	-11 15** 1582 -10 1225 -1259 -9 565 -573	-8 826 -879 -7 823 988 -6 1355 1568
14 1253 1315	4 970 -1046 6 3533 3947	-13 3129 3355 -12 192• -34	11 1492 1648 12 523 -611	5 1435 1575 6 690 -710	-1- 176+ 100	9+2+6	7 816 885 8 745 813	0 1900 1933	11+3+6	3.4.6	-5 187• 94 -7 315 251	-5 2044 -144 -4 1874 2177
-14 1941 1975	10 520 -621	-11 608 600 -10 314 -299 -9 328 -332	8+1+6	7 1383 1532 8 173• 152	-12 290 -297 -11 2632 2739	-12 1225 -1179 -11 1073 -1102	10 2461 2543	3 3725 -3824	-10 707 735 -9 765 -701	-13 757 -851 -12 382 364	-5 3241 3423	-2 1467 -1632 -1 635 660
-10 2059 -2194 -8 207+ 49	-10 2203 2176	-7 5650 5145 -6 218 -252	-13 2010 1941 -12 181* 78	-6 262 -194	-9 191+ 236 -8 1139 -1139	-9 178+ -74 -8 473 448	13 495 529 14 712 766	6 512 537 7 281 -281 8 2986 3074	-7 1037 1021 -6 2220 2260	+10 1947 -2159 -9 1032 -1172 -8 1934 -150	-2 485 -505 -1 559 579 0 1974 110	1 458 479 2 1946 2298 3 342 -309
-4 5322 -5710 -2 3430 -3696	-6 1943 1507 -6 1771 1757	-3 255+ -270	-10 187* -101 -9 3056 3013	-5 515 496 -4 393 -357 -3 1349 1337	-6 1059 1158 -5 2987 3126	-6 157• -27 -5 1299 -1318	1.3.5	9 2807 -2810 10 295 +256	-4 2707 2679	-7 436 -463 +6 993 1151 +5 1509 -1771	1 4341 4442 2 1236 -1229 3 2058 -2047	4 1323 -1478 5 2034 -208
2 5647 -6070 4 6665 -7519	0 675 838 2 500 457	-1 7722 7999 0 530 -595	-7 3100 3055 -5 195* 76	+1 1290 1230 0 178+ 95	-3 +45 360 -2 2148 -2186	-3 193* 47 -2 1484 1435	-13 266 168 -12 1980 2114	12 416 -435 13 177• 51	-1 777 755 0 2572 2570 1 1834 -252	-4 2348 -2695 -3 476 -471 -2 1364 -1510	4 739 -736 5 307 253 6 334 343	7 195+ 112 8 1792 2028 9 189+ -205
8 3635 -3938 10 5809 -6135	6 177 -93 8 657 -736	2 1296 1334 3 584 -633	-5 1550 1527 -4 330 297 -3 2390 2359	2 343 -339 3 174 27	0 3112 3136 1 2375 2398	0 1654 1572 1 392 -413	-10 1687 1801 -9 2464 -2671	6+3+L	2 3740 3821 3 1918 -2005	-1 1250 1405 0 1900 2033	7 3133 3268 8 593 -525 9 1801 1844	10 386 -358
14 1555 -1580	10 749 -818 12+3+L	4 975 -1120 5 4744 5141 6 674 -655	-1 2603 2513 0 716 515	5 170 -73 5 174 184	2 2283 -2255 3 221+ -26 4 2040 -2028	2 534 562 3 584 593 4 1217 1278	-7 208 -41 -6 1599 1732	-12 1035 -1033 -11 1482 -1552	5 303 224 6 1392 1499	2 1709 -1749 3 1623 1726	10 802 -868 11 442 -405	13 275 -192
-14 754 -714	-10 2348 -2332	8 995 1025 9 939 -959	2 403 -384	15+1+L	6 3499 3692 7 1123 1151	6 2222 2410 7 479 417	-4 2360 2531 -3 4142 -4457	-9 1204 -1212 -8 506 425	8 2810 3044 9 1464 -1623	5 2730 2898 6 1474 1539 7 1303 1381	9,4.2	+13 1129 1242 -12 1454 1727
-12 1988 -2002 -10 15+1 -16+9 -5 393 -36+	-5 1412 1457 -4 2442 -2390 -2 197+ 178	10 155+ -201 11 829 944 12 424 -307	5 395 433 5 325 262	-3 1938 -1937 -2 1116 -1136	9 418 405 10 795 -800	9 702 730 10 700 728	-1 389 353 0 250+ -1	-6 888 -982 -5 796 -796	12.3.L	8 464 -510 9 2073 2204	-9 181• -27 -8 489 520	-11 677 -8×4 -10 1389 1697
