

# $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub>: Compound Containing a New Three-Dimensional Borate Anion

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Single crystals of synthetic  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> or Tl<sub>6</sub>B<sub>12</sub>O<sub>21</sub> were obtained by heating its hydrated precursor Tl<sub>2</sub>[B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>]·2H<sub>2</sub>O. The compound is triclinic, space group *P*-1; the unit cell parameters are  $a = 6.742(1)$  Å,  $b = 13.225(2)$  Å,  $c = 13.389(2)$  Å,  $\alpha = 119.093(3)^\circ$ ,  $\beta = 92.288(3)^\circ$ ,  $\gamma = 91.012(3)^\circ$ ;  $Z = 6$ . The crystal structure was solved from 2893 reflections until  $R = 0.0312$ . It exhibits a three-dimensional framework containing a new complex borate anion (B<sub>12</sub>O<sub>21</sub>)<sup>6-</sup> formed by six BO<sub>3</sub> triangles ( $\Delta$ ) and six BO<sub>4</sub> tetrahedra (T), which are disposed on two and three B<sub>3</sub>O<sub>3</sub> rings; this leads to an anion with the shorthand notation: 12:  ${}^3_\infty[(5: 2\Delta + 3T) + (7: 4\Delta + 3T)]$ . This new anion is different from those described in alkaline tetraborates M<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, and especially K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and Rb<sub>2</sub>B<sub>4</sub>O<sub>7</sub> where the M<sup>+</sup> cations have a size close to that of Tl<sup>+</sup>. This difference may be due to the stereochemical role of the 6s<sup>2</sup> lone pairs of Tl<sup>+</sup> cations, which has been pointed out. Upon heating at around 500°C,  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> transforms into a second form of thallium tetraborate,  $\alpha$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. © 2001 Academic Press

## INTRODUCTION

In recent years, borate compounds have received great attention due to their promising physical properties (1). In our group, a lot of work has been devoted to hydrated and anhydrous thallium borates. The latter could be synthesized by two different methods: (i) dehydration of hydrated precursor prepared via aqueous solution and (ii) classical high-temperature ceramic route. Several compounds have been reported in the Tl<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub> binary system (Fig. 1) (2). Among them, the structures of Tl<sub>3</sub>BO<sub>3</sub> (3), TlBO<sub>2</sub> (4), TlB<sub>3</sub>O<sub>5</sub> (5), and TlB<sub>5</sub>O<sub>8</sub> (6) were solved. Structural analogy with CsB<sub>3</sub>O<sub>5</sub> (CBO) (7) was confirmed for the thallium triborate TlB<sub>3</sub>O<sub>5</sub> (TBO) (5). In agreement with their non-centrosymmetric structure, both triborates compounds are

actively studied (8–10) because they exhibit interesting second-harmonic generation properties. Regarding the thallium tetraborate, a previous study (11) showed that the dehydration of Tl<sub>2</sub>[B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>]·2H<sub>2</sub>O led to amorphous Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and then to two successive crystalline forms of Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. Their crystallographic data were obtained some time ago by the classical photographic study (Weissenberg camera) of single crystals:  $\alpha$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> orthorhombic with  $a = 12.338$  Å,  $b = 5.347$  Å,  $c = 12.925$  Å,  $Z = 4$ , space group *Amm*2 or *Ammm*;  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> trigonal with hexagonal parameters  $a = 13.692$  Å,  $c = 6.725$  Å,  $Z = 6$ , space group *P*3 or *P*-3 (12). However, some further examination of this last compound showed a triclinic symmetry that might lead to an analogy with alkaline tetraborates with a cationic radius close to that of Tl<sup>+</sup>, as K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (13) and Rb<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (14), which exhibit the same structure. So, this paper deals with the study of the  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> structure.

## EXPERIMENTAL

### Synthesis

The hydrated thallium tetraborate Tl<sub>2</sub>[B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>]·2H<sub>2</sub>O was obtained from an aqueous solution of dissolved Tl<sub>2</sub>CO<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub> in stoichiometric proportions; CO<sub>2</sub> being released, its evaporation under constant stirring and heating led to the wanted compound. The latter was then dehydrated, melted at 615°C, slowly cooled down to 500°C at 0.1°C/min, annealed at this temperature for 48 h, slowly cooled down to 300°C at 0.1°C/min, and finally cooled down to room temperature at 1°C/min. To avoid oxidation and/or carbonation, this experiment was carried out under argon atmosphere. Single crystals of the title compound were isolated from the biphased preparation, also containing TlB<sub>3</sub>O<sub>5</sub>.

By heating Tl<sub>2</sub>[B<sub>4</sub>O<sub>6</sub>(OH)<sub>2</sub>]·2H<sub>2</sub>O at 430°C for 96 h under argon, a powder of  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> was obtained with very good purity as proven by the excellent experimental powder pattern. The 430°C temperature was chosen

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TABLE 1

Crystal Data and Intensity Collection Conditions for  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$ 

Formula weight (g/mol)	563.98
Space group	$P-1$ ( $N^{\circ}2$ )
Unit cell parameters ( $\text{\AA}$ , $^{\circ}$ )	$a = 6.7415(12)$ ; $b = 13.225(2)$ ; $c = 13.389(2)$
	$\alpha = 119.093(3)$ ; $\beta = 92.288(3)$ ; $\gamma = 91.012(3)$
$V$ ( $\text{\AA}^3$ ); $Z$	1041.3(3); 6
Density ( $\text{g/cm}^3$ )	$D_x = 5.398(1)$ , $D_m = 5.3$ (12)
Crystal size ( $\text{mm}^3$ )	$0.065 \times 0.130 \times 0.160$
Collection method	$\varphi$ and $\omega$ scans
Temperature	298 K
$\theta$ range ( $^{\circ}$ )	1.74–23.25
Range in $h, k, l$	$-7 \leq h \leq 7$ ; $-14 \leq k \leq 14$ ; $-14 \leq l \leq 14$
Absorption coefficient ( $\text{mm}^{-1}$ )	$\mu(\text{MoK}\alpha) = 46.358$
Reflections collected	6492
Independent reflections	2893
$R_{\text{int}}$	0.0384
Refinement method	Full-matrix least-squares on $F^2$ —SHELX-97
Number of variables	188
Goodness-of-fit on $F^2$	0.919
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0312$ , $wR_2 = 0.0677$
$R$ indices (all data)	$R_1 = 0.0422$ , $wR_2 = 0.0697$
Largest difference map peak and hole ( $\text{e.\AA}^{-3}$ )	3.140 and $-1.748$
Largest difference map peak and hole ( $\text{e.\AA}^{-3}$ ) when B atoms are not located	6.50 and $-2.1$

