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## Refinement of the Crystal Structure of Caesium Triborate, Cs<sub>2</sub>O·3B<sub>2</sub>O<sub>3</sub>

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Caesium triborate, Cs<sub>2</sub>O·3B<sub>2</sub>O<sub>3</sub>, crystallizes in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with unit-cell dimensions *a* = 6·213 (1), *b* = 8·521 (1), *c* = 9·170 (1) Å and *Z* = 2. The calculated density is 3·357 g cm<sup>-3</sup>. The structure has previously been determined from film data in two projections (Krogh-Moe, 1960). A refinement with three-dimensional diffractometer data has now confirmed the early determination. The *R* index obtained in the refinement is 0·039. The borate anion of the structure forms a three-dimensional framework built up from triborate groups. The boron–oxygen bond lengths (standard deviation 0·009 Å) show a normal distribution in the framework. The caesium atoms are surrounded by oxygen atoms at distances upwards of 3·030 Å.

### Introduction

The crystal structure of caesium triborate was determined by Krogh-Moe in 1960. Since this determination was based on film data in projections along two axes only, a complete three-dimensional refinement was considered desirable. A new data set was recorded with Mo *K*<sub>α</sub> radiation, on a Picker on-line single-crystal diffractometer. The crystal used for data collection

was synthesized as previously described by Krogh-Moe (1960). It had an approximately prismatic shape, 0·010 × 0·017 × 0·046 cm, with edges corresponding to the *a*, *b* and *c* axes respectively, *c* being aligned with the goniometer axis.

Unit-cell dimensions and standard errors, *a* = 6·213 ± 0·001, *b* = 8·521 ± 0·001 and *c* = 9·170 ± 0·002 Å, were obtained by the method of least squares from angle data recorded at 22°C for 12 high-angle reflexions

(based on the wavelength 0.7093 Å for Mo  $K\alpha_1$ ). With two formula units of  $\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$  in the cell, the calculated density is 3.357 g cm<sup>-3</sup>. Observed intensities were measured at 1262 different reciprocal lattice points and converted to structure factors in the usual manner. A correction for absorption was applied, with a linear absorption coefficient of 81.4 cm<sup>-1</sup>. The maximum and minimum absorption factors required to correct the observed structure factors were 2.07 and 1.48 respectively.

Starting with the parameters from the earlier work, the structure was refined by the method of least squares. The full-matrix program in the X-RAY 71 system (Stewart, Kruger, Kundell & Baldwin, 1971) was used. The atomic scattering factors for O and B were taken from *International Tables for X-ray Crystallography* (1962). The atomic scattering factors for Cs<sup>+</sup> were taken from the tables published by Cromer (1965). A dispersion correction of -0.53 for the real term and 2.49 for the imaginary term was applied to the Cs<sup>+</sup> curve (Cromer & Waber, 1965). A weighting scheme based on the statistical counting errors com-

pounded with errors assumed to be 1% of the observed intensity was used. Reflexions from all the measured reciprocal lattice points, excluding only the systematic extinctions, were initially included in the refinement. A refinement, using all reflexions, was also carried out in the Friedel mirror, but a slightly higher *R* index was obtained in this case. The nine reflexions with the strongest intensities were seen to be affected by extinction and removed from the data set during the last cycles of refinement. An *R* index of 0.039 (with reflexion multiplicity accounted for) was then obtained. The weighted *R* index is 0.052. The maximum shift to error ratio during the last cycle was 0.045. The final atomic coordinates and the thermal parameters are given in Table 1.\*

\* A list of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30330 (24 pp., 1 microfiche). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 *Final atomic parameters*

The anisotropic temperature factors are of the form  $\exp \{-2\pi^2[U_{11}(ha^*)^2 + U_{22}(kb^*)^2 + U_{33}(lc^*)^2 + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*]\}$ . Positional parameters are expressed as fractions of the cell edges. All values are multiplied by 10<sup>4</sup>.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Cs	9804.4	2588.4	1292.6	161	207	274	13	1	12
O(1)	4143	5656	565	143	89	167	7	-96	4
O(2)	6679	5306	2449	88	49	128	-15	-14	41
O(3)	7480	7147	589	220	50	144	22	96	28
O(4)	4624	7720	2328	153	48	117	21	53	6
O(5)	6270	9786	974	153	55	180	-4	86	0
B(1)	7658	8710	306	156	47	118	3	21	17
B(2)	4712	9247	1949	97	49	108	-9	17	-14
B(3)	5755	6490	1477	93	47	100	12	2	27

Standard deviations:									
Cs	0.8	0.6	0.6	2	2	2	2	2	2
O	9	6	6	20	20	20	18	18	18
B	13	8	8	26	26	26	23	23	23

