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Crystal Structure of Thallium Triborate, TlB_3O_5

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Thallium triborate, TlB_3O_5 (TBO), crystallizes in the orthorhombic system, space group $P2_12_12_1$ with unit cell dimensions $a = 5.2099(3)$ Å, $b = 8.248(1)$ Å, and $c = 10.206(2)$ Å; $Z = 4$. The structure was solved from 1340 independent reflections to $R = 0.038$ and $R_w = 0.041$. The borate anion of the structure forms a three-dimensional framework built up from B_3O_3 rings; its shorthand notation is $3:\infty^3(2\Delta + T)$, where Δ is a BO_3 triangle and T is a BO_4 tetrahedron. This compound is isostructural with CsB_3O_5 (CBO) but some differences exist in the oxygenated surroundings of cesium and thallium cations due to the larger size of Cs^+. Like CBO, TBO may be a good candidate for nonlinear optical applications as a second harmonic generator.

INTRODUCTION

During the past few years, numerous investigations concerning new nonlinear optical crystals have been undertaken. In a very recent paper, Xia *et al.* (1) calculated the microscopic SHG coefficients for different types of borate anions and found that the B_3O_7 group is a good candidate for this use. Indeed, two important NLO crystals where this group exists have already been widely studied: LiB_3O_5 (LBO) (2) and CsB_3O_5 (CBO) (3). Another compound, TlB_3O_5 (TBO), might have a similar property because, in a previous study (4), one of us found an isotypy with CBO (5). However, there are some differences in their cell parameters. So, before examining the crystal growth and the physical properties of TBO, an accurate determination of its structure was necessary. Furthermore, a comparison with its hydrated precursor, $Tl[B_3O_4(OH)_2] \cdot 0.5H_2O$, the structure of which is known (6), and the parent compounds LBO and CBO will be presented.

EXPERIMENTAL

Sample Preparation

Stoichiometric amounts of reagent-grade Tl_2CO_3 and H_3BO_3 were mixed and ground. The powder was put in a platinum crucible and a slow heating to 300°C was performed to allow CO_2 release. Then the powder was heated to 650°C, above the melting point of 627°C (7), and left at this temperature for 12 h. After slow cooling, beautiful colorless single crystals were obtained.

Single Crystal X-Ray Diffraction Study

Data from a small single crystal of $0.042 \times 0.064 \times 0.096$ mm were collected using an Enraf–Nonius CAD-4 diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) isolated with a graphite monochromator. The crystal system is orthorhombic and the lattice constants were determined and refined from 25 reflections to be $a = 5.2099(3)$ Å, $b = 8.248(1)$ Å, and $c = 10.206(2)$ Å; $V = 438.53(9)$ Å^3; $M = 316.803$ g/mol; $D_m = 4.6$, $D_x = 4.798$; $Z = 4$; $F(000) = 544$. Systematic extinctions of $h00$, $0k0$, and $00l = 2n + 1$ reflections confirmed the $P2_12_12_1$ space group found previously (4). Intensity data were collected using the 2θ-ω scanning method up to $2\theta = 70°$, with $-8 \leq h \leq 8$, $-13 \leq k \leq 13$, and $0 \leq 1 \leq 16$. Standard reflections $1\,-2\,1$, $-1\,-2\,-1$, $-1\,2\,-1$ were monitored every 200 reflections and no significant intensity deviation was detected. Of 4028 measured reflections, 2862 had an intensity greater than three times their standard deviation and 1340 independent reflections were kept corresponding to the noncentrosymmetric space group ($R_{\text{int}} = 0.073$). Absorption corrections were performed according to De Meulenaer and Tompa's method (8) after indexing of the crystal faces ($\mu = 370.06\ \text{cm}^{-1}$); the transmission factor varied between 0.127 and 0.273 and R_{int} became 0.045. The Patterson function led to the

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coordinates of the thallium atom. Successive refinements and Fourier difference syntheses gave the positions of five oxygen atoms and two boron atoms. The last boron atom was found after the absorption correction. An extinction correction (type II crystals) was also introduced. The final *R* values with anisotropic thermal vibrations for all the atoms are $R = \sum|F_{\mathrm{obs}} - F_{\mathrm{cal}}|/\sum|F_{\mathrm{obs}}| = 0.038$ and $R_{\mathrm{w}} = (\sum w(F_{\mathrm{obs}} - F_{\mathrm{cal}})^2/\sum wF_{\mathrm{obs}}^2)^{1/2} = 0.041$ for 83 refined parameters. The scattering factors used are those for neutral atoms taken from the International Tables for X-ray Crystallography (9). Correction for anomalous dispersion was applied. The weighing scheme used is taken from the counting statistics $\sigma(I) = (I + L + R + 0.04(I - L - R)^2)^{1/2}$, where *I*, *L*, and *R* are the total intensity, left background, and right background, respectively. The atomic coordinates and the thermal motion parameters are reported in Table 1. Significant bond lengths and angles are listed in Table 2.

