

Indium Polytelluride $\text{In}_2\text{Te}_5(\text{II})$

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$\text{In}_2\text{Te}_5(\text{II})$, $M_r = 867.64$, monoclinic, $C2/c$; $a = 16.66(1)$, $b = 4.36(1)$, $c = 41.34(1)$ Å, $\beta = 100.1(5)^\circ$, $D_c = 5.91$ g cm⁻³, $U = 2926.56$ Å³, $Z = 12$, $F(000) = 4296$. The structure was solved by Patterson syntheses with Mo $K\alpha$ X-ray data and refined by block-diagonal least squares to $R = 9.61\%$ for 2595 structure factors. The material is composed of distinctly separate planar sheets of atoms stacked perpendicular to c^* . These sheets, which are similar to those found in $\text{In}_2\text{Te}_4(\text{I})$, are about 7 Å thick and consist of chains of four-membered In–Te rings in which each In is tetrahedrally coordinated indicating sp^3 hybridization with an average In–Te length of 2.849(5) Å. The rings alternate with and are cross-linked by groups of three Te atoms which, on an ionic description, are $(\text{Te}_3)^{2-}$ polyanions. The average Te–Te bond in this anion is 2.854 Å with an included angle of 101.6(2)°. The polyanions are linked by bonds of intermediate strength to form continuous chains of Te atoms running across the sheets of atoms.

Introduction

A previous investigation of the In–Te system (Sutherland, Hogg & Walton, 1976)[†] reported the crystal structure of a phase In_2Te_5 prepared by heating an

intimate mixture of In and Te, in the correct proportion to produce In_2Te_5 , in a sealed evacuated pyrolysed tube to 550°C. This temperature was maintained for 24 h and the sample directionally frozen at 2 mm h⁻¹ to 400°C, at which point it was held before being allowed to cool to room temperature. The resultant samples contained regions of black shiny lamellar material which proved to be In_2Te_5 . In addition, further investi-

[†] In this paper the parameters for Te(3) and Te(4) were inadvertently interchanged in Table 1.



Fig. 1. $\text{In}_2\text{Te}_5(\text{II})$. A projection of the structure down b showing the method of bonding. The atoms are scaled to the respective ionic radii of In^{3+} (0.81 Å) and Te^{2-} (2.22 Å). Shaded and non-shaded atoms lie near $y = \frac{1}{2}$ and 0 respectively.

gation revealed the presence of small quantities of black shiny crystals which, though similar in appearance to those of In_2Te_5 , had different cell parameters. Structure analysis has shown that they also have the formula In_2Te_5 and that the two structures are related. We propose to call the previously reported phase $\text{In}_2\text{Te}_5(\text{I})$ and the subject of this paper $\text{In}_2\text{Te}_5(\text{II})$.

Table 1. Fractional coordinates ($\times 10^4$) with *e.s.d.*'s in parentheses

	X/a	Y/b	Z/c
In(1)	-63 (2)	593 (13)	557 (1)
In(2)	1355 (2)	5584 (13)	1119 (1)
In(3)	2965 (2)	1256 (13)	2202 (1)
Te(1)	367 (2)	588 (12)	1267 (1)
Te(2)	923 (2)	5565 (12)	406 (1)
Te(3)	3028 (2)	5100 (11)	1331 (1)
Te(4)	3145 (2)	913 (11)	807 (1)
Te(5)	3304 (2)	5107 (12)	289 (1)
Te(6)	1847 (2)	6213 (11)	2082 (1)
Te(7)	4425 (2)	636 (12)	1974 (1)
Te(8)	0 (0)	1544 (16)	2500 (0)

Table 3. Other interatomic distances (Å)

Columns 1 and 2 contain comparable bonds in $\text{In}_2\text{Te}_5(\text{II})$; column 3 lists corresponding bonds in $\text{In}_2\text{Te}_5(\text{I})$.