according to the binary diagram  $\text{Tl}_2\text{O}-\text{B}_2\text{O}_3$  (Fig. 1) (2), which shows the existence of a  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7 \rightleftharpoons \alpha$ - $\text{Tl}_2\text{B}_4\text{O}_7$  phase transformation at  $500^{\circ}\text{C}$ . The studied compound was characterized by X-ray powder diffraction (Siemens D5000 diffractometer;  $\lambda_{\text{CuK}\alpha_1} = 1.5406 \text{ \AA}$ ).

*Thermal Analyses*

This compound was also characterized by thermal analyses using temperature-resolved X-ray powder diffraction (TRXPD), carried out with a Guinier–Lenné camera operating with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ); experiments were performed under air with a heating rate of  $0.1^{\circ}\text{C}/\text{min}$ . TG-DTA measurements were carried out with a Setaram TGDTA 92 instrument using platinum crucibles, heating rates of 1 and  $10^{\circ}\text{C}/\text{min}$ , in air, between 25 and  $600^{\circ}\text{C}$ , and samples weighing about 20 mg.

*Single-Crystal Structure Determination*

The crystals in the preparation had no clear-cut faces but rather contorted forms. This can be due to the growth conditions (incongruent melting). The intensity data were collected on a Bruker AXS SMART three-circle

TABLE 2

Final Atomic Coordinates and Equivalent Thermal Isotropic Displacement  $U_{\text{eq}}$  ( $\text{\AA}^2 \times 10^3$ ) of  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$  with e.s.d.'s in Parentheses

Atoms	$x$	$y$	$z$	$U_{\text{eq}}^a$
Tl(1)	0.03001(9)	0.59992(6)	0.94630(6)	27(1)
Tl(2)	0.44248(10)	0.73290(7)	0.63419(6)	33(1)
Tl(3)	0.68915(9)	0.94333(5)	0.06948(6)	27(1)
Tl(4)	0.60391(10)	0.66684(7)	0.11176(6)	35(1)
Tl(5)	0.22388(10)	0.97728(6)	0.55870(7)	37(1)
Tl(6)	0.11433(11)	0.53436(6)	0.40614(6)	34(1)
O(1)	0.9796(13)	0.8066(8)	0.6240(8)	14(2)
O(2)	0.6621(13)	0.8747(8)	0.5978(8)	13(2)
O(3)	0.4364(14)	0.5807(8)	0.8556(8)	11(2)
O(4)	0.7111(13)	0.9966(8)	0.7962(9)	15(2)
O(5)	0.2054(14)	0.7132(8)	0.8742(9)	19(2)
O(6)	0.0909(13)	0.8445(8)	0.8085(8)	12(2)
O(7)	0.3392(13)	0.5669(8)	0.1762(8)	12(2)
O(8)	0.2366(14)	0.7442(8)	0.2036(9)	20(2)
O(9)	0.0720(15)	0.6588(9)	0.3008(9)	22(3)
O(10)	0.5409(13)	0.7480(8)	0.8412(8)	13(2)
O(11)	0.7284(14)	0.6763(8)	0.4797(8)	14(2)
O(12)	0.8808(14)	0.7846(8)	0.9150(8)	14(2)
O(13)	0.2366(14)	0.4112(8)	0.2110(8)	14(2)
O(14)	0.9049(14)	0.7980(8)	0.2649(9)	15(2)
O(15)	0.9178(14)	0.8201(8)	0.4544(9)	15(2)
O(16)	0.1709(14)	0.9128(8)	0.0084(9)	17(2)
O(17)	0.8006(14)	0.7215(8)	0.7162(8)	14(2)
O(18)	0.4822(14)	0.5519(8)	0.3358(9)	17(2)
O(19)	0.1684(14)	0.9435(8)	0.3328(9)	19(2)
O(20)	0.7176(15)	0.6676(9)	0.2987(9)	24(3)
O(21)	0.0487(14)	0.8469(8)	0.1316(9)	18(2)
B(1)	0.3960(23)	0.6831(14)	0.8569(15)	10(4)
B(2)	0.0794(23)	0.8170(14)	0.9020(14)	10(4)
B(3)	0.2143(25)	0.6554(15)	0.2275(16)	17(4)
B(4)	0.9052(26)	0.7398(15)	0.3329(16)	19(4)
B(5)	0.1643(24)	0.9187(14)	0.1113(15)	11(4)
B(6)	0.0848(24)	0.8303(14)	0.2323(15)	12(4)
B(7)	0.6471(25)	0.6324(15)	0.3701(16)	17(4)
B(8)	0.4051(26)	0.4837(15)	0.2145(16)	18(4)
B(9)	0.7364(25)	0.9758(15)	0.6862(16)	17(4)
B(10)	0.7511(23)	0.7109(14)	0.8185(15)	10(4)
B(11)	0.8312(25)	0.7922(15)	0.5358(15)	15(4)
B(12)	0.9536(26)	0.7892(15)	0.7165(16)	19(4)

<sup>a</sup> $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

diffractometer using a graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and equipped with a CCD two-dimensional detector. Crystal data and conditions of intensity collections are given in Table 1. The triclinic symmetry is confirmed, although the found parameters are close to those reported above for a hexagonal unit cell (12). As the absorption rate was very high ( $\mu = 46.36 \text{ mm}^{-1}$ ), the best solution was to cut out a crystal with a cutter blade to get the faces as parallel as possible. The data collection was carried out on a crystal limited by the approximate faces  $0\ 1\ -3$ ,  $0\ -1\ 3$ ,  $0\ 5\ -1$ ,  $0\ -5\ 1$ ,  $4\ -1\ 0$  and  $-4\ 1\ 0$  with

**TABLE 3**  
Anisotropic Thermal Vibration Parameters<sup>a</sup> ( $\text{\AA}^2 \times 10^3$ )  
(e.s.d's in Parentheses) for Thallium Atoms of  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