-6 480 -427 -4 668 -538 -2 573 566	2 1565 -1519	13 2800 2971 14 646 657 15 956 -939	5 490 -529 9 443 -499	-1 1330 1423 0 437 -332 1 184+ -27	12 2678 2755 13 334 281	12 1276 1403	2 2592 2708 3 2762 -2976	-3 1298 -1356 -2 1443 1558	-7 1155 1089	11 2781 2942 12 702 714	-6 980 1076 -5 480 -544 -5 1591 -1731	-8 2158 2609 -7 1717 2010 -6 2859 2915
0 332• 155 2 794 590 4 973 955	6 2496 2921 3 617 +699	4,1,6	10 313 221 11 537 -579 12 176* -155	2 299 289 3 1921 -1989	14 1747 1862 5,2,L	-11 2135 2166	5 217 -107 6 1174 -1269	0 744 758	-% 876 -999 -3 180* -118	4+4+L	-3 187+ 149 +2 292 -157	-5 356 363 2277 2620
6 260* 546 8 63* 731 10 190* 6*	-8 939 -909	-14 532 539 -13 251 -103 -12 342 -281	13 399 -340 9+1+L	0 5970 7547	-14 1993 2039 -15 1105 1122	-9 181• 29 -8 770 757	8 1828 2027 9 808 -867	3 1157 -1173 4 2378 2477	-1 1660 1634 0 180+ 106	-13 1314 1355 -12 187* -109	0 1983 2024 1 192* 142 2 1010 =1005	-2 3020 3++6 -1 2036 2277
14 433 381	-6 2866 -2842 -4 2845 -2689 -2 1782 -1671	-11 1381 -1455 -10 725 -703 -9 572 -574	-12 339 -215 -11 725 -591	2 3251 3235 3 55+ 588	-12 1336 1415 -11 183* -140 -10 104* 1059	-6 1440 1413 -5 2042 2004	11 327 -123 12 882 -869	6 2055 2168 7 1418 1487	2 558 -669	-10 575 -996 -9 550 495	3 1149 1127 4 645 -714 6 1954 2030	1 1675 1990 2 2037 2258
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2 3081 -3200	-2 499 396	2 2672 -2796	0 955 -972 1 2511 2544	14 1224 1319 15 1005 1099	1 618 567	6 2617 2848 7 180 218	-9 190 -61 -8 3756 4109 -7 2290 2394	-12 2694 2660 -11 1098 -1142 -10 2103 2196	-5 387 -342 -4 1010 995 -3 655 -645	2 651 -626 3 319 -130 4 392 90	-9 485 433 -8 885 871 -7 533 495	3,5,2
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14 2133 2253	15.3.6	8 1417 -1515 9 329 -375	5 639 -564 7 2392 2555	-14 836 893 -13 531 485 -12 265 19	7 586 -628 8 193• 257 9 187• -149	11,2,1	-3 921 -902 -2 4927 5267 -1 1955 2013	-6 2281 2363 -5 394 -424 -4 2438 2532	1 268 285 2 444 436 3 952 -999	8 493 413 9 507 453 10 498 -489	-3 185 -276 -2 715 798 -1 1222 -1250	-9 275 306 -8 2708 -3135 -7 187• -30
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-10 2139 2217 -8 3485 3507 -6 2406 2401	4 2139 2273	14 815 -940 5e1eb	12 295 +303	-8 205+ 280 -7 35+ 1+1 -5 220+ 273	13 806 -437 14 461 512	-7 754 791 -6 1660 1556 -5 321 -504	3 1228 -1222 4 2965 3150 5 716 732	0 632 583 1 1023 1079 2 1873 1960	14.3.6	5.4.6	3 913 -941 4 378 302 5 2524 -2603	-3 409 -470 -2 3405 -3655 -1 376 -259
