Journal of Alloys and Compounds, 183 (1992) 393–402
JALCOM 7029

Synthesis and structure of $Na_3B_5O_8S$, the first oxothioborate*

A. Hammerschmidt and B. Krebs
Anorganisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 8, D-4400 Münster (FRG)

(Received August 2, 1991; accepted August 19, 1991)

Abstract

$Na_3B_5O_8S$ was prepared from the reaction of sodium sulphide with boron oxide and sodium carbonate at 500 °C in a graphitized silica tube. It is the first oxothioborate that could be synthesized and characterized by single-crystal X-ray diffraction. $Na_3B_5O_8S$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.390(2)$ Å, $b = 6.249(1)$ Å, $c = 10.934(2)$ Å and $\beta = 93.94(2)°$. In the structure, polymeric $[B_5O_8S^{3-}]_n$ anions form two-dimensionally infinite layers containing groups of two spirocyclically connected six-membered B_3O_3 rings with one exocyclic sulphur atom bonded to one of them. Two of the five boron atoms are in tetrahedral BO_4 coordination (B–O = 1.433–1.504 Å) and three have trigonal planar BO_3 or BO_2S coordination (B–O = 1.353–1.393 Å, B–S = 1.813 Å). The three types of sodium cations between the layers are coordinated by 7 O, 4S + 2O and 1S + 6O atoms.

1. Introduction

In recent years considerable progress has been observed in the chemistry and structural chemistry of binary and ternary boron sulphides and selenides. This was made possible by the development and improvement of current methods of synthesis and crystallization. Besides the binary compounds B_2S_3 [1–6], $(BS_2)_n$ and $(BSe_2)_n$ [1, 7, 8] and the porphin-like B_8S_{16} [1, 7–9], numerous thioborates were synthesized and their structures determined (Table 1). Boron chalcogenides show a great structural variety. B–O and B–S compounds both contain trigonally and tetrahedrally coordinated boron, but the constitution of polymeric anions is different. In contrast to edge-sharing BS_4 tetrahedra forming B_2S_2 four-membered rings, no edge-sharing BO_4 tetrahedra have been observed so far. A novel connecting link between B–O and B–S chemistry is represented by the compound $Na_3B_5O_8S$.

2. Sample preparation and properties

The synthesis of well-defined and highly pure binary, ternary and quarternary boron sulphides is rather difficult because of the high reactivity of

---

*Dedicated to Professor W. Bronger on the occasion of his 60th birthday.

0925-8388/92/$5.00

TABLE 1

Thioborates with known structures[a]

M_mS_s/B_2S_3 M^I:$m=2$, $s=1$ M^{II}:$m=1$, $s=1$	Compound(s)	Reference(s)	Coordination of boron
3:1	Tl_3BS_3	[10]	Trigonal
	$Sr_3[BS_3]_2$	[11]	Trigonal
2:1	$Pb_4B_4S_{10}$	[1, 12–14]	Tetrahedral
1:1	$Na_3B_3S_6$	[1, 15–17]	Trigonal
	$K_3B_3S_6$	[1, 15–17]	Trigonal
	$Rb_3B_3S_6$	[18]	Trigonal
	$LiSrB_3S_6$	[18]	Trigonal
	$TlBS_2$	[19–21]	Tetrahedral
	SrB_2S_4	[21, 22]	Tetrahedral
5:7	$Li_5B_7S_{13}$	[12]	Tetrahedral
3:5	$Ag_6B_{10}S_{18}$	[16]	Tetrahedral
	$Li_{6+2x}[B_{10}S_{18}]S_x$ ($x \approx 2$)	[23]	Tetrahedral

[a] The first perthioborate with a known structure is $TlBS_3$ [19, 20].

boron sulphides towards most of the usual container materials. The silica tubes usually employed are attacked by boron sulphides above 300–400 °C, Si–S compounds being formed by complete B–Si exchange. Pure samples can be obtained from protected silica tubes. The inner walls of the quartz glass crucible are coated with a tight layer of glassy carbon by anaerobic pyrolysis of acetone vapour at about 1000 °C.

