Acta Cryst. (1984). C**40**, 1114–1116

Structure Determination on a Twinned Crystal of Cesium Pentaborate Tetrahydrate, $Cs[B_5O_6(OH)_4].2H_2O$

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(*Received* 4 *August* 1983; *accepted* 8 *February* 1984)

Abstract. $M_r = 387 \cdot 0$, monoclinic, $P2_1/c$, $a = 11 \cdot 584\,(2)$, $b = 7 \cdot 174\,(1)$, $c = 13 \cdot 959\,(3)$ Å, $\beta = 94 \cdot 61\,(2)°$, $V = 1156 \cdot 2\,(3)$ Å^3, $Z = 4$, $D_x = 2 \cdot 15$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 32 \cdot 26$ cm^{-1}, $F(000) = 736 \cdot 89$, room temperature, $R = 0 \cdot 04$ for 1035 non-overlapping symmetrically independent reflections. $Cs[B_5O_6(OH)_4].2H_2O$ belongs to the class of soroborates and contains isolated pentaborate groups $[B_5O_6(OH)_4]$ which are held together by a hydrogen-bond system which includes the water molecules. The structure is isotypic with thallium pentaborate tetrahydrate; the larger Cs atom has 5 + 6 coordination to O atoms compared with the distorted octahedral coordination of the Tl atom.

Introduction. A series of borate compounds $M[B_5O_6(OH)_4].xH_2O$ (M = Li, Na, K, Rb, Cs, NH_4, Tl) has been reported (*Gmelins Handbuch der Anorganischen Chemie,* 1975) and a summary of the hitherto known crystal structures has been given in a previous work (Behm, 1984). The structures of Li and Cs pentaborate were then still unknown. Cesium pentaborate tetrahydrate had been assumed (Rollet & Andres, 1930) to be isotypic with the K and Rb pentaborate tetrahydrates of santite type. Borates of this type are $K[B_5O_6(OH)_4].2H_2O$ (Zachariasen & Plettinger, 1963), α-$NH_4[B_5O_6(OH)_4].2H_2O$ (Domenech, Solans & Solans, 1981) and $Rb[B_5O_6(OH)_4].2H_2O$ (Behm, 1984). The K and Rb pentaborates crystallize in space group $Aba2$, the α-NH_4 pentaborate in space group Pn. Additionally, a Cs pentaborate with formula $Cs[B_5O_6(OH)_4].2Me_2SO$ has been reported by Frohnecke, Hartl & Heller (1977). As a further step in a systematic study of the influence of the cation on the structure of hydrated pentaborates, the analogous cesium pentaborate tetrahydrate has been synthesized and its structure determined.

Experimental. $Cs[B_5O_6(OH)_4].2H_2O$ prepared from aqueous sodium pentaborate solution to which a cesium chloride solution had been added, precipitate dissolved in hot water and crystallized by slow cooling; crystals very small and appeared optically perfect; thin plates, form {100} most prominent; max. diameter 0·2 mm, max. thickness 0·05 mm. Precession photographs showed that all crystals were twinned in such a way that two individuals (designated I and II) share their *bc* plane. The twinning operation is the reflection in this *bc* plane. The resulting angle between $c_{\rm I}^*$ and $c_{\rm II}^*$ is 9·22 (2)°. Fig. 1 shows the *h*0*l* zone, indices are given for both lattices. In this zone all reflections with $l = 2n + 1$ are extinct because of the glide plane *c*. Reflections with $l = 0$ coincide for the two lattices. There is again coincidence for a hypothetical $l = 7 \cdot 5$ and its multiples. It follows that reflections with l = 7, 8, 15, ... from both single crystals are located near to each other. These reflections could not be separated during the data collection.