DESCRIPTION OF THE STRUCTURE

In this compound the boron atoms are surrounded by three (B(1) and B(2)) or four (B(3)) oxygen atoms. The BO_3 triangles and the BO_4 tetrahedron are almost regular, as the mean values of O–B–O angles are 120° and 109°, respectively (Table 2). The oxygenated environment of the thallium atoms is more difficult to determine; indeed if we consider the Tl–O distances inferior to the shorter Tl–B distance (3.19 Å), only four oxygen atoms form the first coordination sphere of thallium atoms. It is interesting to note that these four oxygen atoms are on the same side of the thallium atom (Fig. 1). This is probably due to the stereochemical effect of the lone pair of Tl^+ ions.

The two BO_3 triangles and the BO_4 tetrahedron are linked by vertices and lead to the classical B_3O_3 ring, which is the unit of borate chains. Thallium atoms are located between these chains, which form a three-dimensional framework (Fig. 2).

DISCUSSION

It is interesting to compare the structure of TlB_3O_5 with that of the only known thallium triborate hydrate, $Tl[B_3O_4(OH)_2] \cdot 0.5H_2O$, which can be considered its precursor. The structure (6) also contains chains of B_3O_3 rings. These cycles are almost the same in these two compounds, as the three boron atoms are very close to the plane formed by the three oxygen atoms: in the hydrated borate, B(1), 0.05 Å; B(2), 0.03 Å; and B(3), 0.16 Å and in the anhydrous borate, B(1), 0.260(8) Å; B(2), 0.022(9) Å; and B(3), − 0.002(8) Å. This B_3O_3 ring geometry is observed in the parent compound, $KB_3O_3(OH)_4 \cdot H_2O$(10), where the isolated $B_3O_3(OH)_4^-$ anion constituted by two BO_3 triangles and one BO_4 tetrahedron exists. The shorthand notation proposed by Christ and Clark (11) and Heller (12) can be used; the isolated unit $3{:}2\Delta + T$ ($\Delta = BO_3$ triangle, $T = BO_4$ tetrahedron) exists in $KB_3O_3(OH)_4 \cdot H_2O$. Polymerization of these units leads to the chains $3{:}\ \infty^1\ (2\Delta + T)$, which occur in $Tl[B_3O_4(OH)_2] \cdot 0.5\,H_2O$. In TlB_3O_5, the chains are linked to form a three-dimensional network $3{:}\infty^3\ (2\Delta + T)$. The successive polymerization can be described by the scheme

$$n[B_3O_3(OH)_4]^- \rightarrow nH_2O + [B_3O_4(OH)_2]_n^{n-}$$

and

$$[B_3O_4(OH)_2]_n^{n-} \rightarrow nH_2O + [B_3O_5]_n^{n-}.$$

In fact, the structural analogy between the thallium triborates is misleading because polymerization cannot be attained by heating the hydrated precursor. Indeed the dehydration of $Tl[B_3O_4(OH)_2] \cdot 0.5H_2O$ leads to an amorphous phase, and crystallized TlB_3O_5 is obtained by annealing at 500°C (6). A more precise comparison of the two thallium triborates structures can be made when the parameters and the space groups are considered. $Tl[B_3O_4$

TABLE 1

Final Atomic Coordinates, Equivalent Isotropic Thermal Vibration Parameters (Å^2), and Anisotropic Thermal Vibration Parameters (× 10^4) (e.s.d.'s in Parentheses)

Atom	*x*	*y*	*z*	*B*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tl	0.02784(10)	0.27599(6)	0.12869(6)	1.81(1)	170(2)	64.3(6)	44.1(4)	− 5.9(9)	− 12(1)	1.2(6)
O(1)	0.5536(18)	0.5512(9)	0.0576(9)	1.1(2)	151(34)	15(10)	32(8)	1(15)	22(15)	− 1(7)
O(2)	0.1831(14)	0.7274(10)	0.0800(8)	1.0(2)	118(27)	21(10)	31(8)	− 24(16)	− 23(12)	9(9)
O(3)	0.3559(16)	0.9939(9)	0.1077(10)	1.3(2)	189(33)	16(10)	32(11)	0(14)	− 27(16)	7(8)
O(4)	0.5652(15)	0.7709(10)	0.2137(8)	1.1(2)	137(28)	9(8)	35(8)	− 4(16)	− 18(12)	2(8)
O(5)	0.2940(16)	0.5367(9)	0.2456(9)	0.9(2)	79(30)	17(11)	31(9)	0(13)	11(14)	10(8)
B(1)	0.539(3)	0.933(1)	0.191(1)	0.9(3)	94(42)	25(15)	24(11)	− 7(24)	− 17(22)	− 19(11)
B(2)	0.196(3)	0.883(2)	0.041(2)	1.2(3)	107(48)	39(20)	31(14)	24(23)	0(22)	4(14)
B(3)	0.397(3)	0.652(2)	0.147(1)	1.1(3)	93(41)	42(19)	24(15)	− 7(20)	− 3(20)	21(13)