In order to improve crystallization, the samples are annealed in pressed carbon or boron nitride (BN) crucibles (length 100 mm, cap/outer/inner diameter 18/12/5 mm) furnished with a tight screw cap. For the high temperature experiment they are inserted into a coated silica tube or into a steel or tantalum tube sealed by welding under an inert gas atmosphere. The inner walls of the outer metal container must be coated by a layer of BN produced by spraying a suspension of BN in CH_3OH–CH_2Cl_2 (Union Carbide) onto the inner walls with subsequent polishing.

$Na_3B_5O_8S$ was prepared from a mixture of anhydrous Na_2S (Alfa Ventron 97.5%), anhydrous Na_2CO_3 (Merck 99.5%) and B_2O_3 (Merck 99.8%, heated at 160 °C and 10^{-5} bar for 2 days). The mixture (ratio $2Na_2S + 5B_2O_3 + Na_2CO_3 \rightarrow 2Na_3B_5O_8S + CO_2$) was heated with an excess of B_2S_3 in a sealed silica tube to 500 °C within 3 h, kept at this temperature for 14 h and then cooled to room temperature. To prepare single crystals, the sample was sealed in a steel crucible and heated for 14 days at 380 °C. Colourless, moisture-sensitive crystals were obtained besides some glassy B_2S_3.

3. Structure determination and refinement

For intensity collection, single crystals of $Na_3B_5O_8S$ were sealed under dry nitrogen into Mark capillaries. The crystal structure of $Na_3B_5O_8S$ was determined from single-crystal X-ray diffraction data collected on a SYNTEX $P2_1$ four-circle diffractometer at 150 K. The unit cell constants were refined by least-squares refinement from diffractometer coordinates of 18 medium angle reflections. The space group $P2_1/c$ was obtained from systematic extinctions and from intensity statistics. The structure was solved by direct statistical methods of phase determination using the SHELXTL PLUS program system on a DEC VAX cluster. The refinement with anisotropic thermal parameters for all atoms with the exception of one oxygen atom (O(6)) converged to a conventional R value of 0.053. Table 2 shows crystal data and details of data collection and structure refinement of $Na_3B_5O_8S$. Table 3 presents atomic coordinates as well as isotropic thermal parameters of $Na_3B_5O_8S$.

TABLE 2

Crystal data and details of data collection and structure refinement of $Na_3B_5O_8S$

Formula	$Na_3B_5O_8S$
Crystal dimensions	$0.05\times0.12\times0.10$ mm^3
Formula weight	283.10 g mol^{-1}
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell constants	$a=11.390(2)$ Å $b=6.249(1)$ Å $c=10.934(2)$ Å $\beta=93.94(2)°$
Volume	776.4(1) Å^3
Z	4
Density (calculated)	2.422 g cm^{-3}
Temperature of measurement	150 K
Radiation	Mo Kα ($\lambda=0.71069$ Å)
Monochromator	Graphite (parallel)
Scan mode	θ–2θ
Scan range	$4°<2\theta<54°$
Scan speed in 2θ	2.60–29.30 deg min^{-1}
Absorption coefficient	0.58 mm^{-1}
Reflections observed	1940
Independent reflections	1770
Reflections with $I>1.96\sigma(I)$	1350
Number of variables	154
Weighting factor	$g=0.0001$
$1/w=\sigma^2(F_{hkl})+g\lvert F_{hkl}\rvert^2$	
with $\sigma(F_{hkl})=\sigma(I)/(2\lvert F_{hkl}\rvert L\ P)$	
R values	$R=0.053$, $R_w=0.052$
$R=(\Sigma\lvert\lvert F_0\rvert-\lvert F_c\rvert\rvert)/\Sigma\lvert F_0\rvert$	
$R_w=[\Sigma w(\lvert F_0\rvert-\lvert F_c\rvert)^2/\Sigma wF_0{}^2]^{1/2}$	

TABLE 3

Atomic coordinates and isotropic thermal parameters (Å^2) for $Na_3B_5O_8S$ with standard deviations