Atoms	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Tl(1)	25(1)	32(1)	32(1)	23(1)	-6(1)	-9(1)
Tl(2)	18(1)	57(1)	33(1)	30(1)	-3(1)	-7(1)
Tl(3)	21(1)	23(1)	31(1)	8(1)	9(1)	-1(1)
Tl(4)	25(1)	60(1)	24(1)	24(1)	-2(1)	-10(1)
Tl(5)	25(1)	46(1)	34(1)	15(1)	-5(1)	7(1)
Tl(6)	44(1)	33(1)	28(1)	17(1)	16(1)	7(1)

<sup>a</sup>The form of the anisotropic thermal parameters is

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})].$$

the dimensions  $0.065 \times 0.130 \times 0.160 \text{ mm}^3$ . Analytical absorption corrections using these indexes and these dimensions lowered the  $R_{\text{int}}$  coefficient from 19.01 down to 3.84%.

The structure resolution proceeded quite smoothly: thallium atoms were found by direct methods (SHELX-97) (15); their position refinement gave  $R_1 = 0.166$  and  $0.127$  with isotropic and anisotropic temperature factors, respectively. The Fourier map revealed the positions of oxygen and boron atoms. The refinement converged to  $R_1 = 0.0312$  and  $wR_2 = 0.0677$ . An attempt with anisotropic factors for oxygen and boron atoms led to negative factors for some of them. On the last difference map, all the maxima are in the vicinity ( $0.7$  to  $1.1 \text{ \AA}$ ) of thallium atoms. This is often the case for highly absorbing crystals when the absorption corrections are not perfect. The atomic coordinates and the thermal motion parameters are reported in Tables 2 and 3; significant bond lengths and angles are listed in Table 4.

## DESCRIPTION OF THE STRUCTURE AND DISCUSSION

### Thermal Behavior

Upon heating, the DTA performed on  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> shows two endothermic peaks at  $533^\circ\text{C}$  (very strong) and  $542^\circ\text{C}$  (weak). These phenomena may be correlated with peritectic reaction and complete melting, as reported in the Tl<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> phase diagram (Fig. 1) (2).

For the TRXPD experiments, the  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> powder was: (i) heated to  $530^\circ\text{C}$  at  $0.2^\circ\text{C}/\text{min}$ , (ii) slowly cooled down to  $480^\circ\text{C}$  at  $0.1^\circ\text{C}/\text{min}$ , (iii) annealed at  $480^\circ\text{C}$  for 12 h, (iv) slowly cooled down to  $430^\circ\text{C}$  at  $0.1^\circ\text{C}/\text{min}$ , and finally (v) cooled to room temperature by turning the furnace off (Fig. 2). The examination of the Guinier-Lenné photograph (Fig. 2) shows that the powder pattern of the starting material  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> is visible until  $500^\circ\text{C}$ ; at this temperature a new powder pattern appears, which corresponds to the  $\alpha$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> phase. The  $\alpha$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> remains stable down to room temperature; no modification of the powder pattern

**TABLE 4**  
Interatomic Distances ( $\text{\AA}$ ) and Angles ( $^\circ$ ) in  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

		BO <sub>3</sub> triangles	
● B(1)-O(5)	1.35(2)	O(3)-B(1)-O(5)	114(1)
-O(10)	1.38(2)	O(3)-B(1)-O(10)	122(1)
-O(3)	1.38(2)	O(5)-B(1)-O(10)	124(1)
Mean	1.37(2)	Mean	120(1)
● B(3)-O(7)	1.36(2)	O(7)-B(3)-O(8)	116(1)
-O(8)	1.37(3)	O(7)-B(3)-O(9)	124(1)
-O(9)	1.39(2)	O(8)-B(3)-O(9)	120(1)
Mean	1.37(2)	Mean	120(1)
● B(5)-O(16)	1.34(3)	O(4) <sup>(ii)</sup> -B(5)-O(16)	119(1)
-O(21)	1.35(2)	O(4) <sup>(ii)</sup> -B(5)-O(21)	118(1)
-O(4) <sup>(ii)</sup>	1.43(2)	O(16)-B(5)-O(21)	124(1)
Mean	1.37(2)	Mean	120(1)
● B(7)-O(20)	1.35(3)	O(11)-B(7)-O(18)	118(1)
-O(11)	1.37(2)	O(11)-B(7)-O(20)	121(1)
-O(18)	1.42(2)	O(18)-B(7)-O(20)	121(1)
Mean	1.38(2)	Mean	120(1)
● B(9)-O(2)	1.35(2)	O(2)-B(9)-O(4)	119(1)
-O(19) <sup>(ii)</sup>	1.37(3)	O(2)-B(9)-O(19) <sup>(ii)</sup>	121(1)
-O(4)	1.38(3)	O(4)-B(9)-O(19) <sup>(ii)</sup>	121(1)
Mean	1.37(3)	Mean	120(1)
● B(12)-O(17)	1.35(2)	O(1)-B(12)-O(6) <sup>(iii)</sup>	117(1)
-O(1)	1.38(3)	O(1)-B(12)-O(17)	121(1)
-O(6) <sup>(iii)</sup>	1.39(2)	O(6) <sup>(iii)</sup> -B(12)-O(17)	122(1)
Mean	1.37(2)	Mean	120(1)
		BO <sub>4</sub> tetrahedra	
● B(2)-O(12) <sup>(iii)</sup>	1.44(2)	O(5)-B(2)-O(6)	108(1)
-O(6)	1.47(3)	O(5)-B(2)-O(12) <sup>(iii)</sup>	107(1)
-O(16) <sup>(iv)</sup>	1.47(2)	O(5)-B(2)-O(16) <sup>(iv)</sup>	106(1)
-O(5)	1.52(2)	O(6)-B(2)-O(12) <sup>(iii)</sup>	113(1)
Mean	1.48(2)	O(6)-B(2)-O(16) <sup>(iv)</sup>	110(1)
		O(12) <sup>(iii)</sup> -B(2)-O(16) <sup>(iv)</sup>	113(1)
		Mean	110(1)
● B(4)-O(15)	1.44(2)	O(9) <sup>(iii)</sup> -B(4)-O(14)	110(1)
-O(14)	1.45(3)	O(9) <sup>(iii)</sup> -B(4)-O(15)	111(1)
-O(20)	1.49(2)	O(9) <sup>(iii)</sup> -B(4)-O(20)	107(1)
-O(9) <sup>(iii)</sup>	1.49(2)	O(14)-B(4)-O(15)	112(1)
Mean	1.47(2)	O(14)-B(4)-O(20)	106(1)
		O(15)-B(4)-O(20)	111(1)
		Mean	110(1)
● B(6)-O(14) <sup>(iii)</sup>	1.43(2)	O(8)-B(6)-O(14) <sup>(iii)</sup>	113(1)
-O(8)	1.46(2)	O(8)-B(6)-O(19)	108(1)
-O(21)	1.48(3)	O(8)-B(6)-O(21)	107(1)
-O(19)	1.52(2)	O(14) <sup>(iii)</sup> -B(6)-O(19)	108(1)
Mean	1.48(2)	O(14) <sup>(iii)</sup> -B(6)-O(21)	111(1)
		O(19)-B(6)-O(21)	109(1)
		Mean	110(1)
● B(8)-O(3) <sup>(v)</sup>	1.44(2)	O(3) <sup>(v)</sup> -B(8)-O(7)	108(1)
-O(13)	1.46(2)	O(3) <sup>(v)</sup> -B(8)-O(13)	114(1)
-O(18)	1.49(2)	O(3) <sup>(v)</sup> -B(8)-O(18)	109(1)
-O(7)	1.49(3)	O(7)-B(8)-O(13)	110(1)
Mean	1.47(2)	O(7)-B(8)-O(18)	108(1)
		O(13)-B(8)-O(18)	107(1)
		Mean	110(1)