	(1)	(2)	(3)
Te(4)–Te(2)	4.290	Te(8 ₁)–Te(6 ₃)	4.296
Te(4)–Te(2 ₂)	4.441	Te(8 ₁)–Te(6 ₁₁)	4.440
Te(4)–Te(1 ₃)	4.359	Te(8 ₁)–Te(6 ₇)	4.296
Te(4)–Te(1 ₁₁)	4.498	Te(8 ₁)–Te(6 ₈)	4.440
Te(4)–In(2)	4.005	Te(8 ₁)–In(3 ₁₀)	3.970
Te(4)–In(2 ₂)	4.159	Te(8 ₁)–In(3 ₉)	4.106
Te(4)–In(1 ₃)	3.901	Te(8 ₁)–In(3 ₁)	4.106
Te(4)–In(1 ₁₁)	4.054	Te(8 ₁)–In(3 ₁)	3.970
Te(1)–Te(2)	4.403	Te(6)–Te(6 ₇)	4.335
Te(1)–Te(2 ₂)	4.413	Te(6)–Te(6 ₈)	4.335
Te(1)–Te(3 ₄)	3.957	Te(6)–Te(7 ₁₃)	3.989
Te(1)–Te(6)	4.531		
Te(1)–Te(6 ₂)	4.261		
Te(1)–Te(7 ₁₃)	4.177		
Te(1)–Te(7 ₄)	4.155		
Te(2)–Te(2 ₁₄)	4.166		
Te(2)–Te(5)	4.084		3.893
Te(2)–Te(5 ₆)	4.161		
Te(2)–Te(5 ₁₂)	3.843		
Te(3)–Te(6)	3.985		3.912
Te(3)–Te(7)	3.754	Te(5)–Te(5 ₆)	3.975
Te(3)–Te(7 ₁)	4.016	Te(5)–Te(5 ₁₂)	3.872
			3.963

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

Columns 1 and 2 contain comparable bonds in $\text{In}_2\text{Te}_5(\text{II})$; column 3 contains corresponding bonds in $\text{In}_2\text{Te}_5(\text{I})$. The subscript code is as follows: (1) $x, y+1, z$; (2) $x, y-1, z$; (3) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (4) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (5) $-x, -y, -z$; (6) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (7) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (8) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (9) $1-x, y, \frac{1}{2}-z$; (10) $1-x, y+1, \frac{1}{2}-z$; (11) $x+\frac{1}{2}, y-\frac{1}{2}, z$; (12) $\frac{1}{2}-x, 1\frac{1}{2}-y, -z$; (13) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (14) $-x, 1-y, -z$.

	(1)	(2)	(3)
In(1)–Te(1)	2.897 (5)	In(3)–Te(6 ₈)	2.921 (5)
In(1)–Te(2)	2.853 (6)	In(3)–Te(6)	2.838 (6)
In(1)–Te(2 ₂)	2.871 (6)	In(3)–Te(6 ₂)	2.866 (6)
In(1)–Te(5 ₄)	2.760 (4)	In(3)–Te(7)	2.771 (5)
Te(1)–In(1)–Te(2)	99.9 (2)	Te(6 ₈)–In(3)–Te(6)	97.6 (2)
Te(1)–In(1)–Te(2 ₂)	99.8 (2)	Te(6 ₈)–In(3)–Te(6 ₂)	97.0 (2)
Te(1)–In(1)–Te(5 ₄)	117.3 (2)	Te(6 ₈)–In(3)–Te(7)	113.5 (2)
Te(2)–In(1)–Te(2 ₂)	99.1 (2)	Te(6)–In(3)–Te(6 ₂)	99.6 (2)
Te(2)–In(1)–Te(5 ₄)	122.4 (2)	Te(7)–In(3)–Te(6)	127.1 (2)
Te(2 ₂)–In(1)–Te(5 ₄)	114.5 (2)	Te(7)–In(3)–Te(6 ₂)	116.7 (2)
In(2)–Te(2)	2.909 (5)	In(3 ₇)–Te(6)	2.921 (5)
In(2)–Te(1 ₁)	2.861 (6)	In(3 ₇)–Te(6 ₇)	2.838 (6)
In(2)–Te(1)	2.859 (6)	In(3 ₇)–Te(6 ₈)	2.866 (6)
In(2)–Te(3)	2.779 (5)	In(3 ₇)–Te(7)	2.771 (5)
Te(2)–In(2)–Te(1 ₁)	99.7 (2)	Te(6)–In(3 ₇)–Te(6 ₇)	97.6 (2)
Te(2)–In(2)–Te(1)	99.5 (2)	Te(6)–In(3 ₇)–Te(6 ₈)	97.0 (2)
Te(2)–In(2)–Te(3)	112.1 (2)	Te(6)–In(3 ₇)–Te(7)	113.5 (2)
Te(1 ₁)–In(2)–Te(1)	99.2 (2)	Te(6 ₇)–In(3 ₇)–Te(6 ₈)	99.6 (2)
Te(1 ₁)–In(2)–Te(3)	125.0 (2)	Te(6 ₇)–In(3 ₇)–Te(7)	127.1 (2)
Te(1)–In(2)–Te(3)	117.3 (2)	Te(6 ₈)–In(3 ₇)–Te(7)	116.7 (2)
Te(4)–Te(3)	2.864 (6)	Te(8 ₁)–Te(7 ₁)	2.845 (6)
Te(4)–Te(5)	2.862 (6)	Te(8 ₁)–Te(7 ₁₀)	2.845 (6)
Te(4)–Te(3 ₂)	3.360 (6)	Te(8 ₁)–Te(7)	3.397 (6)
Te(4)–Te(5 ₂)	3.354 (6)	Te(8 ₁)–Te(7 ₉)	3.397 (6)
Te(3)–Te(4)–Te(5)	100.8 (2)	Te(7 ₁)–Te(8 ₁)–Te(7 ₄)	102.4 (2)
Te(3)–Te(4)–Te(3 ₂)	88.5 (1)	Te(7 ₁)–Te(8 ₁)–Te(7)	88.1 (1)
Te(5)–Te(4)–Te(5 ₂)	88.6 (1)	Te(7 ₆)–Te(8 ₁)–Te(7 ₉)	88.1 (1)
Te(3 ₂)–Te(4)–Te(5 ₂)	82.1 (1)	Te(7)–Te(8 ₁)–Te(7 ₉)	81.5 (1)
Te(3)–Te(4)–Te(5 ₂)	170.5 (2)	Te(7 ₁)–Te(8 ₁)–Te(7 ₉)	169.5 (2)
Te(5)–Te(4)–Te(3 ₂)	170.7 (2)	Te(7 ₁₀)–Te(8 ₁)–Te(7)	169.5 (2)