Atom	x	y	z	U_{eq}[a]
S(1)	0.01046(9)	0.25479(18)	0.36483(9)	0.0098(3)
Na(1)	0.47377(15)	−0.19238(26)	−0.30279(15)	0.0118(5)
Na(2)	−0.02161(16)	0.21732(28)	0.10869(15)	0.0158(6)
Na(3)	−0.21183(17)	0.0777(3)	0.35344(18)	0.0190(6)
O(1)	0.1864(3)	0.1804(5)	0.2095(3)	0.0077(9)
O(2)	0.3805(3)	0.5527(4)	−0.0108(3)	0.0081(9)
O(3)	0.3820(3)	0.1826(4)	−0.0659(3)	0.0084(9)
O(4)	0.3635(3)	−0.0235(4)	0.2669(3)	0.0077(9)
O(5)	0.2784(3)	−0.0454(4)	0.0636(3)	0.0092(9)
O(6)	0.3208(3)	−0.1512(4)	−0.1403(3)	0.0078(9)
O(7)	0.3693(3)	0.2897(4)	0.1409(2)	0.0080(9)
O(8)	0.1906(3)	−0.0461(5)	0.3853(3)	0.0086(9)
B(1)	0.3796(4)	0.3420(8)	0.0224(5)	0.0083(16)
B(2)	0.1405(4)	0.1181(8)	0.3174(4)	0.0080(17)
B(3)	0.3258(4)	−0.0105(8)	−0.0449(4)	0.0075(16)
B(4)	0.3130(5)	−0.1143(7)	0.3733(5)	0.0080(17)
B(5)	0.2990(4)	0.0952(7)	0.1724(5)	0.0084(17)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} matrix.

Further details of the crystal structure determination (anisotropic temperature factor coefficients, structure factor tables) are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-Technische Zusammenarbeit m.b.H., D-7514 Eggenstein-Leopoldshafen 2, F.R.G. on quoting the depository number CSD-55591, the names of the authors and the journal citation.

4. Description of the structure

$Na_3B_5O_8S$ crystallizes in the monoclinic space group $P2_1/c$. $[B_5O_8S^{3-}]_n$ anions build up a two-dimensional network parallel to the (100) plane. The polymeric $[B_5O_8S^{3-}]_n$ anion contains subunits of two spirocyclically linked six-membered B_3O_3 rings with an exocyclic sulphur atom in one ring (Fig. 1). Additional oxygen atoms connect the bicyclic subunits to a layer system of composition $[B_5O_8S^{3-}]_n$ (Figs. 2 and 3), which leads to a distorted octahedral or sevenfold coordination of the sodium cations located between the layers. Two of the boron atoms are in tetrahedral BO_4 coordination; the three others are trigonal planar with BO_3 or BO_2S coordination. The sulphur atoms are located on a straight line parallel to the c axis with $a \approx 0$.

The coordination spheres of the three sodium cations in the asymmetric unit differ in number and kind of chalcogen atoms. The first sodium cation is coordinated by 7O, the second by 6O + 1S and the third by 4O + 2S atoms (Fig. 4). In Table 4 the Na–O and Na–S distances are listed. The interactions between the sodium cations and the chalcogen atoms are largely ionic, with

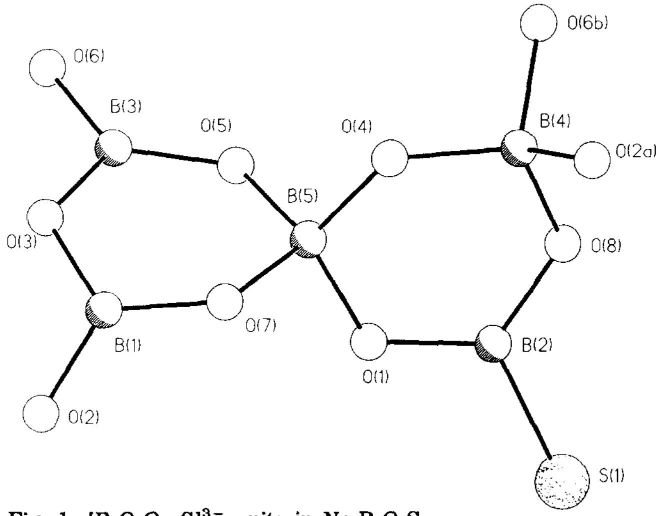

Fig. 1. $[B_5O_6O_{4/2}S]^{3-}$ units in $Na_3B_5O_8S$.