-4 2449 2445 -2 3082 3142 0 361+ 1436	1 295• 235	-14 791 -790	-12 408 -308	-5 2776 -2980 -4 1414 -1523 -3 1839 -1921	6+2+L	-4 869 740 -3 501 519 -2 1787 1690	6 1933 2013 7 1441 1600 8 1974 -186	3 1616 -1653 # 2330 -2435 5 1549 1566	-5 175 -16 -4 710 -727 -3 178 -23	-13 1445 1484 -12 919 977 -11 714 734	6 1176 1251 7 342 22 8 180• 94	0 1145 -121* 1 475 -457 2 912 967
2 1230 1295 4 1115 1155 6 420 327	3 292+ -501 4 936 1039 5 947 -1018	-12 333 352 -11 890 -995 -10 462 470	-10 190+ -97 -9 1199 -1157 -8 550 503	-2 798 -758 -1 1400 -1371 0 826 591	-13 1125 -1156 -12 1747 1774 -11 181+ 103	-1 1039 1108 0 1508 1465 1 355 -323	9 688 -686 10 954 920 11 186+ +171	5 1105 -1111 7 1859 1954 8 920 937	-1 1196 1196 0 265 135	-9 1662 1701 -9 926 978	11.4.6	4 2240 -2448 5 538 -569
8 458 358 10 323 -321 12 299 -234	6 1227 1201 7 215+ -109 8 206+ -112	-9 2505 -2522 -9 733 -755 -7 2541 2604	-7 1909 -1970 -6 313 -230 -5 3629 -3533	1 4925 -4918 2 600 -555 3 2317 -2465	-10 995 -996 -9 2273 -2419 -6 1800 1868	2 313 -196 3 181 279 4 257 211	13 1182 1223 14 1091 -1171	10 1743 -1820	2 599 -617 3 956 -973	-6 2097 2199	-8 1031 995 -7 897 931	7 405 -214 8 1398 1438
1+ 179+ 207 6+0+L	9 465 -495 10 1395 1482 11 1355 -1490	-6 996 1929 -5 1989 -1059 -4 1409 1396	-4 997 -961 -3 2769 -2695 -2 548 520	4 758 -710 5 1710 -1777 6 701 776	-7 2651 -2769 -6 3870 4829 -5 310 147	5 873 1013 6 403 405 7 570 -659	3+3+1	8+3+L	0:4+L	-3 2196 2195	-5 345 -412	10 733 -Ru7 11 388 -409
-14 1813 1804 -12 2007 2022	12 768 780 13 690 -714 14 181+ 229	-3 6294 -6393 -2 578 -494 -1 563 576	-1 2543 -2510 0 471 -437 1 3252 -3212	7 3414 -3493 8 561 579 9 2395 -2470	-3 2265 -2355 -2 1691 1703	8 493 -538 9 308 -278 10 815 -890	-13 1704 1892 -12 1820 -66	-12 178• 28 -11 382 305	0 1924 2073 1 2431 2700	0 3186 3286	-2 452 442	41512
-10 1636 -1642 -8 2848 2806 -5 5266 5352	15 598 -521 1+1+L	0 1407 1351 1 1626 -1609 2 1833 1950	2 1252 -1273 3 2720 -2795 4 1834 -45	10 191 -279 11 538 -498 12 362 432	0 5486 5549 1 730 726	15.5.1	-10 549 -548 -9 1944 13	-9 945 931 -8 1784 1951 -7 2531 2557	3 924 1072 4 776 -526 5 1778 -2339	3 1591 1566	1 298 -184 2 977 -987	-12 179• -281 -11 323 -311 +10 1052 -1305
-2 2356 2281 0 8205 8529	-15 2449 -2598	5 1961 -2129	5 1612 -1458 5 563 -407 7 1602 -1757	14 726 865 15 1143 -1161	3 1101 -1203 4 426 377 5 2166 -2312	-8 499 469 -7 2106 -2943	-7 3609 3826 -6 634 -680 -5 1969 1533	-6 938 896 -5 1027 1034 -6 1898 58	6 1252 1455 7 1922 2131 8 983 930	6 2340 2472 7 191• -73 8 320 288	4 455 -430 5 664 725 6 1553 1629	-9 956 -1223 -8 565 -723 -7 2444 2754
