SHORT STRUCTURAL PAPERS

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An Accurate Refinement of the β-Rhombohedral Boron Structure

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Abstract. β-Rhombohedral boron, $R\bar{3}m$, hexagonal, $a = 10{\cdot}9251$ (2), $c = 23{\cdot}8143$ (8) Å, $V = 2461{\cdot}6$ Å^3. (Rhombohedral unit cell: $a = 10{\cdot}139$ Å, $\alpha = 65{\cdot}20°$, $V = 820{\cdot}5$ Å^3.) Conventional $R = 0{\cdot}053$. The hexagonal unit cell contains 314·7 B atoms.

Introduction. Crystalline boron (from H. C. Starck, Goslar; claimed purity 99·8%) was melted under purified argon in an arc furnace. The single crystal used in this investigation was taken from the rapidly solidified melt. It was known that the melt contained Hf and Fe as the major metal impurities. Consequently the crystal was analysed for these elements with an electron-probe microanalyser (Cameca MS 46). The concentrations were, however, below the detection limit of the instrument (0·05 wt% for these metals). This corresponds to a maximum of 0·01 Hf and 0·03 Fe atoms per unit cell.

Cell parameters for the single crystal were calculated from a least-squares fit of the 2θ values of 22 different reflexions. The 2θ values were measured with an accurate X-ray diffraction technique described by Andersson & Callmer (1974). The cell dimensions obtained are in good agreement with those measured by Andersson & Lundström (1970) [$a = 10{\cdot}9253$ (5), $c = 23{\cdot}8103$ (16) Å] with the Guinier–Hägg technique.

Intensities were recorded with a computer-controlled Stoe–Philips four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), and an ω–2θ scan technique. The background was measured on each side of the scanning interval of 1·60°. Instrumental stability and crystal setting were checked with three standard reflexions remeasured every 50 reflexions. The intensity variations of the standard reflexions were entirely within the limits of counting statistics. Crystal quality and symmetry were checked with Weissenberg photographs. The crystal shape was triangular pyramidal (shortest edge 0·05 mm, longest edge 0·11 mm). The linear absorption coefficient for Mo $K\alpha$ was calculated to be 0·9 cm^{-1}. Corrections for absorption were thus considered unnecessary. All reflexions with h, k and $l \geq 0$ satisfying the condition $-h + k + l = 3n$ (hexagonal indexing) were measured up to $2\theta = 60°$. Altogether 1001 reflexions were measured. This set included some equivalent reflexions which were averaged after correction for Lorentz and polarization effects. Two reflexions were excluded because of experimental errors. These procedures left 920 independent structure factors. 719 of these had $\bar{F}_o^2 > 2\sigma(F_o^2)$. Initial atomic coordinates were taken from Hoard, Sullenger, Kennard & Hughes (1970). The coordinates were refined with an overall scale factor and individual isotropic temperature factors by the full-matrix least-squares program *UPALS*. Calculations were performed on IBM 370/155 and IBM 1800 computers with programs described by Lundgren (1975). Furthermore, occupation parameters for two atoms, B(13) and B(16), were refined giving a total of 52 refined parameters. The atomic scattering factors for B of Hanson, Herman, Lea & Skillman (1964) were used. The function minimized was $\chi^2 = \Sigma\, w(|F_o^2| - |F_c^2|)^2$. Weights were used according to $w = 1/[\sigma^2(F_o^2) + (cF_o^2)^2]$ with $\sigma(F_o^2)$ obtained from counting statistics. Values for c between 0·02 and 0·07 were tested; a value of 0·06 was used in the final refinement as giving the most even distribution of mean χ^2 values for different F^2 and $\sin\theta$ intervals. No extinction correction was applied. The final agreement indices for the 719 reflexions with $F_o^2 > 2\sigma(F_o^2)$ were: $R(F) = 0{\cdot}053$, $R(F^2) = 0{\cdot}077$, $R_w(F^2) = 0{\cdot}131$, and for all 920 reflexions: $R(F) = 0{\cdot}072$, $R(F^2) = 0{\cdot}082$, $R_w(F^2) = 0{\cdot}138$, where $R(F) = \Sigma\,(|F_o| - |F_c|)/\Sigma\,|F_o|$, and $R_w(F^2) = [\Sigma\, w(|F_o|^2 - |F_c|^2)^2/\Sigma\, w|F_o|^4]^{1/2}$. $R(F^2)$ is defined in a similar manner as $R(F)$, but F^2 replaces F in the formula. The final shifts were all smaller than 1% of the standard deviations. The atomic parameters based on the refinement with the 719 reflexions are given in Table 1.* In Table 2 interatomic distances are given. A refinement with anisotropic temperature factors for all 16