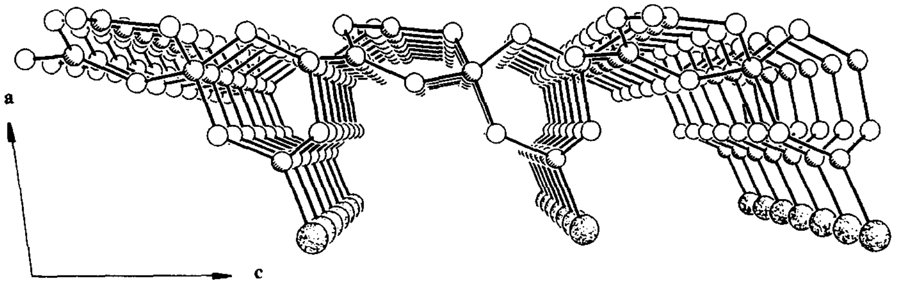

Fig. 2. Perspective view of the $[B_5O_8S^{3-}]_n$ anions of $Na_3B_5O_8S$ along [010].

the Na–O (Na–S) distances being close to the sum of the ionic radii of Na^+ and O^{2-} (S^{2-}): $d(Na^+–O^{2-})=2.42$ Å and $d(Na^+–S^{2-})=3.14$ Å [24, 25].

Tables 5 and 6 show the bond lengths and bond angles in the polymeric anions. The trigonal (tetrahedral) B–O bond lengths vary from 1.353(6) to 1.393(5) Å (1.433(5) to 1.504(5) Å); the B–S bond length are 1.813(5) Å. The B–O values are in good accordance with numerous data in other borates as well as with the standard Shannon and Prewitt [24] values after consideration of covalent bonding and hybridization of the boron atoms (d(B–O) = 1.38 Å for trigonally planar coordinated boron and 1.48 Å for tetrahedrally coordinated boron). The theoretical B–S single-bond distance for trigonal planar coordination can be estimated to be about 1.85 Å. The B–S distance observed in $Na_3B_5O_8S$ is remarkably shorter, implying significant partial pπ bonding. Very similar observations are made in the thioborates studied so far (Table 1), where similarly short B–S distances are observed in trigonal planar BS_3 groups; they invariantly indicate significant pπ–pπ overlap in the B–S bonds.

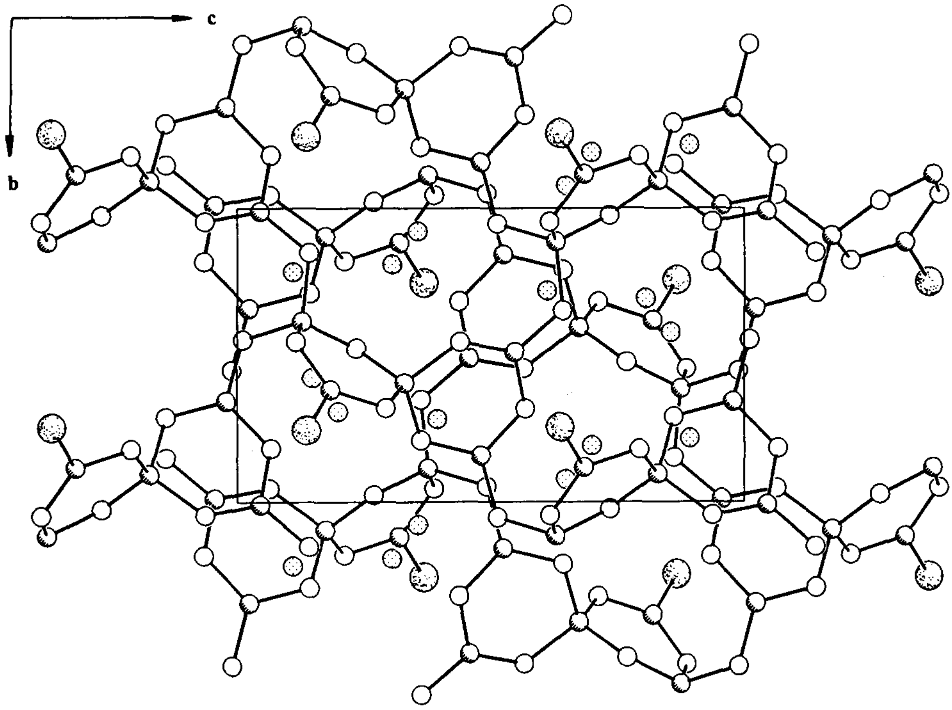

Fig. 3. Projection of the unit cell of $Na_3B_5O_8S$ along [100].