TABLE 2
Interatomic Distances (Å) and Angles (°) with e.s.d.'s in Parentheses

	B triangles		
● B(1)–O(3)	1.37(2)	O(3)–B(1)–O(4)	122(2)
–O(4)	1.36(1)	O(3)–B(1)–O(5$^{\rm i}$)	120(2)
–O(5$^{\rm i}$)	1.38(2)	O(4)–B(1)–O(5$^{\rm i}$)	118(2)
Mean value	1.37	Mean value	120
O(3)–O(4)	2.40(1)		
O(3)–O(5$^{\rm i}$)	2.39(1)		
O(4)–O(5$^{\rm i}$)	2.35(1)		
Mean value	2.38		
● B(2)–O(1$^{\rm ii}$)	1.36(2)	O(1$^{\rm ii}$)–B(2)–O(2)	120(2)
–O(2)	1.35(2)	O(1$^{\rm ii}$)–B(2)–O(3)	125(2)
–O(3)	1.41(2)	O(2) –B(2)–O(3)	115(2)
Mean value	1.37	Mean value	120
O(1$^{\rm ii}$)–O(2)	2.40(1)		
O(1$^{\rm ii}$)–O(3)	2.34(1)		
O(2) –O(3)	2.39(1)		
Mean value	2.38		
	B tetrahedron		
B(3)–O(1)	1.48(2)	O(1)–B(3)–O(2)	112(2)
–O(2)	1.45(2)	O(1)–B(3)–O(4)	109(2)
–O(4)	1.48(2)	O(1)–B(3)–O(5)	105(1)
–O(5)	1.48(2)	O(2)–B(3)–O(4)	113(2)
Mean value	1.47	O(2)–B(3)–O(5)	108(1)
		O(4)–B(3)–O(5)	109(1)
		Mean value	109
O(1)–O(2)	2.43(1)		
O(1)–O(4)	2.41(1)		
O(1)–O(5)	2.35(1)		
O(2)–O(4)	2.44(1)		
O(2)–O(5)	2.38(1)		
O(4)–O(5)	2.42(1)		
Mean value	2.41		
	B–B distances in a B_3O_3 cycle		
B(1)–B(2)	2.39(2)		
B(1)–B(3)	2.47(2)		
B(2)–B(3)	2.43(2)		
	Tl–O distances < 3.5 Å		
Tl–O(4$^{\rm iii}$)	2.662(8)		
–O(5)	2.823(8)		
–O(5$^{\rm iv}$)	2.890(8)		
–O(3$^{\rm v}$)	2.895(8)		
–O(2$^{\rm iv}$)	3.195(8)		
–O(3$^{\rm ii}$)	3.198(9)		
–O(1$^{\rm vi}$)	3.304(8)		
–O(1$^{\rm vii}$)	3.433(9)		
–O(4$^{\rm iv}$)	3.484(8)		
Angles O–Tl–O (only for the four closest oxygen atoms)			
O(4$^{\rm iii}$)–Tl–O(5)	50.6(3)		
–Tl–O(5$^{\rm iv}$)	100.6(5)		
–Tl–O(3$^{\rm v}$)	64.0(3)		
O(5)–Tl–O(5$^{\rm iv}$)	128.1(6)		
–Tl–O(3$^{\rm v}$)	110.7(5)		
O(5$^{\rm iv}$)–Tl–O(3$^{\rm v}$)	80.0(4)		

TABLE 2—*Continued*

Other distances	
Tl–B(1$^{\rm iii}$)	3.19(1)
–B(3$^{\rm iv}$)	3.35(1)
–B(2$^{\rm v}$)	3.48(2)
Tl–Tl($^{\rm vi}$)	3.724(1)

Symmetry code
(i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, 3/2 - y, -z$;
(iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (v) $x, y - 1, z$;
(vi) $x - \frac{1}{2}, \frac{1}{2} - y, -z$; (vii) $x - 1, y, z$

