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The Crystal Structure of Calcium Borate Chloride $\text{CaCl}_2 \cdot \text{Ca}_3(\text{BO}_3)_2$

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The structure of $\text{CaCl}_2 \cdot \text{Ca}_3(\text{BO}_3)_2$ has been determined by direct methods. The effect of rationally dependent atomic coordinates on the phase-determining procedure is described. The structure consists of Ca^{2+} , Cl^- and BO_3^{3-} ions arranged in distinct, mutually alternating anionic and cationic layers parallel to (102). The BO_3 groups are practically planar with $\text{B}-\text{O} = 1.403, 1.391$ and 1.390 Å. The sevenfold coordination around Ca is represented by two types of polyhedra, CaCl_3O_4 and CaCl_2O_5 . Each O atom is surrounded by three Ca atoms and one B atom in the form of a slightly distorted tetrahedron. The e.s.d.'s for the bond lengths are 0.001–0.003 Å, for the bond angles 0.02–0.25°. The final R is 0.037.

Introduction

$\text{Ca}_2\text{BO}_3\text{Cl}$ is an intermediate phase in the system $\text{Ca}_3(\text{BO}_3)_2-\text{CaCl}_2$ (Majling, Figusch, Čorba & Hanic, 1974). The existence of two different coordination numbers, triangular or tetrahedral, in borate structures and the fact that the O atoms in oxy-ions may be replaced by halogen atoms to form oxy-halide ions, $\text{MO}_a\text{X}_b^{n-}$, raised a question as to whether $\text{Ca}_2\text{BO}_3\text{Cl}$ is calcium borate chloride $\text{CaCl}_2 \cdot \text{Ca}_3(\text{BO}_3)_2$, or calcium chloroborate, $\text{Ca}_2(\text{BO}_3\text{Cl})$.

Crystallographic and intensity data

Recently, the crystal data for $\text{Ca}_2\text{BO}_3\text{Cl}$ were published (Majling *et al.*, 1974): $a = 3.9484$ (4), $b = 8.692$ (2), $c = 12.402$ (2) Å, $\beta = 100.27$ (1)°, $V = 418.8$ Å³, $Z = 4$, $D_m = 2.76$ (1), $D_x = 2.77$ g cm⁻³, space group $P2_1/c$.

Single crystals prepared according to Majling *et al.* (1974) were twinned, (010) being the plane of twinning as determined from Weissenberg photographs. The crystal used for the structure determination had to be cut from a twin in the form of a triangular prism with

length 0.04 cm and the triangle side 0.02 cm. The intensities of 1243 independent reflexions (up to $2\theta = 60^\circ$) were collected on a four-circle fully automated Picker FACS-1 diffractometer by a θ - 2θ scan technique (scan speed 1° min^{-1} with 20 s background count on each side of the peak) with Zr-filtered Mo $K\alpha$ radiation. Two standard reflexions were measured after every 50 reflexions to check stability. The 1125 reflexions which had $I > 3\sigma(I)$ were considered to be observed; the remaining 118 were assumed to be unobserved. Intensities were converted to structure factors with application of Lorentz, polarization and absorption corrections (Coppens, Leiserowitz & Rabinovich, 1965) with $\mu = 30.7 \text{ cm}^{-1}$. The normalized structure factors were calculated by estimating the statistical relationship between the mean intensity within limited ranges of $\sin^2 \theta$ values and the sum of the squares of the scattering factors of all atoms in the unit cell. The scattering factors of Ca^{2+} , Cl^- , O^- , and B were from Cromer & Mann (1968).

Structure determination and refinement

A characteristic feature of the Patterson function $P(uvw)$ was the occurrence of maxima on the planes parallel to (010) at $v = 0, \frac{1}{4}$, and $\frac{1}{2}$. Such an interatomic vector distribution imposes a limitation upon the possible y_i coordinates of the heavy atoms in Fourier space which can only be close to ± 0.125 and ± 0.375 . It means that the structure contains i atoms with rational coordinates y_i satisfying the condition

$$\sum_{i=1}^v m_i y_i = u,$$

where u and m_i are integers. However, any two atoms in general positions, having as a difference of any of their corresponding coordinates, say Δy_i , a rational number, represent also a rationally dependent pair. The characteristic effect of the existence of rationally dependent atoms is that $\langle |E_s|^2 \rangle_s$ differs significantly from unity over subsets of hkl (Hauptman & Karle, 1959).

In the present work, if k is even then $\langle |E_{hkl}|^2 \rangle_{k=2n} = 1.372$; if k is odd, then $\langle |E_{hkl}|^2 \rangle_{k=2n+1} = 0.714$. The average $\langle |E_h|^2 \rangle_h$ over all the vectors in reciprocal space still remains unity. Phase-determining formulae such as \sum_1 and \sum_2 maintain their validity provided that re-