4 2144 -97 6 5590 6225	-12 971 947 -11 3049 -3291	7 590 -659 8 1+28 1575	9 1219 -1349 10 275 -170	2+2+2	6 3819 4097 7 977 1071 8 761 776	-5 435 -357 -4 2000 -1984 -3 2013 -2021	-4 2144 48 -3 2344 -238 -2 4521 -4765	-3 195* 223 -2 236* 2488 -1 2336 2391	9 1633 1956 10 699 -753 11 1120 -1150	9 325 -245 10 1010 -1059 11 339 214	7 355 -391 8 534 -545	-6 1507 -1715 -5 606 733 -4 2420 -2643
10 1303 -1394 12 2328 2441	-9 5311 -5792 -8 708 -749 -7 433 418	10 393 -369 11 2591 -2779 12 1774 -55	11+1+1	-14 1495 1544 -13 593 -617 -12 1670 1839	9 487 522 10 1156 -1215 11 1233 -1322	-2 183* 204 -1 2473 -2421 0 2071 2011	-1 4165 4354 0 1123 -1097 1 3240 3320	0 1175 1210 1 1412 1303 2 1954 -245	12 490 543 13 764 6+5 14 657 823	12 1415 1520 13 1072 -1079	12,4,1 -7 2529 -2547	-3 1951 -2107 -2 2525 -2595 -1 2073 2173
7.0.6	-5 780 956 -5 2511 -27+3 -4 1219 1303	13 180+ 121 14 827 861	-11 1069 -1021 -10 455 436 -9 1223 -1183	-11 1349 1423 -10 2078 -2184 -9 884 -940	12 1840 1918 13 710 728	1 174• 118 2 1319 -1319 3 1205 -1210	2 1713 1721 3 475 -520 4 2799 -2885	3 734 -714 4 1296 1390 5 1201 1254	1.4.2	-12 182* 242	-6 182* 29 -5 602 -548 -4 998 -873	0 2626 -2776 1 1449 1593 2 3299 -3592
-14 196* 152 -12 1709 -1579 -10 1765 -1808	-3 7307 -8079 -2 1574 -1711 -1 2954 414	6+1+2 -14 174+ 101	-9 270 -516 -7 2249 2249 -6 952 952	-8 741 716 -7 908 -945 -6 2143 2239	7.2.2	6 116 - 549 5 1614 - 1745 6 1767 2005	5 1953 2026 6 965 -984 7 3030 3127	6 586 582 7 1039 1078 8 852 -901	-14 851 997 -13 594 659 -12 1198 1317	-11 180* -74 -10 390 -373 -9 3059 -3192	-3 2885 -2913 -2 182* 203 -1 2924 -2971	3 2398 -2603 4 2765 -3083 5 784 814
-9 1126 -1130 -6 3183 -3209 -4 3581 -3574	0 291+ -110 1 1031 1200 2 1537 1494	-13 1296 -1299 -12 510 -521 -11 2050 -2056	-5 719 -598 -4 1050 990 -3 2789 -2781	-5 2661 2547 -4 3917 -4150 -3 244+ 241	-12 955 -998 -11 1067 -1035 -10 1605 -1659	7 506 614 8 579 -651 9 176• 165	9 2111 2229 9 678 -676 10 1032 -1016	9 803 -785 10 248 177 11 178+ -91	-11 1110 -1254 -10 1155 -1249 -9 616 -685	-3 1055 1097 -7 3079 -3290 -6 1145 1211	0 3+3 331 1 190+ -33 2 1091 -103+	6 2549 -2771 7 1526 1649 8 2494 -2734
-2 2663 -2638 0 3598 -3512 2 3580 -3733	3 6105 -6201 4 1441 -1489 5 1245 1282	-10 781 -775 -3 594 -521 -8 345 102	-2 285 51 -1 1715 1795 0 1133 1153	-2 3395 -3422 -1 1333 -1335 0 2590 2566	-9 187• -207 -8 653 -713 -7 191• -29	13.5.6	11 307 321 12 753 +745 13 1515 1571	12 323 -346 9.3.L	-8 590 717 -7 658 -699 -6 2102 2445	-5 19604 -4 721 -773 -3 3004 -3245	3 1446 -1469 4 295 -233 5 2239 -2293	9 2014 -2184 10 1394 -1755 11 326 -441
4 2480 -2688 6 1473 -1625 8 1507 -1744	6 706 -555 7 3843 4035 8 875 572	-7 418 -276 -6 608 -572 -5 1159 -1125	1 411 -264 2 1375 1367 3 3567 -3978	1 3044 3000 2 5253 -5314 3 723 707	-6 1541 -1546 -5 2032 -2048 -4 2901 -2933	-8 916 -795 -7 876 875 -6 1749 -1709	14 1599 1667 4+3+L	-11 703 -603 -10 1407 -1485	-5 2601 -3108 -4 1489 -1705 -3 2998 -3305	-2 781 798 -1 4062 -4205 0 1369 1359	6 370 345 7 679 759	12 1517 -1712 5+5+1