$(OH)_2]\cdot 0.5H_2O$(H) belongs to the *Pnma* space group with $a_H = 13.41$ Å, $b_H = 16.17$ Å, $c_H = 5.43$ Å, and $Z = 8$. We can observe that $c_H \approx a$, $b_H \approx 2b$, and $a_H > c$. There is a great analogy between these two compounds; in the hydrate, thallium atoms and water molecules are located between the $[B_3O_4(OH)_2]_n^{n-}$ chains while in the anhydrous borate, thallium atoms are located in large interstices formed by the intercrossed $[B_3O_5]_n^{n-}$ chains, which form a three-dimensional network. On the other hand, the change from $Tl[B_3O_4(OH)_2]\cdot 0.5H_2O$ (space group $Pnma = P2_{1/n}2_{1/m}2_{1/a}$) to TlB_3O_5 (space group $P2_12_12_1$) shows that the dehydration and the chain polymerization involve the disappearance of planes and centers of symmetry in the structure of the anhydrous borate where only the twofold screw axes exist.

The main structural features of TlB_3O_5 are found in the isostructural compound CsB_3O_5 (5) and also in LiB_3O_5 (13). The crystal data are $a = 6.213$ Å, $b = 8.521$ Å, $c = 9.170$ Å, $Z = 4$, space group $P2_12_12_1$ for CsB_3O_5 and $a = 8.447$ Å, $b = 7.3789$ Å, $c = 5.1408$ Å, $Z = 4$, space group $Pna2_1$ for LiB_3O_5. It is interesting to note that in CsB_3O_5 there are seven oxygen atoms around Cs^+ at distances between 3.030 and 3.342 Å; this is very different from the

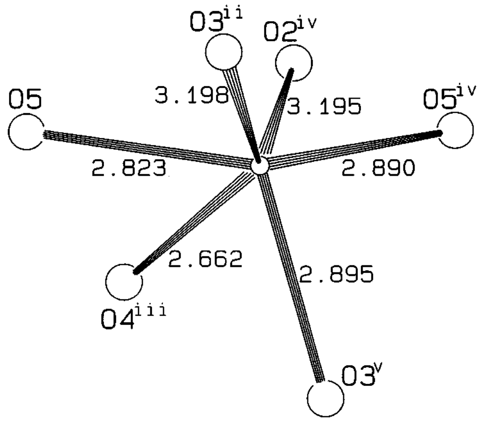

FIG. 1. Oxygenated environment of a thallium atom with distances in Å.

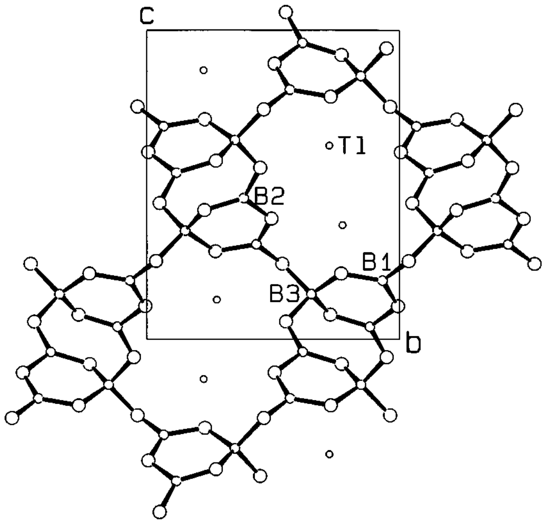

FIG. 2. Projection of the crystal structure of TlB_3O_5 onto the (100) plane; only B–O bonds are shown.

oxygenated environment of Tl^+ in TlB_3O_5 (see Fig. 1 and Table 2).

Another way to describe the structure of these three triborates is to consider that it is made up of a continuous helical network of B_3O_7 groups (one B_3O_3 ring and all the oxygen atoms linked to the boron atoms) along the axes, with thallium, cesium, or lithium atoms located in the interstices of the helical network. This description was used in the study of the lattice vibrational spectra of LiB_3O_5 (14) and also in the determination of the second harmonic generator coefficient of the borate group by Xia *et al.* (1). We can observe that TlB_3O_5 is a good candidate for use as a nonlinear optical material; it melts congruently at moderate temperature (627°C)—lower than CsB_3O_5 (842°C) (15) —while LiB_3O_5 melts incongruently and presents many problems in its crystal growth (16–19). With TlB_3O_5, the Czochralski procedure could easily be used to obtain suitable single crystals. A test performed at room temperature on powder has evidenced the second harmonic ($\lambda = 0.53$ μm) of a Nd:YAG laser radiation ($\lambda = 1.06$ μm).

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