TABLE 4—Continued

• B(10)–O(12)	1.43(2)	O(10)–B(10)–O(12)	110(1)
–O(13) <sup>(v)</sup>	1.47(2)	O(10)–B(10)–O(13) <sup>(v)</sup>	110(1)
–O(17)	1.49(3)	O(10)–B(10)–O(17)	105(1)
–O(10)	1.50(2)	O(12)–B(10)–O(13) <sup>(v)</sup>	112(1)
Mean	1.47(2)	O(12)–B(10)–O(17)	111(1)
		O(13) <sup>(v)</sup> –B(10)–O(17)	108(1)
		Mean	110(1)
• B(11)–O(15)	1.45(3)	O(1)–B(11)–O(2)	107(1)
–O(1)	1.45(2)	O(1)–B(11)–O(11)	113(1)
–O(11)	1.48(2)	O(1)–B(11)–O(15)	110(1)
–O(2)	1.56(2)	O(2)–B(11)–O(11)	103(1)
Mean	1.49(2)	O(2)–B(11)–O(15)	111(1)
		O(11)–B(11)–O(15)	113(1)
		Mean	110(1)
Environments of thallium atoms (< 3.2 Å)			
• Tl(1)–O(5)	2.450(13)	• Tl(2)–O(2)	2.607(11)
–O(13) <sup>(vi)</sup>	2.660(11)	–O(17)	2.650(10)
–O(12) <sup>(iii)</sup>	2.864(12)	–O(11)	2.724(10)
–O(21) <sup>(iv)</sup>	2.986(8)	–O(10)	2.733(12)
–O(3)	3.006(9)		
–O(7) <sup>(vi)</sup>	3.117(8)		
–B(1)	3.186(19)		
• Tl(3)–O(12) <sup>(vii)</sup>	2.538(8)	• Tl(4)–O(20)	2.583(13)
–O(16) <sup>(viii)</sup>	2.746(13)	–O(7)	2.612(11)
–O(6) <sup>(i)</sup>	2.818(8)	–O(14)	2.723(9)
–O(10) <sup>(vii)</sup>	3.000(8)	–O(8)	2.793(10)
–O(21) <sup>(iii)</sup>	3.028(11)	–O(3) <sup>(viii)</sup>	3.191(10)
–O(4) <sup>(i)</sup>	3.196(10)	–B(3)	3.141(19)
• Tl(5)–O(15) <sup>(iii)</sup>	2.707(9)	• Tl(6)–O(13)	2.498(9)
–O(19)	2.842(12)	–O(9)	2.649(14)
–O(14) <sup>(viii)</sup>	2.931(8)	–O(18)	2.733(10)
–O(15) <sup>(viii)</sup>	2.943(12)	–O(17) <sup>(v)</sup>	3.036(9)
–O(19) <sup>(ix)</sup>	3.021(10)	–O(11) <sup>(iii)</sup>	3.137(9)
		–B(8)	3.107(20)

Note. Symmetry code: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $x + 1, y, z$ ; (iii)  $x - 1, y, z$ ; (iv)  $x, y, z + 1$ ; (v)  $-x + 1, -y + 1, -z + 1$ ; (vi)  $-x, -y + 1, -z + 1$ ; (vii)  $x, y, z - 1$ ; (viii)  $-x + 1, -y + 2, -z$ ; (ix)  $-x, -y + 2, -z + 1$ .

occurs during cooling. We can note that no peak corresponding to the  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub>  $\leftrightarrow$   $\alpha$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> transformation appears on the DTA curve. This is probably due to the heating rate used in DTA (1 and 10°C/min) being faster than that used in TRXPD (0.1 and 0.2°C/min).

### Borate Anion

The structure of the complex borate  $\beta$ -Tl<sub>2</sub>B<sub>4</sub>O<sub>7</sub> consists of a three-dimensional framework of BO<sub>3</sub> triangles ( $\Delta$ ) and BO<sub>4</sub> tetrahedra (T) linked to each other, every oxygen atom being common to two polyhedra (Fig. 3). The mean values for B–O bonds are 1.37(2) Å for the six BO<sub>3</sub> triangles and 1.47(2) Å for the six BO<sub>4</sub> tetrahedra with distances between 1.34(2) and 1.43(2) Å in the triangles and between 1.43(2) and