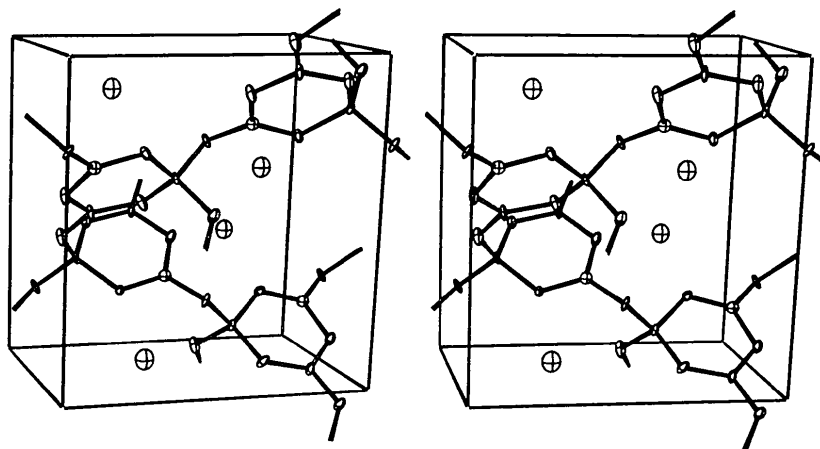


Fig. 1. A stereo pair, showing the structure of caesium triborate. The solid lines connecting vibration ellipsoids represent the boron-oxygen bonds. The isolated vibration ellipsoids represent the caesium atoms. The unit cell is oriented with the *a* axis out of the plane of the paper, the *b* and *c* axes are horizontal and vertical respectively, approximately in the plane of the paper.

### Results and discussion

The borate anion in caesium triborate forms a single three-dimensional framework. Part of the framework can be seen as a stereo pair in Fig. 1. The framework is built up from triborate groups. The boron-oxygen bond lengths reported in Table 2, exhibit normal systematic variations, depending on surroundings. Thus the B(1)-O(5) and B(2)-O(5) bonds (average length 1.397 Å) are longer than the remaining boron-oxygen bonds extending from the threefold coordinated boron atoms (average length 1.352 Å). The longer B(1)-O(5) and B(2)-O(5) bonds are the only ones where two BO<sub>3</sub> triangles share corners. The remaining oxygens [all except O(5)] bridge between a threefold, B(1) and

B(2), and a fourfold coordinated boron, B(3). Similar variations in bond lengths have been reported (Krogh-Moe, 1972). One of the two intergroup bond angles [B(1)-O(1)-B(3)] is 127.5° which is similar to values found previously (Krogh-Moe, 1972). The other intergroup bond angle [B(2)-O(2)-B(3)] is only 117.0°, however, a comparatively small value.

The thermal vibrations are indicated as vibration ellipsoids in Fig. 1. One may note that the ring atoms of the triborate group have the long axis of their vibration ellipsoids approximately perpendicular to the ring system.

The caesium atoms do not have a well defined coordination sphere of oxygens. If the coordination is arbitrarily taken to include all caesium-oxygen distances below 4 Å, each caesium atom is surrounded by ten oxygens in the range 3.030 Å to 3.967 Å (Table 2). *International Tables for X-ray Crystallography* (1962) indicates caesium-oxygen distances in the range 3.00 to 3.59 Å for caesium coordinated by eight oxygens and distances in the range 3.28 to 3.42 for caesium coordinated by twelve oxygens. With the upper limit of 3.59 Å quoted above, the caesium coordination number is seven in the present case. Since the closest mutual approach of two caesium atoms is 3.911 Å, it would seem justified to select a limit lower than 4 Å to define the oxygen coordination shell around the caesium atoms.

Table 2. *Interatomic distances and bond angles*

Boron-oxygen bond lengths (standard deviation 0.009 Å), caesium-oxygen distances (standard deviation 0.006 Å), caesium-caesium distances (standard deviation 0.001 Å) and oxygen-boron-oxygen and boron-oxygen-boron bond angles (standard deviation 0.6°)

B(1)-O(1)	1.336 Å	Cs-Cs'	3.911 Å
B(1)-O(3)	1.361	Cs-Cs''	4.809
B(1)-O(5)	1.399		
B(2)-O(2)	1.366	O(1)-B(1)-O(3)	124.5°
B(2)-O(4)	1.348	O(1)-B(1)-O(5)	115.0
B(2)-O(5)	1.396	O(3)-B(1)-O(5)	120.5
B(3)-O(1)	1.485	O(2)-B(2)-O(4)	120.5
B(3)-O(2)	1.464	O(2)-B(2)-O(5)	118.7
B(3)-O(3)	1.458	O(4)-B(2)-O(5)	120.7
B(3)-O(4)	1.484	O(1)-B(3)-O(2)	106.1
		O(1)-B(3)-O(3)	111.4
Cs-O(4)'	3.030	O(1)-B(3)-O(4)	108.4
Cs-O(2)'	3.144	O(2)-B(3)-O(3)	108.4
Cs-O(5)'	3.187	O(2)-B(3)-O(4)	110.6
Cs-O(2)	3.203	O(3)-B(3)-O(4)	111.8
Cs-O(5)	3.257		
Cs-O(1)'	3.273	B(1)-O(1)-B(3)	127.5
Cs-O(3)'	3.342	B(2)-O(2)-B(3)	117.0
Cs-O(4)''	3.663	B(1)-O(3)-B(3)	122.8
Cs-O(1)	3.813	B(2)-O(4)-B(3)	121.8
Cs-O(5)''	3.967	B(1)-O(5)-B(2)	119.5
Cs-O(2)''	4.061		

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