The density could not be measured experimentally since only a very small quantity of the phase could be isolated. 2595 reflections, of which 967 were recorded as zero, were collected from Weissenberg photographs taken about \mathbf{b} with multiple-film packs and Mo $K\alpha$ radiation. Intensities were measured visually since the proximity of the reflections, due to the 42 Å spacing, and the use of Mo $K\alpha$ radiation precluded the use of microdensitometry. Data were corrected for Lorentz and polarization factors. No absorption correction was made since the crystal had a fairly regular cross-section with $\mu R \sim 0.5$.

The structure was solved from minimum functions based on Patterson syntheses. The systematic absences indicate space groups Cc or $C2/c$. Block-diagonal least-squares refinement was performed in both groups leading to very similar R factors and final atomic parameters which were the same to within an e.s.d., with the exception of those for Te(8). This atom occupies a special position ($x = 0, z = \frac{1}{4}$) in $C2/c$. On refinement in Cc it moved to within three e.s.d.'s of either side of this position depending on its initial coordinates. It was concluded that this phase has space group $C2/c$ whereas $\text{In}_2\text{Te}_5(\text{I})$ is Cc .

The final R in $C2/c$ was 0.096 where $R = \sum |F_o| - |F_c| / \sum |F_o|$. Scattering factors were from *International Tables for X-ray Crystallography* (1974). Table 1 gives the atomic parameters,† Table 2 the bond lengths and angles within the two unique sheets of atoms, and Table 3 other interatomic distances. Tables 2 and 3 also contain equivalent bonds and angles in $\text{In}_2\text{Te}_5(\text{I})$. The atom designation and system of bonding for $\text{In}_2\text{Te}_5(\text{II})$ are shown in Fig. 1.

Discussion

This material is composed, as in $\text{In}_2\text{Te}_5(\text{I})$, of continuous separate sheets of atoms, approximately 7 Å thick, lying in the xy plane. The sheets are formed by endless chains of four-membered In–Te rings In(1), Te(1), In(2), Te(2), which alternate with and are cross-linked by tightly bound Te(3)–Te(4)–Te(5) groups. $\text{In}_2\text{Te}_5(\text{II})$ consists of repeated groups of six such sheets stacked perpendicular to \mathbf{c}^* . The sheets in isolation contain alternating twofold and twofold-screw axes which appear as pseudo axes in the structure, with the exception of those contained in the layers lying along $z = \frac{1}{4}$ and $\frac{3}{4}$ which are genuine axes in space group $C2/c$. In $\text{In}_2\text{Te}_5(\text{I})$ only pseudo axes are present. The unique b axis in $\text{In}_2\text{Te}_5(\text{II})$ is the short 4.4 Å axis; the β angle is formed by symmetry operations involving translations of successive layers in directions parallel to the plane of

the original layer. However, in $\text{In}_2\text{Te}_5(\text{I})$, the 4.4 Å direction becomes the non-unique a axis and the β angle is formed by a shearing action on the layers in a direction perpendicular to the plane of the layers. This leads to a distortion of the layer structure.