Data collection: crystal approximately 0·04 × 0·15 × 0·15 mm, lattice constants and extinctions indicating space group $P2_1/c$ from precession photographs, lattice parameters refined from 25 Bragg reflections centered on a Syntex $R3$ diffractometer; 7406 reflections, $3 < 2\theta < 65°$, $\bar{h}k\bar{l}$–hkl, Syntex $R3$ four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, ω scan, variable scan speed, min. 4° per min, max. 10° per min, scan range 0·8°,

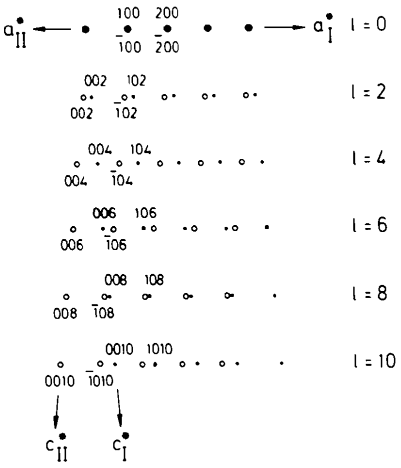

Fig. 1. Indexed *h*0*l* zone; for individual I, points with indices given above; for individual II, circles with indices given below.

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background/scan ratio 0·5, 3 standard reflections every 100 reflections with variation ±2%; Lorentz and polarization corrections and all further calculations with *SHELXTL* (Sheldrick, 1981) on a NOVA 3 computer; absorption correction using Gaussian quadrature method of *SHELXTL* with 128 sampling points and optically measured crystal dimensions as above, max. transmission 0·86, min. 0·64; averaging gave 1301 symmetrically independent reflections with $F > 5\sigma_{F_o}$ (σ_{F_o} from counting statistics), $2\theta < 50°$, $R(\text{merge}) = 0{\cdot}043$ (unit weight) and $R(\sigma) = 0{\cdot}049$, $R(\sigma) = \sum\sigma_{F_o}/\sum F_o$ and $R(\text{merge}) = (\sum\{N\sum[F(\text{mean}) - F_o]^2\}/\sum[(N-1)\sum(F_o^2)])^{1/2}$; atomic scattering factors and dispersion coefficients for Cs, O, B and H from *International Tables for X-ray Crystallography* (1974); structure solved with Patterson methods; although certain intensity data contain contributions from both crystals the whole structure could be recognized from Fourier map after Cs atom correctly located; all nonhydrogen atoms refined (on F), anisotropic thermal parameters, $R = 0{\cdot}066$; as expected, reflections with $l = 0,7,8,15$ showed large differences between obs. and calc. structure factors and were eliminated from data set, leaving 1035 symmetrically independent reflections due to only one of the two individuals; $R = 0{\cdot}042$; from difference Fourier map H atoms found; structure refined anisotropically for Cs, O and B and isotropically for H; $R = 0{\cdot}040$, $R_w = 0{\cdot}033$, $w = (1/\sigma_F^2)$, $S = 1{\cdot}22$, normal probability slope 1·03; max. final Δ/σ 0·010, mean 0·002; max. height in final difference map 0·7 e Å^{-3} in neighborhood of the Cs atom, min. −0·6 e Å^{-3}; volume ratio of the two individuals determined from *hk*0 intensities to be approximately equal; it follows from the type of twinning that these intensities contain contributions from both individuals. The final atomic parameters are listed in Table 1.*

Discussion. $\mathrm{Cs[B_5O_6(OH)_4].2H_2O}$ is a soroborate which is found to be isotypic with thallium pentaborate tetrahydrate described by Woller & Heller (1981). The previously assumed isotypism with the santite structure is not confirmed. The interatomic distances are given in Table 2 and compared with the values for Tl pentaborate from which the atomic numbering is adopted. The packing of the structure is shown in Fig. 2. The twinning is caused by the layer-like packing of the Cs atoms and the pentaborate groups. The twin mirror plane is expected to lie in a section parallel to the *bc* plane at $x = 0{\cdot}25$, 0·75. A reflection of the structure in this plane leaves the interatomic distances almost invariant.

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* Lists of structure factors, bond angles and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39254 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atom coordinates and temperature factors* (Å^2)