10 1161 -1309 12 750 -838	9 1924 -1959 10 594 -584 11 884 888	-4 705 -679 -3 219• 102 -2 927 833	4 151+ 200 5 438 366 6 712 772	4 5676 -5980 5 1970 -2025 6 410 315	-3 1539 -1531 -2 2038 -2044 -1 766 -759	-5 412 -440 -4 2530 -2439 -3 182• 102	-14 868 862 -13 892 947	-9 365 -225 -8 3783 -3848 -7 1838 1902	-2 525 -460 -1 2414 -2651 0 2965 3263	1 320 294 2 208+ +345 3 1325 -1343	13+4+L -5 400 -399	-12 561 584 -11 913 -941
8.0.L -12 1293 1254	12 545 -487 13 3589 3795 14 726 744	-1 1422 1392 0 2254 -225 1 912 863	7 354 308 8 1023 1195 9 2862 -3263	7 1451 1539 8 2771 -2847 9 679 673	0 1761 -1689 1 3094 -3128 2 2763 -2744	-2 1555 -1469 -1 647 660 0 1690 -1691	-12 438 -448 -11 734 -806 -13 1089 -1117	-6 1359 -1349 -5 168+ -112 -4 1428 -1440	1 4071 -4572 2 928 -959 3 3952 -4474	4 325 -333 5 3353 -3442 6 1191 1234	-4 1648 -1680 -3 1834 99 -2 278 -240	-10 270 235 -9 179+ -120 -8 1289 -1324
-10 2520 -2451 -9 604 300 -6 2147 2149	15 367 342 2+1+L	2 2140 87 3 944 994 4 1038 1085	10 175+ -60 12+1+L	10 4801 -4914 11 1751 -1845 12 535 -552	3 1686 -1756 4 1796 -1939 5 980 -991	1 780 -854 2 2267 -2287 3 342 -298	-9 919 -1001 -8 195• -214 -7 977 1007	-3 919 -920 -2 4398 -4571 -1 2211 2250	5 2451 -2711 6 2045 2226	9 413 406	0 857 884 1 504 -639	-6 1237 1356 -5 783 -843
-2 2367 -2327 0 2592 2087	-15 1368 1493 -14 985 999	5 1250 1340 6 567 925 7 1353 1443	-10 375 -376 -9 606 569	13 282 58 14 903 -918 15 372 352	6 1071 -1123 7 2244 -2434 8 1048 -1096	6 793 -852	-5 810 -830 -4 2922 -3083	0 1/2/ =1653 1 614 695 2 185• =13	9 2526 -2842	10 cJB -750 11 1750 -1791 12 407 391	2 1/50 -1689 3 373 -438 4 857 -815 5 175- 10	-3 385 -378 -2 859 -848
2 4283 -4532 4 3843 -4208 6 408 512	-13 1295 1482 -12 435 494 -11 744 802	8 190+ 237 9 9+5 1741 10 1221 1294	-9 376 327 -7 666 556 -5 182239	3+2+6	9 1491 -1604 10 1217 -1350 11 350 -296	7 771 -913 14+2+L	-2 1358 -1416 -1 606 617	4 2977 -3155 5 1034 1060	11 1379 -1558 12 818 940	7.4.L	144445	0 1571 1644 1 2034 169 2 2918 2005
B 2570 -2658 10 3811 -4227 12 1814 279	-10 1010 1045 -9 1855 2022 -8 1441 1598	11 575 545 12 852 878 13 793 870	-5 190* -86 -4 470 -575 -3 1419 1382	-14 575 -344 -13 371 -407 -12 1221 -1229	12 142* -234	-6 1026 1057 -5 2275 2276	1 352 -260 2 4608 -4681	7 1125 1142 8 1085 1168	2.4.2	-11 1175 -1195	-2 495 351 -1 1193 1103	3 1974 -52
	-7 2102 2319 -6 1125 1150	14 295 232	-2 396 377 -1 2221 2195	-11 1896 -1987 -10 1752 -1827	8+2+1	-4 1441 -1462 -3 810 759	3 2344 -2560 4 1996 -2058	10 1105 -1209	-13 888 -956	-9 552 556	1 3213 3288	5 -11 373

Table 2 (cont.)