1.56(2) Å in the tetrahedra (Table 4). These mean values are comparable to those found in parent compounds as K<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (13) and Rb<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (14) for which the longer B–O bonds are 1.51 and 1.50 Å, respectively. A great difference comes from the structural formula of these two last compounds, which is M<sub>4</sub>B<sub>8</sub>O<sub>14</sub> with M = K or Rb instead of Tl<sub>6</sub>B<sub>12</sub>O<sub>21</sub>, which was found in the thallium borate, taking into consideration the crystallographically independent atoms. The triclinic unit cells and other crystallographic data of these two alkaline borates are reported in Table 5. We note that the unit cell volume of the thallium borate (Table 1) is 1.5 times larger than that of the alkaline borates in agreement with the big channels existing in the structure of Tl<sub>6</sub>B<sub>12</sub>O<sub>21</sub> as evidenced in Figs. 3 and 4. In the framework of this compound, two types of complex boron–oxygen anions, containing two and three classical B<sub>3</sub>O<sub>3</sub> rings having one and two boron atoms in common, can be found (Fig. 4); their shorthand notations (16, 17) are 5: 2 $\Delta$  + 3T with B(1), B(2), B(8), B(10), and B(12) and 7: 4 $\Delta$  + 3T, with the other boron atoms corresponding to the (B<sub>5</sub>O<sub>6</sub>O<sub>3</sub>)<sup>3-</sup> and (B<sub>7</sub>O<sub>9</sub>O<sub>3</sub>)<sup>3-</sup> borate anions, respectively. In these anions, the first oxygen atoms refer to those that are in the B<sub>3</sub>O<sub>3</sub> rings and the second ones to those linked to two rings following the three space directions: O(5) shares two (B<sub>5</sub>O<sub>9</sub>)<sup>3-</sup> anions and O(2) two (B<sub>7</sub>O<sub>12</sub>)<sup>3-</sup> anions; O(1), O(7), O(16), and O(18) link two different anions with five and seven boron atoms. It is interesting to note that if the first anion with five boron atoms appears in numerous borates such as, for example, Ca<sub>2</sub>(B<sub>5</sub>O<sub>9</sub>)Br (18) and Ba<sub>2</sub>(B<sub>5</sub>O<sub>9</sub>)Cl·0.5H<sub>2</sub>O and Ba<sub>2</sub>[B<sub>5</sub>O<sub>8</sub>(OH)<sub>2</sub>]OH (19), the second anion with seven boron atoms was, to our knowledge, described in one compound only, Tl<sub>4</sub>[B<sub>8</sub>O<sub>12</sub>(OH)<sub>4</sub>]·H<sub>2</sub>O with the shorthand notation 8:  $\frac{1}{\infty}$ [(7: 3 $\Delta$  + 4T) +  $\Delta$ ] (20). Complex borate anions with seven boron atoms are described in two heptaborates, but in AgSrB<sub>7</sub>O<sub>12</sub>, the shorthand notation is 7:  $\frac{2}{\infty}$ [(4-1: 2 $\Delta$  + 2T) + 2 $\Delta$  + T] (21) and in Li<sub>3</sub>B<sub>7</sub>O<sub>12</sub>, it is 7:  $\frac{3}{\infty}$ [(3: 2 $\Delta$  + 1T) + (3:  $\Delta$  + 2T) +  $\Delta$ ] (22). Borates with the same or a superior number of boron atoms are very scarce; they are often formed by the association of small borate anions with three, four, or five boron atoms as indicated by Burns *et al.* (23). Some examples are reported by Heller (17), and interestingly a new isolated anion [B<sub>9</sub>O<sub>12</sub>(OH)<sub>6</sub>]<sup>3-</sup> with nine boron atoms containing four B<sub>3</sub>O<sub>3</sub> rings was recently found in guanidinium and imidazolium borates (24); its shorthand notation is 9: 6 $\Delta$  + 3T. The structure of the two alkaline tetraborates M<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (with M = K or Rb) is different because their framework contains three types of boron–oxygen anions whose shorthand notation is given in parentheses: BO<sub>3</sub> triangles ( $\Delta$ ), B<sub>3</sub>O<sub>3</sub> rings (3:  $\Delta$  + 2T) and two B<sub>3</sub>O<sub>3</sub> rings linked together (4-1: 2 $\Delta$  + 2T) leading to 8:  $\frac{3}{\infty}$ [(4-1: 2 $\Delta$  + 2T) + (3:  $\Delta$  + 2T) +  $\Delta$ ] for the structural formula M<sub>4</sub>B<sub>8</sub>O<sub>14</sub> (13, 14). Other complex borate anions with eight boron atoms were found in other tetraborates such as