As in $\text{In}_2\text{Te}_5(\text{I})$ the In atoms occur in environments which are typically trivalent. Each is surrounded by four Te atoms in approximately tetrahedral coordination, which indicates that the In atoms are sp^3 hybridized. Since the In sites are well separated, valence saturation requires the formation of the triatomic anions Te(3)–Te(4)–Te(5) and Te(7)–Te(8₁₁)–Te(7₉), which are arranged in chevron formations approximately in the yz plane. The two polyanions in $\text{In}_2\text{Te}_5(\text{II})$ have similar configurations; the average bond length in the Te(3)–Te(4)–Te(5) ion is 2.863 Å with an included angle of 100.8°, compared with the appropriate values for Te(7)–Te(8₁₁)–Te(7₉), 2.845 Å and 102.4°. For $\text{In}_2\text{Te}_5(\text{I})$ these values are 2.832 Å and 100.1°. Other compounds containing mutually bonded Te atoms show bond lengths very similar to the above whilst in elemental Te the average Te–Te bond is 2.86 Å with a bond angle of 102°. The closest distances of approach between the polyanions in a chevron occur between the centre atom of an anion and, for example, in sheets one and two, the two end members of the anion below it. In both chevrons in $\text{In}_2\text{Te}_5(\text{II})$ these distances are almost identical and average 3.377 Å compared with 3.366 Å for $\text{In}_2\text{Te}_5(\text{I})$ and 3.47 Å for the interchain distance in elemental Te. The In–Te distances in $\text{In}_2\text{Te}_5(\text{II})$ average 2.849 Å; the corresponding figure for $\text{In}_2\text{Te}_5(\text{I})$ is 2.832 Å, for In–Te it is 2.819 Å (Hogg & Sutherland, 1976) and for In_3Te_4 , 2.88 Å (Hogg & Sutherland, 1973).

Both faces of the sheet of atoms which occur in In_2Te_5 types (I) and (II) consist of a packed array of Te atoms. The layers themselves may be packed together in only four different ways given that the Te atoms of one layer must lie in the interstices between the Te atoms of the neighbouring layer.

In $\text{In}_2\text{Te}_5(\text{II})$ layer 1 ($z = \frac{1}{12}$) and layer 2 ($z = \frac{1}{4}$) are related by reflection of sheet 1 across the junction between them followed by a translation of sheet 2 in the negative x direction of approximately 6.6 Å. In this way Te(1₃) is transposed to Te(6). Sheet 2 and sheet 3 ($z = \frac{5}{12}$) are similarly related across the plane $z = \frac{1}{3}$. A second position for layer 2 exists which does not occur in $\text{In}_2\text{Te}_5(\text{II})$ but which does in $\text{In}_2\text{Te}_5(\text{I})$. This involves a further translation of the whole of this layer along x until Te(7) has the same x parameter as that previously held by Te(6). These two possible positions are symmetrically related producing an identical set of inter-layer contacts. A third method of packing occurs between sheet 3 and sheet 4 ($z = \frac{7}{12}$) in $\text{In}_2\text{Te}_5(\text{II})$, where the two layers are related by inversion centres. As a fourth possibility there should exist a second position for sheet 4 which could be brought about by a 4.4 Å translation of the sheet in the positive x direction. This

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32925 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

would lead to the end members of neighbouring polyanions in sheets 3 and 4 being at the same height in y , a situation which is not observed in either form of In_2Te_5 .