5+5+6	8+5+L	5 1072 1112	1+6+L	-4 2400 -2814	6 2644 2745	-1 613 591	3 2725 -2900	-7 1100 -1217	6.7.1	0 845 -813	3.8.1	♦ 1191 -1359
6 721 732 7 691 701	-10 317 222 -9 1386 -1424	7 1123 1181 8 994 -1033	-11 178* 16 -10 1144 -1238	-2 1403 -1576 -1 1920 -83	7 543 557 8 178• 193 9 263 181	0 190+ -140 1 2635 2669 2 365 341	4 357 -346 5 183• 101 6 180• 231	-6 179: -177 -5 175: -1957 -4 387 -290	-8 641 -614 -7 1622 1746	1 1253 -1250 2 722 -728 3 648 -632	-7 584 -590 -6 1270 1468	5 761 -841
9 497 338 10 181• -214 11 181• 112	-7 1630 1732 -6 1018 1139 -5 324 -275	11.5.L	-8 817 861 -7 1247 -1482 -6 2893 3202	0 2008 2215 1 1209 1366 2 2012 -2367 3 87* 1020	10 1059 -1096 6+6+L	3 1493 1460 4 934 889 5 428 403 6 582 509	7 1448 1625 8 1577 1714 9 1461 -1612	-3 1242 -1378 -2 1184 -1268 -1 1853 -1968 0 568 -498	-6 779 858 -5 1920 -199 -4 1052 1099 -3 2394 -2599	4 1455 -1532 13+7+L	-5 16+3 1778 -4 1321 -1333 -3 183+ -107	-4 177• 168 -3 1945 -1786
12 399 -354 6+5+L	-4 687 684 -3 1941 -2059 -2 1198 1271	-6 1998 2047 -5 954 -970 -9 2143 2215	-5 990 -1135 -4 995 -1169 -3 1838 -2210	4 2110 -2527 5 796 811 6 1672 1775	-10 183* -225 -9 2003 -2161	7 1903 1919 8 812 812	1.7.6	1 1915 -2028 2 183* -95	-2 538 -524 -1 831 797	-2 1426 -1553 -1 2753 2422	-1 1072 -1074 0 1067 1175	-1 1441 -1528 0 2680 2858
-11 810 -753 -10 817 -885	-1 1946 2008 0 995 985 1 821 844	-3 259 -214 -2 688 637 -1 885 389	-2 323 -302 -1 2618 -3072	7 1798 1926 8 669 -712	-7 1706 -1856 -6 1221 -1330	9+6+L	-10 577 630 -9 1712 1893	4 1052 -1088 5 1554 -1673	1 1844 -54 2 1935 2073	1 1751 1920 2 350 214	2 1133 -1174 3 605 665	2 412 363 3 471 -533
-9 1512 -1531 -9 307 -294 -7 1602 1668	2 546 484 3 1912 -1917	0 2489 2524 1 433 -384	1 2019 -2348 2 611 -729	10 2052 -2173 11 1062 1079	-4 673 -694 -3 2158 -2330	-6 1267 1336 -5 658 658	-7 1253 1406 -5 1150 1221	5 642 -645 7 1300 -1379 8 276 149	3 2876 -3045 4 182• 171 5 270 -286	C.S.L	4 1451 -1576 5 937 -1039 6 933 1085	8.8.2
-6 157• 2+1 -5 368 -331	5 1449 1470 6 333 113	3 183 -30 4 829 751	4 1535 -1822 5 2832 -3215	4+6+L	-2 /91 -791 -1 2501 -2643 0 1492 -1497	-4 2081 -2227 -3 184* 67 -2 692 -752	-5 1208 1277 -4 1058 1121 -3 1739 1686	9 475 -507 4.7.L	6 849 971 7 490 521 8 1913 2042	0 2102 -2255 1 225* 151 2 1821 -1994	7 1392 1552 4+8+L	0 642 690 0.9.L
-3 2710 -2919 -2 489 503	8 348 -358 9 1389 -1358	6 1921 196% 7 300 251	7 2026 -2228	-10 701 751 -9 476 537	1 355 -370 2 1302 -1333 3 1399 -1443	-1 594 594 0 1384 1436 1 1308 1384	-2 268 191 -1 968 1020 0 768 848	-9 530 -528 -8 1819 -2019	7.7.L	3 288 97 4 1671 -1923 5 457 -473	-6 695 759 -5 762 886	1 387 453
0 1092 1170 1 336 308	9+5+L	12.5.L	9 1498 -1637 10 2018 -2136 11 1847 -1973	-8 1195 1368 -7 853 891 -6 733 788	4 626 -693 5 2042 -2120 6 1190 -1223	2 2183 -2305 3 712 693 4 1841 -1876	1 615 660 2 1216 1288 3 849 924	-7 2484 2618 -6 182220 -5 1176 1266	-7 726 759 -5 1251 1304 -5 409 304	6 1695 -1967 7 411 -497	-9 1020 1072 -3 565 566 -2 1119 1159	3 939 -1036 9 1312 -1450