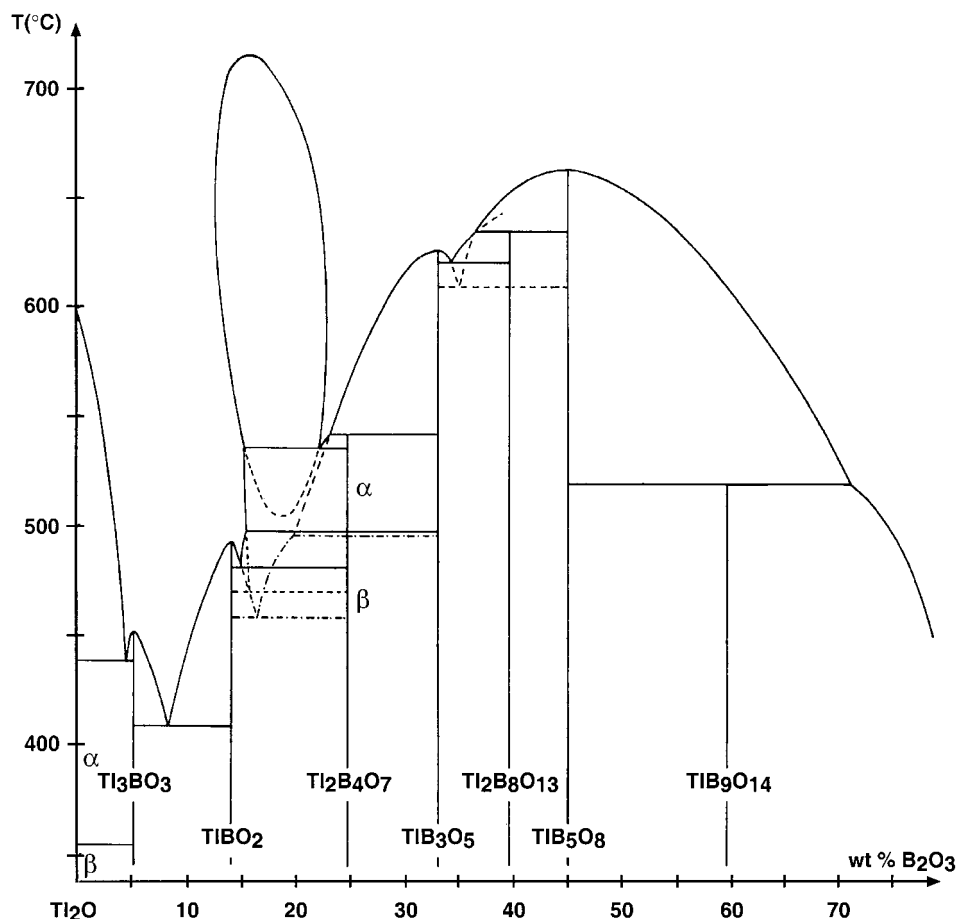


FIG. 1.  $\text{Tl}_2\text{O}$ - $\text{B}_2\text{O}_3$  binary system (2).

$\text{Na}_2\text{B}_4\text{O}_7$  (25) and  $\text{BaB}_4\text{O}_7$  (26). Therefore, the shorthand notation of the complex borate anion existing in  $\text{Tl}_6\text{B}_{12}\text{O}_{21}$  ( $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$ ) can be written as  $12: \frac{3}{\infty} [(5: 2\Delta + 3\text{T}) + (7: 4\Delta + 3\text{T})]$ . This anion is different from those found in two

hydrated dodecaborates,  $\text{Ag}_6[\text{B}_{12}\text{O}_{18}(\text{OH})_6] \cdot 3\text{H}_2\text{O}$  (27) and in  $\text{Na}_8[\text{B}_{12}\text{O}_{20}(\text{OH})_4]$  (28), whose shorthand notation is  $12: 2(6: 3\Delta + 3\text{T})$ .

#### Thallium Environments

Figure 3 shows the positions of the thallium atoms; they are located in the large channels existing in the three-dimensional borate framework. In Table 4, the thallium atoms' environments are given up to a distance of  $3.2 \text{ \AA}$ . We can see that the shortest Tl-B distance is  $3.107(20) \text{ \AA}$  for Tl(6)-B(8). Therefore, only the oxygen atoms with shorter Tl-O bonds will be considered in the oxygenated environment of the thallium atoms. The numbers of coordination four are found for Tl(2), Tl(4), and Tl(6) and five for Tl(1), Tl(3), and Tl(5). As shown in Fig. 5, all the oxygen atoms are located on the same side of the thallium atoms. So, the  $6s^2$  lone pairs of the  $\text{Tl}^+$  cations are stereochemically active as found in other complex thallium oxides such as, for example,  $\text{Tl}_3\text{BO}_3$  (3),  $\text{TlBO}_2$  (4), or  $\text{Tl}_8\text{Ge}_5\text{O}_{14}$  (29). These pairs are located on the other side of oxygen atoms in the channels existing in this structure. Interestingly, the shortest

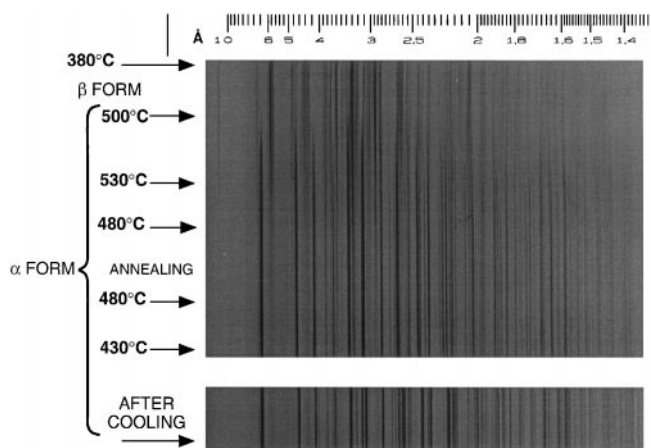


FIG. 2. Guinier-Lenné photograph of  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$ ; see text for the heating and cooling conditions.