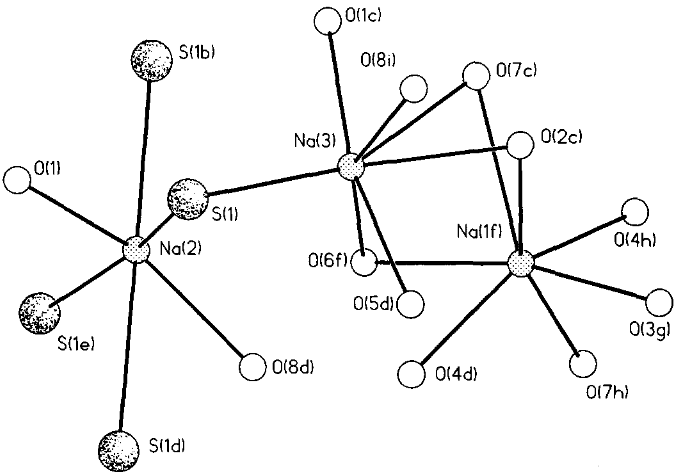

Fig. 4. Coordination of the sodium cations in $Na_3B_5O_8S$.

The O–B–O and B–O–B bond angles (Table 6) within the six-membered rings differ rather strongly from 120° (from 115.2(1)° to 124.8(1)°) and the angles at the tetrahedral boron atoms vary in a wide range from 97.8(1)° to 113.6(1)°, but as with the distances, the angle distortions are similar to

TABLE 4

Na–O and Na–S distances (Å) for $Na_3B_5O_8S$ with standard deviations

Na(1*f*)–O(2*c*)	2.594(3)	Na(3)–S(1)	2.760(2)			
Na(1*f*)–O(3*g*)	2.386(3)	Na(3)–O(1*c*)	2.598(3)			
Na(1*f*)–O(4*h*)	2.301(3)	Na(3)–O(2*c*)	2.666(3)			
Na(1*f*)–O(4*d*)	2.335(3)	Na(3)–O(5*d*)	2.653(3)			
Na(1*f*)–O(6*f*)	2.588(3)	Na(3)–O(6*f*)	2.606(3)			
Na(1*f*)–O(7*h*)	2.500(3)	Na(3)–O(7*c*)	2.547(3)			
Na(1*f*)–O(7*c*)	2.833(3)	Na(3)–O(8*i*)	2.856(4)			
Na(2)–O(1)	2.552(3)	*c*		$-x$	$-\tfrac{1}{2}+y$	$\tfrac{1}{2}-z$
Na(2)–O(8*d*)	2.432(3)	*d*		$-x$	$\tfrac{1}{2}+y$	$\tfrac{1}{2}-z$
Na(2)–S(1)	2.808(2)	*e*		x	$\tfrac{1}{2}-y$	$-\tfrac{1}{2}+z$
Na(2)–S(1*c*)	2.907(2)	*f*		$-x$	$-y$	$-z$
Na(2)–S(1*d*)	3.372(2)	*g*		$-1+x$	$\tfrac{1}{2}-y$	$\tfrac{1}{2}+z$
Na(2)–S(1*e*)	2.723(2)	*h*		$-1+x$	y	z
		i		$-x$	$-y$	$1-z$