Bonding between the layers concerns only Te atoms, the contacts between the end members of polyanions in adjacent layers being shorter than other Te—Te contacts. Each end member is interleaved with the end members of two polyanions in the neighbouring layer but does not lie equidistant from them. In $\text{In}_2\text{Te}_5(\text{I})$ and in the present compound between layers 1 and 2 and 2 and 3 these two contacts on average differ by 0.26 Å. At approximately 3.7 Å, the shorter of the two is about 0.5 Å less than the usual Te—Te contact between the layers indicating some form of intermediate bonding similar to that which occurs in polyiodide chains. This bonding occurs at each end of the polyanion to form a linked continuous chain of Te atoms extending throughout the structure (Fig. 2). This would suggest the presence within the chain of a three-membered

resonance-hybrid form of the Te polyanion which contains the bond between polyanions in adjacent sheets. This would involve the polyanion $\text{Te}(5)$, (4), (3) alternating with $\text{Te}(4)$, (3), (7) and likewise throughout the chain. The included angle of the resonance form $\text{Te}(4)$, (3), (7) is 95.2° , close to the 100.7° value for $\text{Te}(5)$, (4), (3). A slightly different situation exists between layers 3 and 4 and layers 1 and 6 in $\text{In}_2\text{Te}_5(\text{II})$. Here the end members of polyanions in adjacent layers are almost symmetrically interleaved, the appropriate bond distances being 3.87 for $\text{Te}(5)$ — $\text{Te}(5_6)$ and 3.97 Å for $\text{Te}(5)$ — $\text{Te}(5_{13})$. A resonance-hybrid polyanion form $[\text{Te}(4)$, (5), (5₆)] accounting for the shorter of these bonds would have an included angle of 131.4° .

In $\text{In}_2\text{Te}_5(\text{I})$ all the polyanion chevrons have their apices pointing in the negative x direction and bond together to form a Te chain which rises stepwise in x as z increases (Fig. 2). In $\text{In}_2\text{Te}_5(\text{II})$ the chevron apices can point along either $\pm y$ and bond to form a kinked