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32449 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic coordinates, isotropic thermal and occupation parameters with standard deviations in parentheses*

	Position	x	y	z	B (Å^2)	Partial occupancy (%)
B(1)	36(*i*)	0·17302 (21)	0·17400 (22)	0·17661 (8)	0·488 (32)	
B(2)	36(*i*)	0·31887 (21)	0·29536 (21)	0·12935 (8)	0·406 (32)	
B(3)	36(*i*)	0·26165 (21)	0·21766 (21)	0·41974 (8)	0·450 (32)	
B(4)	36(*i*)	0·23496 (21)	0·25151 (21)	0·34689 (8)	0·420 (31)	
B(5)	18(*h*)	0·05436 (16)	0·10872 (16)	0·94389 (11)	0·392 (42)	
B(6)	18(*h*)	0·08640 (15)	0·17280 (15)	0·01309 (12)	0·397 (42)	
B(7)	18(*h*)	0·10981 (15)	0·21961 (15)	0·88617 (12)	0·390 (42)	
B(8)	18(*h*)	0·17017 (16)	0·34034 (16)	0·02778 (12)	0·445 (42)	
B(9)	18(*h*)	0·12873 (16)	0·25746 (16)	0·76625 (11)	0·397 (42)	
B(10)	18(*h*)	0·10211 (15)	0·20421 (15)	0·69851 (12)	0·376 (41)	
B(11)	18(*h*)	0·05652 (15)	0·11303 (15)	0·32659 (11)	0·395 (43)	
B(12)	18(*h*)	0·08962 (16)	0·17924 (16)	0·39902 (12)	0·419 (43)	
B(13)	18(*h*)	0·05784 (24)	0·11568 (24)	0·55385 (18)	0·83 (10)	73·4 (15)
B(14)	6(*c*)	0	0	0·38535 (21)	0·381 (70)	
B(15)	3(*b*)	0	0	$\frac{1}{2}$	1·02 (12)	
B(16)	18(*h*)	0·05574 (62)	0·11147 (62)	0·11727 (45)	0·33 (27)	24·8 (16)

atoms was carried out. However, the anisotropy was not significant and the correlations between the thermal and the two occupational parameters were strong. In addition, a significance test (Hamilton, 1965) was applied to the $R_w(F^2)$ values from two refinements. It indicated that the introduction of anisotropic temperature parameters gave an insignificant decrease of the R value. For these reasons thermal anisotropy was omitted in the final calculations. Atom B(15) had the most anisotropic character. In a final three-dimensional difference synthesis over the whole asymmetric unit the largest deviation from zero for the electron density corresponded to 7% of a B maximum in an F_o synthesis. The peak values were obtained by integrating over 0·2 Å^3.

Table 2. *Interatomic distances up to* 2·38 Å *with standard deviations in parentheses*