TABLE 5

B–O and B–S bond lengths (Å) for $Na_3B_5O_8S$ with standard deviations

B(1)–O(2)	1.360(5)	B(4)–O(2*a*)	1.492(5)			
B(1)–O(3)	1.392(5)	B(4)–O(4)	1.443(6)			
B(1)–O(7)	1.353(6)	B(4)–O(6*b*)	1.475(5)			
		B(4)–O(8)	1.476(6)			
B(2)–S(1)	1.813(5)	B(5)–O(1)	1.472(6)			
B(2)–O(1)	1.382(6)	B(5)–O(4)	1.437(5)			
B(2)–O(8)	1.369(5)	B(5)–O(5)	1.486(5)			
		B(5)–O(7)	1.504(5)			
B(3)–O(3)	1.393(5)					
B(3)–O(5)	1.353(6)	*a*		x	$\tfrac{1}{2}-y$	$\tfrac{1}{2}+z$
B(3)–O(6)	1.360(5)	*b*		x	$-\tfrac{1}{2}-y$	$\tfrac{1}{2}+z$

those in other known sterically constrained borates and thioborates with trigonally planar and tetrahedrally coordinated boron.

The anion structure in crystals of $Na_3B_5O_8S$ is similar to that of oxoborates containing the pentaborate anion. Exchange of the sulphur to an oxygen atom leads to a hypothetic $Na_3B_5O_9$. Although this prototype has not been synthesized yet, a related derivative is realized in $Na_3B_5O_8(OH)_2 \cdot H_2O$ [26]. In the crystal structure of this pentaborate the position of the sulphur atom in $Na_3B_5O_8S$ is replaced by two hydroxyl groups (Fig. 5). $Na_3B_5O_8(OH)_2 \cdot H_2O$ crystallizes in the orthorhombic space group *Pbca*, the polymeric anions running parallel to the (010) plane. The coordination of the sodium cations is somewhat different from that in $Na_3B_5O_8S$. Similar pentaborate anions exist in the minerals $NaCa[B_5O_6(OH)_6] \cdot 5H_2O$ (Ulexit) [27, 28], $NaCa[B_5O_7(OH)_4] \cdot 3H_2O$ (Probertit) [29, 30], $Na_2Ca_3Cl(SO_4)_2[B_5O_8(OH)_2]$ (Heidornit) [31] and $NaBa_3[Si_2B_7O_{16}(OH)_4]$ (Garrelsit) [32].

TABLE 6

O–B–O, O–B–S and B–O–B bond angles (deg) for $Na_3B_5O_8S$ with standard deviations

O(2)–B(1)–O(7)	119.4(1)	O(2*a*)–B(4)–O(6*b*)			108.2(1)
O(2)–B(1)–O(3)	120.6(1)	O(2*a*)–B(4)–O(8)			106.3(1)
O(3)–B(1)–O(7)	119.8(1)	O(4)–B(4)–O(6*b*)			106.7(1)
		O(4)–B(4)–O(8)			97.8(1)
O(1)–B(2)–S(1)	118.5(1)	O(2*a*)–B(4)–O(4)			111.8(1)
O(1)–B(2)–O(8)	120.3(1)	O(6*b*)–B(4)–O(8)			111.0(1)
O(8)–B(2)–S(1)	121.2(1)				
		O(1)–B(5)–O(4)			113.6(1)
O(5)–B(3)–O(6)	124.8(1)	O(1)–B(5)–O(7)			105.1(1)
O(3)–B(3)–O(5)	120.0(1)	O(5)–B(5)–O(7)			110.6(1)
O(3)–B(3)–O(6)	115.2(1)	O(5)–B(5)–O(4)			108.5(1)
		O(1)–B(5)–O(5)			109.8(1)
B(1)–O(7)–B(5)	120.0(1)	O(4)–B(5)–O(7)			109.2(1)
B(5)–O(1)–B(2)	120.3(1)				
B(3)–O(3)–B(1)	118.4(1)	*a*	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
B(4)–O(4)–B(5)	124.8(1)	*b*	x	$-\frac{1}{2}-y$	$\frac{1}{2}+z$
B(5)–O(5)–B(3)	123.7(1)				
B(4)–O(8)–B(2)	122.2(1)				