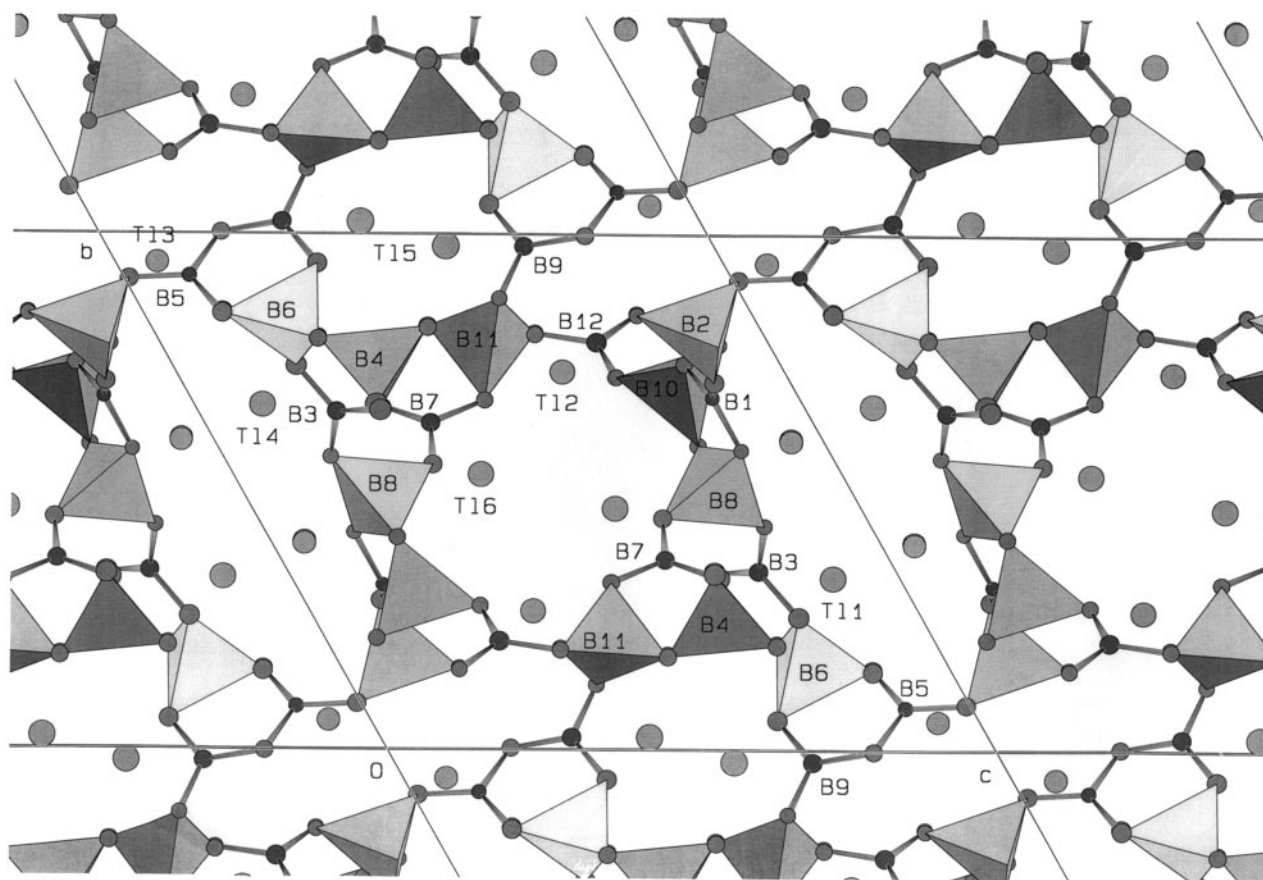


FIG. 3. Projection of the structure of  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$  on the (100) plane.

Tl–O bond in  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$  is observed for Tl(1)–O(5) at 2.450(13) Å; this value is comparable to that found in  $\text{Tl}_3\text{BO}_3$ , 2.45 Å (3),  $\text{TlBO}_2$ , 2.48 Å (4), and  $\text{Tl}_8\text{Ge}_5\text{O}_{14}$ , 2.46 Å (29). The shortest Tl–O bonds existing in other anhydrous thallium borates are 2.665 and 2.900 Å for  $\text{TlB}_3\text{O}_5$  (5) and  $\text{TlB}_5\text{O}_8$  (6), respectively. The more or less great

stereochemical activity of the lone pair of  $\text{Tl}^+$  in these compounds seems to be linked to the value of the shorter Tl–O bond found in their structures and in the number of oxygen atoms close to and on the same side of the  $\text{Tl}^+$  cations. That also explains the analogy or the difference in the structures of the thallium borates with the alkaline borates that have the same chemical formula. So,  $\text{TlB}_5\text{O}_8$  (6) is isostructural of  $\beta$ - $\text{KB}_5\text{O}_8$  (30) and no stereochemical activity of the  $\text{Tl}^+$  lone pair occurs. However, although a weak stereochemical activity of the  $\text{Tl}^+$  lone pair is observed in  $\text{TlB}_3\text{O}_5$  (5), it does not prevent it from being isostructural of  $\text{CsB}_3\text{O}_5$  (7). For all the other anhydrous thallium borates, with  $\text{B}/\text{Tl} < 3$ , the stereochemical activity of the  $\text{Tl}^+$  lone pair increases when this ratio decreases; for the oxygenated environment of  $\text{Tl}^+$  cations, the number of coordination is three for  $\text{Tl}_3\text{BO}_3$  (3), three and four for  $\text{TlBO}_2$  (4), and four and five for  $\beta$ - $\text{Tl}_2\text{B}_4\text{O}_7$  (Table 4). A similar behavior has been observed for other oxygenated thallium compounds as, for example, thallium germanates (31), for which the stereochemical activity starts with  $\text{Tl}_8\text{Ge}_5\text{O}_{14}$ , a compound with  $\text{Ge}/\text{Tl} = 0.625$  (29); therefore it seems that the charge of the counterions,  $\text{B}^{3+}$  or  $\text{Ge}^{4+}$ , has an

TABLE 5  
Crystallographic Data of  $M_4\text{B}_8\text{O}_{14}$  ( $M = \text{K}, \text{Rb}$ )

Compounds	$\text{K}_4\text{B}_8\text{O}_{14}$ (14)	$\text{Rb}_4\text{B}_8\text{O}_{14}$ (13)
Formula weight (g/mol)	466.88	652.35
Space group	$P-1$	$P-1$
$a$ (Å)	9.604	9.860
$b$ (Å)	10.413	10.653
$c$ (Å)	6.484	6.649
$\alpha$ (°)	102.7	103.4
$\beta$ (°)	101.2	101.4
$\gamma$ (°)	89.2	89.1
$V$ (Å <sup>3</sup> )	619.9	665.5
$Z$	2	2
$D_x$ (g/cm <sup>3</sup> )	2.501	3.26