B(1)–B(16)	1·797 (9)	B(7)–B(9)	1·826 (4)
B(7)	1·828 (3)	2B(1)	1·828 (3)
B(9)	1·845 (3)	B(8)–B(6)	1·623 (4)
B(2)	1·855 (3)	2B(4)	1·734 (3)
B(2)	1·858 (3)	2B(3)	1·795 (3)
B(1)	1·880 (4)	B(10)	1·831 (4)
B(1)	1·912 (4)	B(9)–B(10)	1·690 (4)
B(2)–B(3)	1·724 (3)	B(7)	1·826 (4)
B(7)	1·795 (3)	2B(1)	1·845 (3)
B(2)	1·798 (4)	2B(2)	1·854 (3)
B(9)	1·854 (3)	B(10)–B(9)	1·690 (4)
B(1)	1·855 (3)	2B(11)	1·780 (2)
B(1)	1·858 (3)	B(8)	1·831 (4)
B(3)–B(2)	1·724 (3)	2B(4)	1·843 (3)
B(12)	1·778 (2)	B(11)–B(14)	1·761 (5)
B(13)	1·790 (4)	2B(10)	1·780 (2)
B(8)	1·796 (3)	B(12)	1·835 (4)
B(4)	1·827 (3)	2B(4)	1·837 (3)
B(3)	1·897 (4)	2B(11)	1·852 (4)
B(4)–B(4)	1·678 (4)	B(12)–B(14)	1·727 (3)
B(8)	1·734 (3)	2B(3)	1·778 (2)
B(3)	1·827 (3)	B(11)	1·835 (4)
B(11)	1·837 (3)	2B(4)	1·853 (3)
B(10)	1·843 (3)	2B(13)	1·865 (4)
B(12)	1·853 (3)	B(13)–B(15)	1·686 (4)
B(5)–B(7)	1·729 (4)	2B(3)	1·790 (4)
B(6)	1·756 (4)	B(14)	1·815 (6)
2B(6)	1·760 (3)	2B(12)	1·865 (4)
2B(5)	1·782 (4)	2B(13)	1·896 (7)
2B(16)	1·791 (10)	B(14)–3B(12)	1·727 (3)
B(6)–B(8)	1·623 (4)	3B(11)	1·761 (5)
2B(6)	1·750 (3)	3B(13)	1·815 (6)
B(5)	1·756 (4)	B(15)–6B(13)	1·686 (4)
2B(5)	1·760 (3)	B(16)–2B(5)	1·791 (10)
B(7)–B(5)	1·729 (4)	2B(1)	1·797 (9)
2B(2)	1·795 (3)	2B(7)	1·801 (4)
2B(16)	1·801 (4)	2B(16)	1·827 (17)

Discussion. A number of single-crystal determinations of solid solutions of metals in β-boron have been reported, *e.g.* for Cr (Andersson & Lundström, 1970); Cu and Mn (Andersson & Callmer, 1974); Cu and Al (Mattes, Marosi & Neidhard, 1970); and Fe (Callmer & Lundström, 1976). In order to examine the extent to which the dissolved atoms change the boron network it is necessary to know the β-boron structure to a high degree of accuracy. Therefore it was felt desirable to complement the report by Hoard *et al.* (1970) with a further investigation. Hoard *et al.* presented a detailed discussion and description of the β-boron structure. Therefore, only a brief description will be given below.

The arrangement of B atoms can be described with B_{84} and B_{10} units. The B_{84} unit has one central icosahedron [consisting of six B(5) and six B(6) atoms], of which the atoms are bonded along quasi-fivefold axes to the vertex atoms of twelve half-icosahedra. In the hexagonal cell the B_{84} units are centred at (0,0,0), $(\frac{1}{3},\frac{2}{3},\frac{2}{3})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{3})$, with their threefold axes parallel to **c**. The six half-icosahedra [2 B(1), 2 B(2), B(7), B(9)] closest to the threefold axis are bonded to the same type of half-icosahedra in neighbouring B_{84} units, forming new complete icosahedra ('rhombohedral'). The other six half-icosahedra [2 B(3), 2 B(4), B(8), B(10)] form

new icosahedra ('equatorial') with six different B_{10} units. Each B_{10} unit [3 B(11), 3 B(12), 3 B(13), B(14)] consists of a condensate of three half-icosahedra. In this manner three B_{84} units are connected through each B_{10} unit, of which there are six in the cell. The linkage of B_{84} and B_{10} units results in a three-dimensional network where all atoms are part of an icosahedron.