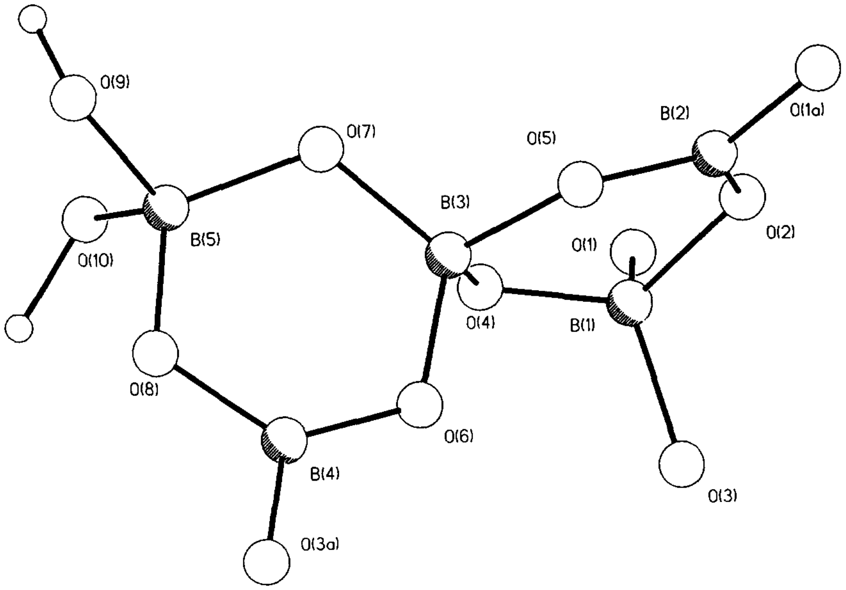

Fig. 5. $[B_5O_6O_{4/2}(OH)_2]^{3-}$ unit in $Na_3B_5O_8(OH)_2 \cdot H_2O$ [26].

5. X-ray powder diffraction of $Na_3B_5O_8S$

A powder diffraction pattern of $Na_3B_5O_8S$ was recorded at 210 K with a Guinier–Simon camera using Cu Kα radiation ($\lambda = 1.540\,56$ Å) with α-quartz as an internal standard. The evaluation of the pattern is shown in

TABLE 7

X-ray powder diffraction data of $Na_3B_5O_8S$

h k l	Calculated			Observed		
	2*θ* (deg)	*d* (Å)	*I* (%)	2*θ* (deg)	*d* (Å)	*I* (%)
1 0 0	7.77	11.36	50	7.78	11.35	50
0 1 1	16.33	5.42	11	16.35	5.42	10
1 1 −1	17.87	4.96	28	17.88	4.97	40
1 1 1	18.35	4.83	13	18.35	4.83	10
3 0 0	23.47	3.79	79	23.47	3.79	80
2 1 2	27.42	3.25	63	27.45	3.25	80
3 1 −1	28.25	3.16	15	28.25	3.16	10
3 1 1	29.19	3.05	14	29.20	3.02	10
3 0 2	29.60	3.02	41	29.65	3.01	50
2 2 0	32.68	2.74	100	32.68	2.74	100
0 0 4	32.81	2.73	28	32.80	2.73	40
3 1 2	32.95	2.72	18	32.95	2.72	10
1 0 −4	33.23	2.69	47	33.25	2.69	50
2 1 3	33.37	2.68	15	33.37	2.68	20
4 0 −2	34.55	2.59	21	34.55	2.59	20
3 1 −3	36.00	2.49	24	36.00	2.49	30
1 2 −3	38.42	2.34	11	38.42	2.34	10
5 0 0	39.62	2.27	20	39.62	2.27	10
2 1 4	40.29	2.24	25	40.30	2.24	20
5 1 −1	42.57	2.12	24	42.58	2.12	20
4 2 −1	43.39	2.08	17	43.39	2.08	20
0 2 4	44.04	2.05	14	44.03	2.05	10
1 1 −5	44.14	2.05	13	44.15	2.05	10
4 4 −2	45.41	2.00	13	45.40	2.00	10
2 3 −1	46.97	1.93	10	46.98	1.93	10
4 0 4	47.76	1.90	21	47.75	1.90	20
2 2 4	47.81	1.90	20	47.80	1.90	20
6 0 0	48.00	1.89	16	48.00	1.89	20
3 2 −4	49.31	1.85	45	49.30	1.85	50
3 2 4	51.66	1.77	21	51.65	1.77	20

Table 7 and is compared with the calculated diffraction data from the single-crystal structure (program LAZY PULVERIX [33]).