3 3245 -3329 4 1726 1915	-9 345 402 -8 3203 -3373	-5 404 -423 -4 195+ -284 -3 1501 -1634	5+9+F	-5 2301 2500 -4 853 921 -3 491 432	7 182• -100 8 733 -698 9 268 -306	5 791 775 6 1143 1157 7 1548 1581	4 284 189 5 182* -216 6 334 423	-4 642 -729 -3 1060 -1076 -2 2550 -2751	-4 815 826 -3 1146 1179 -2 184+ 189	1.5.L	-1 701 776 0 552 543 1 949 1072	1.9.L
6 1732 1753 7 1157 1100	-7 193* 148 -6 1287 -13*2 -5 854 -785	-2 181• 186 -1 125• 12•0 0 570 555	-11 402 292 -10 457 -442 -9 1051 -1113	-2 1199 1298 -1 267 -267 0 292 291	10 398 -402 7.6.L	10+6+6	7 390 -313 8 1030 1195 9 177* -156	-1 2470 2566 0 1353 -1444 1 1752 1932	-1 615 580 0 741 695 1 291 84	-5 1875 2092 -5 952 1003 -4 584 -574	2 291 183 3 652 738 4 348 243	-2 734 725 -1 1015 1170 0 706 837
9 2080 -2234	-3 347 -291 -2 3677 -3826	2 192 • 76 3 2103 -2175	-3 179• 125 -7 615 -703 -6 477 -577	1 1639 1808 2 751 845 3 590 624	-9 1083'-1151 -9 1144 1244	-6 179 123 -5 1593 1711 -4 444 495	10 474 432 2+7+L	2 363 -347 3 1537 -1670 4 2233 -2457	2 613 605 3 396 394 4 384 -322	-3 1069 -1179 -2 269 -133 -1 1975 -2201	5 501 573 6 482 -567	1 902 850 2 630 764 3 292 219
7+5+6	0 1664 -1645 1 748 -666	5 678 690	-4 197* 87	5 1055 -1104 6 1850 -143	-5 509 -568	-2 1031 1044 -1 412 -356	-10 1160 1265 -9 2149 -2406	5 1235 1302 6 1669 -1829 7 1562 1727	5 185* -207 6 185* 16 7 502 -500	0 2014 2142 1 701 691 2 590 -613	5+8+1 -6 174* 76	2+9+L
-11 182 -245 -10 1956 1956 -9 82 817	3 857 -796 4 2628 -2634	-2 1420 -1512	-1 909 -1092	8 191+ +86 9 52+ 569	-3 1533 -1657 -2 569 515	0 188* 194 1 944 943 2 185* 275	-8 180* 211 -7 1009 1047 -6 1862 2082	8 177• -142 9 1457 -1601	8.7.1	3 545 -587 4 974 -1061 5 2734 -2569	-5 1800 1977 -6 2015 -2216 -3 182* -266	-3 1295 -1495 -2 1673 -1812 -1 370 267
-8 181• 68 -7 752 818	6 1173 -1167 7 564 -514 8 747 745	0 152• 167 1 328 219	2 767 935 3 347 318	11 821 -835	0 3312 3523 1 1041 -1124	3 562 -495 4 535 507 5 1415 -1350	-2 5241 -5250 -7 5241 -5250	5.7.L -9 277 201	-6 1007 1129 -5 1080 -1117 -4 644 633	6 1193 1295 7 385 259	-2 1084 -1214 -1 955 -982 0 1047 1078	0 178+ 21 1 179+ 201 2 1455 1639
-5 189+ +95 -4 2025 2132 -3 664 700	9 476 -478	0.6.L	5 1152 -1266 6 791 484 7 522 527	-10 2288 -2674	3 1578 -1667 4 624 -646	6 151+ -53 11+6+L	-2 296 -168 -1 1207 1250 0 1437 1567	-9 765 -793 -7 365 -337 -6 504 413	-3 2491 -2650 -2 972 -1049 -1 773 730	2.8.L -7 278 -343	1 1578 1693 2 1179 -1245 3 182• 67	3 1039 -1150 3.9.L
-2 1130 -1192 -1 970 930 0 741 805	-8 180+ 93 -7 1992 2075	1 1253 1328 2 1155 -1353 3 398 435	9 1455 1614 9 538 549 10 961 973	-8 576 -557 -7 1264 1487 -6 1131 1242	6 2458 2550 7 1015 -1022 8 321 -221	-4 2193 -2337 -3 445 -437 -2 592 -599	1 1393 1469 2 2193 2390 3 1894 -2047	-5 182 -206 -4 330 313 -3 849 943	0 552 606 1 381 359 2 919 857	-5 178* -45 -5 403 -400 -4 378 435	* 893 -925 5 1296 -1410 6 1455 1606	-2 179• 73 -1 1445 -1626