Two further B atoms occur in the cell, namely B(15) and B(16). B(15) is octahedrally surrounded by atoms [B(13)] from two B_{10} units. B(16) occupies a hole situated in the B_{84} unit outside the central icosahedron and close to the threefold axis. There are seven more holes large enough to accommodate interstitial atoms (Andersson & Lundström, 1970) but none of these is occupied in pure β-boron. Because of the partial occupancy of B(13) and B(16), the cell content is reduced from 333 to 314·7 atoms. This is calculated from the refined occupation parameters of B(13) and B(16) which are different from those assumed by Hoard *et al.*

To make a comparison between the present refinement and the structure presented by Hoard *et al.* [$R(F) = 0{\cdot}098$], the non-rounded-off coordinates and standard deviations corresponding to those published have been used (Hughes, 1968). For all parameters and interatomic distances $\Delta = D/\sigma_D$ has been calculated. D is the modulus of the observed difference and $\sigma_D = (\sigma^2_{\text{Hughes}} + \sigma^2_{\text{this report}})^{1/2}$. The probability that an observed difference is significant is 99·0% and 99·9% when Δ is 2·6 and 3·3 respectively. Systematic errors may, however, invalidate the conclusions made on the basis of these calculations.

The average standard deviation of the atomic coordinates in this refinement is 75% of that given by Hoard. The greatest changes in coordinates (0·008 to 0·016 Å) are found for B(2)'s Y coordinate, B(3)'s X, B(4)'s Y and Z, B(5)'s Y, B(7)'s X and Y, and B(10)'s Z. All these have Δ between 2·7 and 5·5. The isotropic temperature factors, B, are in general lower in the present refinement and the average standard deviation is 80% of that of Hoard. For B(4) ad B(6) the decrease of the temperature factor is significant with $\Delta = 3{\cdot}3$ and 2·7 respectively.

Interatomic distances in Hoard's structure with $a = 10{\cdot}944 \pm 0{\cdot}005$ Å and $c = 23{\cdot}81 \pm 0{\cdot}01$ Å have been calculated and compared with the corresponding distances from the present work. The greatest differences are presented in Table 3.

In brief, one can say that the central icosahedron is slightly more regular and the intericosahedral distance B(4)—B(4) even shorter than that obtained by Hoard *et al.*

The histogram in Fig. 1 shows the great range in interatomic bonding distances occurring in the β-boron structure. The overall average distance is 1·803 (1·804) Å (the values in parentheses were calculated from Hoard *et al.*). The average distances within the central, rhombohedral and equatorial icosahedra are 1·762 (1·768), 1·840 (1·849) and 1·808 (1·805) Å respectively. Within the B_{10} unit the average distance is 1·827 (1·822) Å. From Fig. 1 it is clearly seen that the

Table 3. *Greatest differences in interatomic distances* (Å)

Δ is defined in the text.

	Hoard *et al.* (1970)	This work	Difference	Δ
B(2)—B(7)	1·814	1·795	0·019	4·5
B(2)—B(9)	1·868	1·854	0·014	2·8
B(4)—B(4)	1·705	1·678	0·027	4·2
B(5)—2B(5)	1·801	1·782	0·019	3·8
B(7)—B(9)	1·847	1·826	0·021	4·2