Acknowledgment

We wish to thank the Fonds der Chemischen Industrie for generous support of our work.

References

1 B. Krebs, *Angew. Chem.*, *95* (1983) 113; *Angew. Chem. Int. Ed. Engl.*, *22* (1983) 113.
2 B. Krebs and H. Diercks, *Acta Crystallogr. A*, *31* (1975) 66.

3 H. Diercks and B. Krebs, *Angew. Chem.*, *89* (1977) 327; *Angew. Chem. Int. Ed. Engl.*, *16* (1977) 313.
4 P. zum Hebel, H. Diercks and B. Krebs, *Z. Kristallogr.*, *185* (1988) 401.
5 P. Hagenmuller and F. Chopin, *C.R. Acad. Sci. Paris*, *255* (1962) 2259.
6 H. Y. Chen, B. R. Conard and P. W. Gilles, *Inorg. Chem.*, *9* (1970) 1776.
7 H.-U. Hürter, *Doctoral Thesis*, Münster, 1981.
8 B. Krebs and H.-U. Hürter, *Acta Crystallogr. A*, *37* (1981) C-163.
9 B. Krebs and H.-U. Hürter, *Angew. Chem.*, *92* (1980) 479; *Angew. Chem. Int. Ed. Engl.*, *19* (1980) 481.
10 B. Krebs and W. Hamann, *J. Less-Common Met.*, *137* (1988) 143.
11 C. Püttmann, P. zum Hebel, A. Hammerschmidt and B. Krebs, *Acta Crystallogr. A*, *46* (1990) C-279.
12 P. Hagenmuller, F. Chopin and B. Castagna, *C.R. Acad. Sci. Paris*, *262* (1966) 418.
13 A. Hardy, *Bull. Soc. Fr. Mineral. Cristallogr.*, *91* (1968) 111.
14 H. Diercks and B. Krebs, *Acta Crystallogr. C*, in press.
15 B. Krebs, P. zum Hebel and H. Diercks, in preparation.
16 P. Hagenmuller and F. Chopin, *C.R. Acad. Sci. Paris*, *256* (1963) 5578.
17 F. Chopin and G. Turrell, *J. Mol. Struct.*, *3* (1969) 57.
18 C. Püttmann and B. Krebs, *Phosphorus, Sulfur and Silicon*, *65* (1992) 1.
19 B. Krebs and W. Hamann, *Acta Crystallogr. A*, *40* (1984) C-217.
20 B. Krebs and W. Hamann, *Z. Kristallogr.*, *162* (1983) 149.
21 C. Püttmann and B. Krebs, *Eur. J. Solid State Inorg. Chem.*, in press.
22 F. Chopin and B. Capdepuy, *Bull. Soc. Chim. Fr.*, *1* (1970) 505.
23 P. zum Hebel, B. Krebs, M. Grüne and W. Müller-Warmuth, *Solid State Ionics*, *43* (1990) 133.
24 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. B*, *25* (1969) 925.
25 L. Pauling, *Die Natur der Chemischen Bindung*, VCH, Weinheim, 1968.
26 S. Menchetti and C. Sabelli, *Acta Crystallogr. B*, *33* (1977) 3730.
27 S. Ghose, Cheng'ng Wan and J. R. Clark, *Am. Mineral.*, *63* (1978) 160.
28 J. R. Clark and D. E. Appleman, *Science*, *145* (1964) 1295.
29 Kh. M. Kurbanov and I. M. Rumanova, *Dokl. Akad. Nauk SSSR*, *152* (1963) 1100.
30 I. M. Rumanova, Kh. M. Kurbanov and N. V. Belov, *Sov. Phys. – Crystallogr.*, *10* (1965) 513.
31 H. Burzlaff, *Neues Jb. Miner. Mh.*, *8* (1967) 157.
32 S. Ghose, Cheng'ng Wan and H. H. Ulbrich, *Acta Crystallogr. B*, *32* (1976) 824.
33 K. Yvon, W. Jeitschko and E. Parthé, *J. Appl. Crystallogr.* *10* (1977) 73.