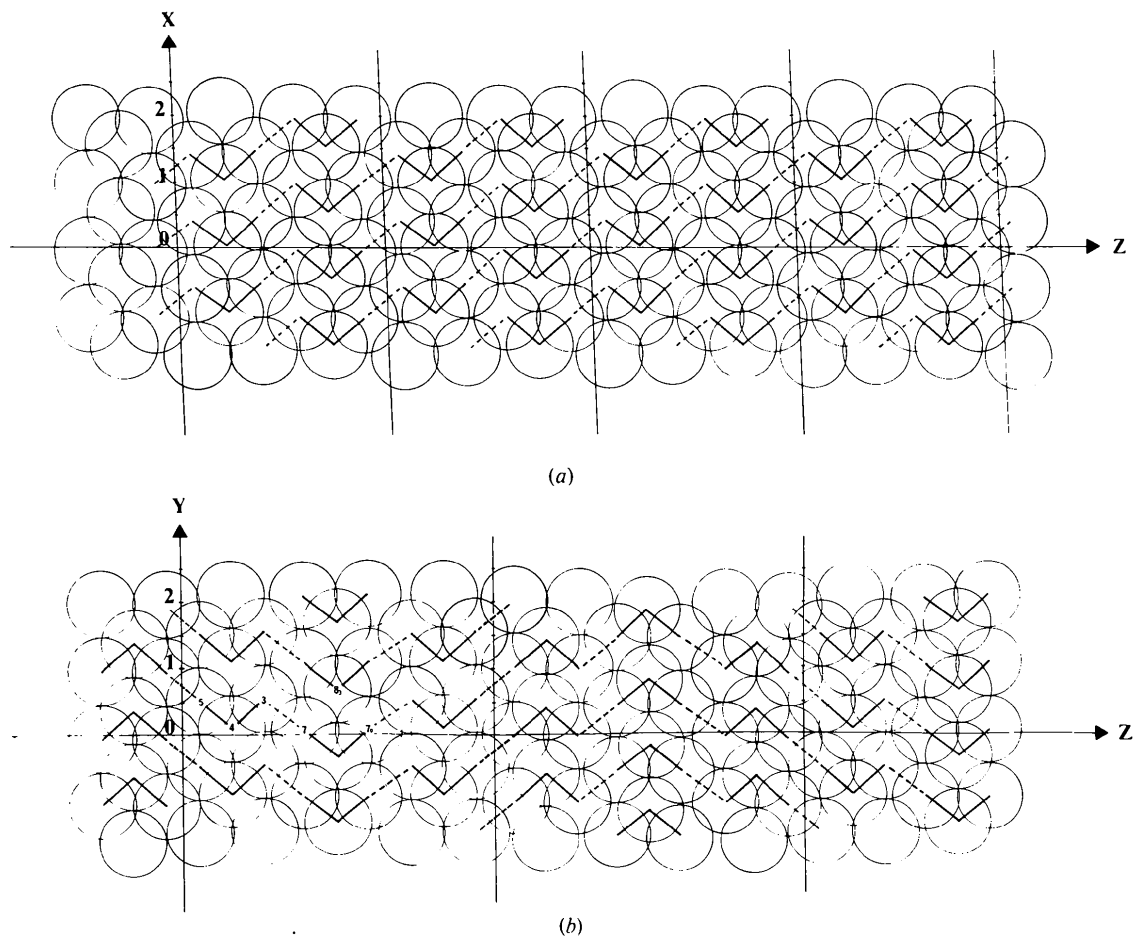


Fig. 2. Schematic sections of the structures of (a) $\text{In}_2\text{Te}_5(\text{I})$ and (b) $\text{In}_2\text{Te}_5(\text{II})$, showing the bonding within the Te polyanion chains.

chain lying in approximately the $(\bar{1}01)$ plane and oscillating about the (010) plane.

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The Crystal Structure of $\text{NaB}_5\text{O}_6(\text{OH})_4$

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The synthetic compound $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ is monoclinic, space group $P2_1/c$, with $a = 8.701(4)$, $b = 8.067(4)$, $c = 12.977(4)$ Å and $\beta = 106.77(2)^\circ$. The crystal structure was determined by means of direct methods from single-crystal X-ray diffractometer data. Refinement was carried out by least-squares calculations, yielding a final R value of 0.051. The basic structural unit is the isolated polyanion $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ formed by one tetrahedron and four triangles in the shape of a double hexagonal ring. The Na atom has six neighbours (three OH and three O) the four closest being arranged in a roughly tetrahedral configuration. The Na polyhedra connect B–O polyanions to form a three-dimensional network. Further connexions are provided by the hydrogen-bonding system. The structural formula is $\text{NaB}_5\text{O}_6(\text{OH})_4$.

Introduction

The crystal study of the title compound is part of a systematic investigation of hydrated sodium borates (Corazza, Menchetti & Sabelli, 1974, 1975*a,b*).

One of the several phases obtained in the $\text{NaOH}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system under hydrothermal conditions at 150°C (Corazza, Menchetti, Sabelli & Stoppioni, 1977) has an X-ray powder pattern identical with the one that Nies & Hulbert (1967) assigned to sodium pentaborate dihydrate; that is the phase with $\text{Na}_2\text{O}:\text{B}_2\text{O}_3:\text{H}_2\text{O}$ molar proportions 1:5:4. In turn these authors pointed out that the 1:5:4 pattern is similar to that of the compound considered as 1:5:2 by Bouaziz (1962). However, Nies & Hulbert gave a different X-ray pattern to the compound with 1:5:2 oxide ratio and therefore there is a high probability that Bouaziz's pattern belongs to the 1:5:4 phase.

The present study confirms the composition found by Nies & Hulbert and allows the 1:5:4 compound to be classified among the soroborates with one tetrahedron and four triangles as the repeat unit. The structural formula is $\text{NaB}_5\text{O}_6(\text{OH})_4$.

Experimental

Crystals of the compound were prepared at $150 \pm 5^\circ\text{C}$, under hydrothermal conditions, by means of a pressure vessel supplied with temperature regulation and pressure read-out. Frequently the 1:5:4 phase was associated with H_3BO_3 and/or $\beta\text{-HBO}_2$. The crystals were rather large (up to 2 mm), but without well defined crystal forms, and were opaque. The unit-cell dimensions were determined from the scattering angles of 25 high-angle reflexions, measured with Mo $K\alpha$ radiation on a Philips single-crystal diffractometer. Systematic absences $l = 2n + 1$ in $h0l$ and $k = 2n + 1$ in $0k0$ uniquely indicate the space group $P2_1/c$. Crystal data are reported in Table 1.

Table 1. *Crystal data*

$\text{Na}[\text{B}_5\text{O}_6(\text{OH})_4]$	$V = 872.1 \text{ \AA}^3$
Space group: $P2_1/c$	$Z = 4$
$a = 8.701(4) \text{ \AA}$	$D_x = 2.178 \text{ g cm}^{-3}$
$b = 8.067(4)$	FW 241.1
$c = 12.977(4)$	$\mu(\text{Mo } K\alpha) = 2.79 \text{ cm}^{-1}$
$\beta = 106.77(2)^\circ$	$F(000) = 480$