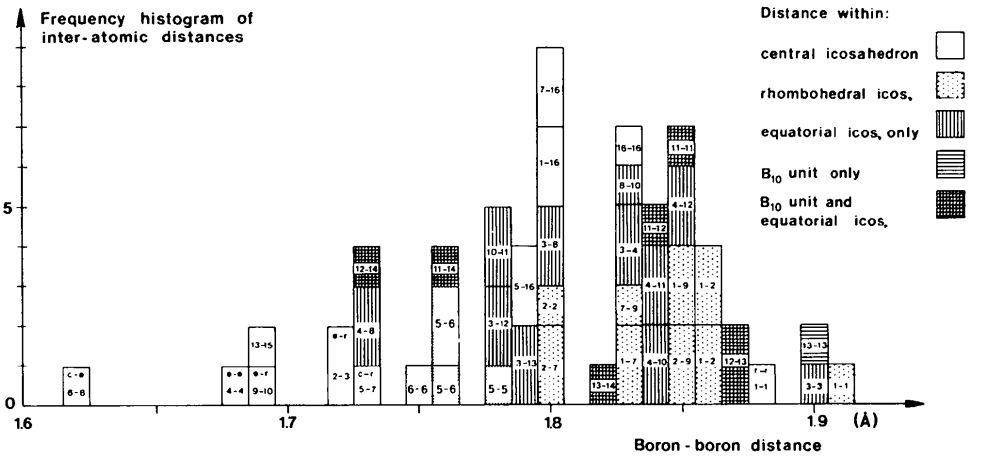

Fig. 1. A histogram of $\frac{1}{18}$ of all interatomic bonding B—B distances in a hexagonal unit cell of β-boron, showing the frequency of distances falling within 0·1 Å intervals; *c–e* is the distance between the central and equatorial icosahedra, *etc.*

only regular polyhedron is the central icosahedron, and that the least regular is the equatorial one. The figure also shows that the bonding distances between the polyhedra are shorter than those within the polyhedra. It should be noted that the coordination is sixfold for most atoms (Table 2) and that a higher coordination in all cases except one involves B(13) and B(16), which are only partially present.

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Potassium and Ammonium Decabromodibismuthate(III) Tetrahydrate

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Abstract. $K_4[Bi_2Br_{10}].4H_2O$: orthorhombic, *Pnma*, $a = 8{\cdot}794$ (1), $b = 22{\cdot}737$ (3), $c = 12{\cdot}860$ (2) Å; $D_o = 3{\cdot}70$ (1), $Z = 4$, $D_c = 3{\cdot}733$ g cm^{-3}. $(NH_4)_4[Bi_2Br_{10}].4H_2O$: orthorhombic, *Pnma*, $a = 8{\cdot}945$ (3), $b = 22{\cdot}887$ (9), $c = 13{\cdot}083$ (1) Å; $Z = 4$, $D_c = 3{\cdot}375$ g cm^{-3}. The title compounds are isomorphous. The structural analysis was carried out for the K compound; $R = 0{\cdot}079$ for 1836 reflexions $[I > 3{\cdot}5\sigma(I)]$. The structure contains binuclear decabromodibismuthate(III) anions with two $BiBr_6$ octahedra sharing an edge.

Introduction. Only a few structures of bromo- and iodobismuthates(III) are known: bis(piperidinium) pentabromobismuthate(III) (McPherson & Meyers, 1968), with chain-anions built of octahedra sharing *cis* vertices; 2-picolinium tetrabromo- and tetraiodobismuthate(III) (Robertson, McPherson & Meyers, 1967), with chain-anions built of octahedra sharing edges; and Cs enneaiododibismuthate(III) (Lindqvist, 1968), with anions built of two octahedra sharing a face. The present investigation is the first part of a systematic study of bromo- and iodobismuthates(III). A number of alkali bromo- and iodobismuthates(III) were synthesized (the methods of preparation will be published elsewhere) in order to study their structures and the conditions for linking the hexahalobismuthate(III) groups into such a variety of polynuclear species. Some of these compounds (*e.g.* the title compounds) were mentioned in the literature towards the end of the nineteenth century (Pascal, 1958).

Pale-yellow crystals were grown by slow evaporation from an aqueous solution obtained by dissolving $Bi(OH)_3$ and K_2CO_3 [or $(NH_4)_2CO_3$] in 1:1 molar ratio in a dilute HBr solution. A well developed crystal of $K_4[Bi_2Br_{10}].4H_2O$, selected for the intensity measurements, was characterized by the planes $\pm\{010\}$, $\pm\{101\}$ and $\pm\{101\}$; its dimensions along [100], [010] and [001] were 0·48, 0·16 and 0·34 mm respectively.

The intensity data were collected at 20 (1)°C with an Enraf–Nonius CAD-4 diffractometer. Experimental conditions were: Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å); ω–2θ scan; $\theta_{min} = 1{\cdot}5°$, $\theta_{max} = 75{\cdot}0°$; 2θ scan width (°): $0{\cdot}8 + 0{\cdot}2 \tan\theta$; aperture (mm): $2{\cdot}5 + 0{\cdot}9 \tan\theta$; maximum scan time 40 s; background: a quarter of the scan time at each of the scan limits. 2618 independent reflexions were recorded and, of these,