1 332 267 2 1546 1564 3 1930 299	-6 195° -157 -5 274 200 -4 1010 -1089	4 1000 -1159 5 944 -1021 6 1315 -1433	11 1053 -1092 3.5.L	-5 1814 2005 -4 2518 -2757 -3 1117 1201	9 855 -920 9+6+L	-1 183* -99 0 1589 15°6 1 379 333	5 998 1032 6 182• 25 7 2019 2153	-1 722 711 0 48b 541	4 1043 -1102 5 926 914 6 409 -377	-2 896 931 -1 393 -516	6+8+L	1 1677 -1892 2 383 -404
• 1834 -1918 5 340 261 6 953 -937	-3 1225 -1269 -2 568 -566 -1 1845 1913	7 797 892 8 544 -623 9 802 842	-11 496 -545 -10 1723 -1859	-2 933 -1057 -1 1114 1233 0 2318 2537	-8 1840 32 -7 453 402	2 1369 -1313 3 314 -337 4 792 -761	8 1333 1504 9 1058 -1100 10 300 -252	2 852 880 3 1542 1755 4 190+ -103	9.7.1	1 341 -309 2 1542 1721 3 182+ -207	-4 1280 -1446 -3 1007 -1048 +2 1008 -1111	4.9.L
7 374 191 9 876 944 9 181• -65	0 666 -690 1 871 948 2 1171 -1253	10 407 -435 11 595 -694	-9 1192 -1332 -9 178* 51 -7 70* -792	1 1545 1734 2 1135 -1200 3 766 843	-6 653 -740 -5 1962 2011 -4 184+ -259	0.7.1	3+7+6	5 1203 1278 6 184• 216 7 1130 1236	-5 977 -1002 -4 1170 -1210 -3 368 -292	4 1479 1579 5 404 -393 6 1408 1629	-1 651 -650 0 1526 -1662	5 1.40 110
10 1378 -1472	3 1710 -1744 4 1040 -1041		-6 1733 1998 -5 198* 194	4 1273 -1428 5 187• 76	-3 467 480 -2 657 590	1 779 851 2 1414 1493	-9 422 -386 -8 934 -968	8 1000 1035	-2 1788 -1777 -1 913 -922	7 396 -217	2 1320 -1356 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 Rvalue 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, ill-y, 1-z,

(a) Boron-oxygen

Dist	ances	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)	$125 \cdot 17(2 \cdot 14)$			
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)

			-8)
$Bi(1) - O(4^{i})$	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 <sup>ii</sup> )	2.199 (14)
$Bi(2) - O(2^{v})$	2.306 (14)	Bi(4) - O(2)	2.249(15)
Bi(2)-O(9 <sup>ii</sup> )	2.334(15)	$Bi(4) - O(1^{i_v})$	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 clearcut maximum coordination distance about 2.67 Å. The Bi(3) atom could be considered to be either fivecoordinated 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  $120.00^{\circ}$  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 Cs<sub>2</sub>UO<sub>2</sub>F<sub>4</sub>.H<sub>2</sub>O

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

 $Cs_2UO_2F_4$ .  $H_2O$  crystallizes in the monoclinic system, space group  $P2_1/c$ : a=8.06, b=12.18, c=9.29 Å,  $\beta=109^{\circ}12'$ . The structure is composed of Cs<sup>+</sup> ions, of water molecules and of dimers with the formula  $U_2O_4F_8^{4-}$ . The dimer is formed by two  $UO_2F_3^{3-}$  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