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
Cs	0·2551 (1)	0·2102 (1)	0·4222 (1)	0·047 (1)*
O(12)	0·6694 (4)	0·1844 (8)	0·3395 (4)	0·032 (2)*
O(13)	0·6904 (4)	0·5192 (7)	0·3673 (4)	0·030 (2)*
O(14)	0·8313 (4)	0·3037 (8)	0·4370 (3)	0·032 (2)*
O(15)	0·8135 (4)	0·3584 (8)	0·2647 (4)	0·032 (2)*
O(23)	0·5056 (4)	0·3728 (7)	0·3655 (4)	0·035 (2)*
O(45)	0·9987 (4)	0·3539 (8)	0·3509 (4)	0·034 (2)*
O(2)	0·4804 (4)	0·0550 (8)	0·3468 (5)	0·044 (2)*
O(3)	0·5263 (4)	0·6970 (8)	0·3918 (4)	0·039 (2)*
O(4)	1·0230 (5)	0·276 (1)	0·5126 (4)	0·045 (2)*
O(5)	0·9819 (4)	0·3896 (9)	0·1827 (4)	0·042 (2)*
O(10)	0·2145 (5)	0·3543 (8)	0·2026 (4)	0·046 (2)*
O(20)	0·7040 (5)	0·191 (1)	0·0961 (4)	0·063 (3)*
B(1)	0·7495 (7)	0·342 (1)	0·3518 (7)	0·031 (3)*
B(2)	0·5544 (7)	0·197 (2)	0·3508 (7)	0·032 (3)*
B(3)	0·5740 (8)	0·529 (1)	0·3732 (7)	0·028 (3)*
B(4)	0·9499 (7)	0·313 (2)	0·4359 (7)	0·034 (3)*
B(5)	0·9308 (7)	0·369 (2)	0·2661 (7)	0·032 (3)*
H(2)	0·528 (5)	−0·035 (9)	0·346 (4)	0·03 (3)
H(3)	0·44 (1)	0·70 (2)	0·395 (8)	0·14 (5)
H(4)	1·006 (7)	0·26 (1)	0·555 (5)	0·03 (3)
H(5)	1·061 (5)	0·406 (9)	0·192 (4)	0·02 (2)
H(11)	0·22 (1)	0·29 (2)	0·167 (8)	0·14 (4)
H(12)	0·27 (1)	0·50 (3)	0·20 (1)	0·24 (8)
H(21)	0·747 (5)	0·173 (8)	0·056 (4)	0·01 (2)
H(22)	0·731 (8)	0·25 (1)	0·151 (6)	0·08 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Interatomic distances* (Å) *for cesium pentaborate tetrahydrate compared with the corresponding values found in thallium pentaborate tetrahydrate*

	Cs	Tl
M–O(4$^{\rm i}$)*	3·097 (6)	3·024 (7)
–O(2)	3·098 (5)	3·011 (8)
–O(45$^{\rm i}$)	3·224 (5)	2·976 (7)
–O(10)	3·233 (6)	2·835 (9)
–O(23)	3·283 (5)	2·972 (7)
–O(20$^{\rm ii}$)	3·491 (8)	2·91 (1)
–O(13$^{\rm iii}$)	3·536 (5)	
–O(3$^{\rm iii}$)	3·541 (5)	
–O(15$^{\rm iv}$)	3·670 (5)	
–O(20$^{\rm iv}$)	3·768 (8)	
–O(5$^{\rm iv}$)	3·785 (6)	
B(1)–O(12)	1·46 (1)	1·49 (1)
–O(13)	1·47 (1)	1·47 (1)
–O(14)	1·49 (1)	1·49 (1)
–O(15)	1·48 (1)	1·46 (1)
B(2)–O(12)	1·36 (1)	1·34 (1)
–O(23)	1·40 (1)	1·40 (1)
–O(2)	1·33 (1)	1·33 (1)
B(3)–O(13)	1·36 (1)	1·37 (1)
–O(23)	1·37 (1)	1·37 (1)
–O(3)	1·36 (1)	1·37 (1)
B(4)–O(14)	1·38 (1)	1·34 (1)
–O(45)	1·39 (1)	1·38 (1)
–O(4)	1·34 (1)	1·36 (1)
B(5)–O(15)	1·36 (1)	1·34 (1)
–O(45)	1·37 (1)	1·38 (1)
–O(5)	1·36 (1)	1·36 (1)

* Symmetry code is given in Table 3.