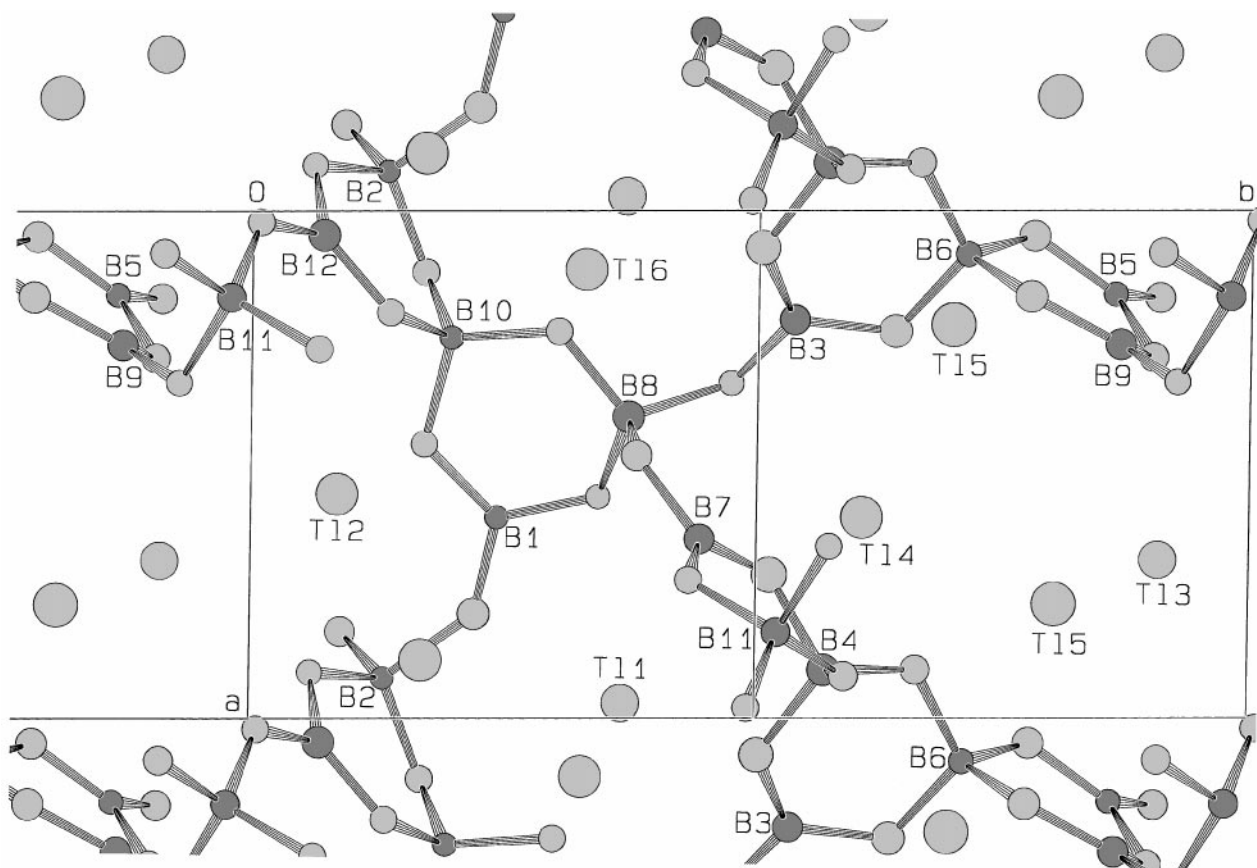


FIG. 4. Projection on (001) plane of the structure of  $\beta\text{-Tl}_2\text{B}_4\text{O}_7$  making it possible to see the complex borate anion  $12: \frac{3}{2}[(5: 2\Delta + 3T) + (7: 4\Delta + 3T)]$ ; for the sake of clarity only half of the content of a unit cell is drawn.

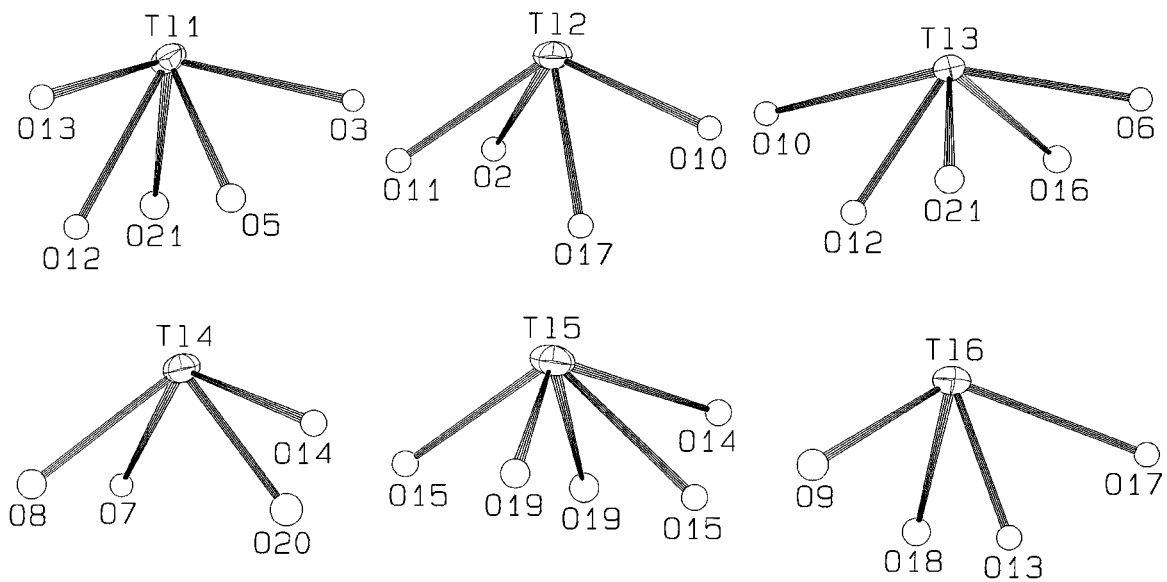


FIG. 5. Oxygenated environment of the six thallium ions in  $\beta\text{-Tl}_2\text{B}_4\text{O}_7$ .

important effect upon the stereochemical activity of the lone pair around the  $Tl^+$  cation. The three thallium borates mentioned above are not isostructural of alkaline borates with the same chemical formula. This is also observed for  $Tl_6B_{12}O_{21}$  ( $\beta$ - $Tl_2B_4O_7$ ), which does not have the same structure as  $K_4B_8O_{14}$  ( $K_2B_4O_7$ ) or  $Rb_4B_8O_{14}$  ( $Rb_2B_4O_7$ ) as discussed before.

### CONCLUSION

A new complex anion borate  $(B_{12}O_{21})^{6-}$  was found in the  $\beta$ -form of the thallium tetraborate  $Tl_2B_4O_7$ , whose structural formula is  $Tl_6B_{12}O_{21}$ ; it consists of two shorter borate anions  $(B_5O_9)^{3-}$  and  $(B_7O_{12})^{3-}$ , which are formed by two and three classical  $B_3O_3$  rings, respectively. An original framework is obtained by the linkage in the three space directions of this complex borate anion that contains six  $BO_3$  triangles ( $\Delta$ ) and six  $BO_4$  tetrahedral (T); its shorthand notation is  $12: \infty[(5: 2\Delta + 3T) + (7: 4\Delta + 3T)]$ . Thallium ions are situated inside the channels formed by the boron–oxygen three-dimensional network, toward the centers of which the stereochemically active  $6s^2$  lone pairs are directed. Upon heating, this compound leads to another form of thallium tetraborate,  $\alpha$ - $Tl_2B_4O_7$ .

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