The interatomic distances within the pentaborate groups agree well with the values for the Tl pentaborate. The mean B—O distance for the trigonally coordinated B atom is 1·36 (1) Å, for the tetrahedrally coordinated B atom 1·48 (1) Å. As has been found for Tl pentaborate the B(2)—O(23) bond in the pentaborate ring is significantly elongated to 1·40 (1) Å. The bond angles in the BO_4 tetrahedron are close to the ideal angle, maximum 112·8 (6), minimum 108·1 (7)°. The O—B—O angles of three of the four BO_3 groups show only small deviations from 120°, maximum 123·4 (8), minimum 116·9 (7)°. Rather large deviations are found for the $B(2)O_3$ group, maximum 125·2 (9), minimum 115·4 (7)°, which seems to be strongly distorted by close contacts with the Cs cation. The O—H distances found in the hydroxyl groups are in the range 0·65 (7) to 1·01 (1) Å as are the O—H distances of the water molecule $H_2O(20)$. The H atoms of the water molecule $H_2O(10)$ have rather high temperature factors and large differences in bond lengths. The uncertainties arising from the separation of the intensity contributions of the two individuals and the deficiencies of the data set prevent a detailed analysis of calculated O—H distances.

In contrast to the distorted octahedral coordination observed for the Tl ion, the bigger Cs atom has a 5 + 6 coordination to O atoms: five Cs—O distances fall in the range 3·097 (6) to 3·283 (5) and six 3·491 (8) to 3·785 (6) Å. Further Cs—O distances are longer than 4·0 Å. The six distances which are comparable to the Tl—O octahedral bonds are approximately 0·28 Å longer than these, in accordance with the larger ionic radius of the Cs ion: [Cs(CN10) = 1·81 and Cs(CN12) = 1·88 Å, Tl(CN6) = 1·50 Å; values given by Shannon & Prewitt (1969)]. Since the Cs—O bonds (O of the pentaborate group) are almost parallel to the *a* direction, this lattice constant increases significantly by about 0·3 Å compared with the Tl compound, while the other constants *b* and *c* are not changed. The Cs ion itself makes a displacement of about 0·26 (1) Å out of the *c* glide plane and about 0·19 (1) Å in the *c* direction to allow for the longer Cs—O distances perpendicular to the *a* direction. The pentaborate groups are held together through a hydrogen-bond system which includes the water molecules. The O—H···O bond distances are listed in Table 3. Except for the higher coordination number of the Cs ion the same arrangement and topology of interatomic bonds is found as in thallium pentaborate tetrahydrate.

Table 3. O—H···O *distances* (Å) *in the hydrogen-bond system of cesium pentaborate tetrahydrate compared with the corresponding values found in thallium pentaborate tetrahydrate*

	Cs	Tl
O(2)–H(2)	0·85 (6)	
O(3)–H(3)	1·0 (1)	
O(4)–H(4)	0·65 (7)	
O(5)–H(5)	0·92 (7)	
O(10)–H(11)	0·7 (1)	
O(10)–H(12)	1·3 (2)	
O(20)–H(21)	0·78 (7)	
O(20)–H(22)	0·91 (9)	
$O(2)–O(3^{i})$	2·687 (8)	2·68 (1)
$O(3)–O(20^{ii})$	2·687 (8)	2·70 (1)
$O(4)–O(5^{vi})$	2·732 (8)	2·73 (1)
$O(5)–O(10^{vii})$	2·699 (8)	2·69 (1)
$O(10)–O(12^{ii})$	2·809 (8)	2·76 (1)
$O(10)–O(13^{iv})$	2·848 (8)	2·82 (1)
$O(20)–O(14^{viii})$	2·763 (8)	2·75 (1)
O(20)–O(15)	2·848 (8)	2·83 (1)

Symmetry code: (i) $-1 + x, y, z$; (ii) $1 - x, 0{\cdot}5 + y, 0{\cdot}5 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $1 - x, -0{\cdot}5 + y, 0{\cdot}5 - z$; (v) $x, -1 + y, z$; (vi) $x, 0{\cdot}5 - y, 0{\cdot}5 + z$; (vii) $1 + x, y, z$; (viii) $x, 0{\cdot}5 - y, -0{\cdot}5 + z$.

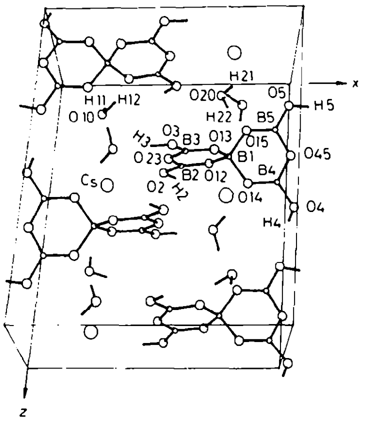

Fig. 2. The structure of $Cs[B_5O_6(OH)_4].2H_2O$ with atomic numbering.

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