normalization has first been carried out (Hauptman & Karle, 1959). In this case, an equal number of the contributors to each subset allows renormalization simply through multiplication of the $|E_{hkl}|_{k=2n}$ values by $(1/1.372)^{1/2}$ and the $|E_{hkl}|_{k=2n+1}$ values by $(1/0.714)^{1/2}$. The phases of 158 E_{hkl} with $|E_h| \geq 1.65$ (72 with $k=2n$ and 86 with $k=2n+1$) could be established with a local version of a tangent formula program *TANFOR* (Drew & Larson, 1968). Originally, there were only 8 reflexions with $k=2n+1$ among 80 E_{hkl} having $|E_h| \geq 1.96$ and their phases remained undetermined. The E map based on 158 E_h coefficients revealed the positions of all atoms. A full-matrix least-squares refinement was performed with the *TLS* program (Novák, 1973), a version of *ORFLS* (Busing, Martin & Levy, 1962). Isotropic refinement decreased the R to 0.23. At this stage, anisotropic temperature factors were introduced and R dropped to 0.057. Since an inspection of the F_o/F_c list indicated the presence of extinction, a correction (Stout & Jensen, 1968) was made. Although this procedure is not fully satisfactory, the agreement between F_o and F_c for 49 affected reflexions improved markedly. Two more cycles of refinement with all 1243 data gave a final $R = 0.037$, $R_w = 0.087^*$ with weights $w_i = 1/\sigma_i^2$ derived from counting statistics. R and R_w for observed reflexions only were 0.034 and 0.079, respectively. The maximum shift in positional parameters during the last cycle was less than $\frac{1}{5}$ of the e.s.d.; the average shift did not exceed $\frac{1}{10}$.

The final coordinates and anisotropic thermal parameters are given in Table 1.†

Description and discussion of the structure

The structure of $\text{CaCl}_2 \cdot \text{Ca}_3(\text{BO}_3)_2$ consists of Ca^{2+} , Cl^- and BO_3^{3-} ions. They are arranged in distinct, mutually alternating anionic and cationic layers parallel to (102). The whole structure also forms infinite columns along y . These columns are bonded into a three-dimensional structure by Ca-O-Cl polyhedra. The dis-

$$* R_w = \left[\sum_i w_i (|F_o| - |F_c|)^2 / \sum_i w_i |F_o|^2 \right]^{1/2}.$$

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31558 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final atom parameters and their estimated standard deviations

The values have been multiplied by 10^4 . The temperature factor is in the form:

$$T_i = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca(1)	2934 (1)	6173 (05)	3605 (04)	86 (5)	19 (1)	8.5 (5)	-0.3 (1)	8 (1)	-2.2 (2)
Ca(2)	3289 (1)	1214 (05)	3836 (05)	80 (5)	19 (1)	7 (05)	1.4 (1)	7 (1)	1.3 (2)
Cl	1989 (2)	8747 (05)	876 (1)	158 (5)	28 (1)	16 (05)	12 (1)	15 (1)	0.2 (3)
O(1)	4804 (5)	3584 (2)	722 (2)	168 (12)	21 (2)	12 (1)	5 (3)	17 (3)	2 (1)
O(2)	2244 (4)	2305 (2)	2053 (1)	109 (10)	24 (2)	10 (1)	-3 (3)	10 (2)	3 (1)
O(3)	1988 (4)	5104 (2)	1878 (1)	140 (10)	17 (2)	11 (1)	3 (3)	7 (2)	-1 (1)
B	2906 (8)	3667 (3)	1560 (3)	87 (7)	37 (3)	8 (2)	-6 (5)	3 (4)	0 (1)

tances between two columns in the x and z directions are 1.580 and 1.985 Å, respectively.

The BO_3 group is practically planar with the B atom 0.025 Å out of the plane defined by the three O atoms. Although this deviation from an ideal triangular arrangement is small, it is eight times the standard deviation of the B atom in the x direction, the least favourable one, and the sum of the O–B–O angles is slightly less than 360° (359.9°). The diversity in O–B–O angles (117.25 , 117.80 , and 124.85°), O–O–O angles (59.02 , 58.77 , 62.21°) and in B–O and O–O distances corrected for the thermal motion (1.403, 1.391, 1.390 Å and 2.371, 2.451, 2.377 Å, respectively) suggest that the O atoms do not form an equilateral triangle and the B atom is not in ideal sp^2 hybridization (Fig. 1). Similar non-planarity of the BO_3^{3-} anion has been observed by Schuckmann (1969) and Vegas, Cano & Garcia-Blanco (1974) in $\text{Ca}_3(\text{BO}_3)_2$ with the B atom 0.031 Å from the plane of O atoms. The whole BO_3 group is coordinated by seven different Ca atoms in an approximately trigonal prismatic arrangement with an extra Ca atom opposite a prismatic face (Table 2, Fig. 2).

Table 2. *Interatomic distances and angles in the BO_3 group and the $(\text{BO}_3)\text{Ca}_7$ coordination polyhedron*

B—O(1)	1.403 (3) Å	O(1)—B—O(2)	117.25 (22)°
B—O(2)	1.391 (3)	O(2)—B—O(3)	124.85 (25)
B—O(3)	1.390 (3)	O(1)—B—O(3)	117.80 (22)
O(1)—O(2)	2.371 (3)	O(1)—O(2)—O(3)	59.02 (7)
O(2)—O(3)	2.451 (3)	O(1)—O(3)—O(2)	58.77 (7)
O(1)—O(3)	2.377 (3)	O(2)—O(1)—O(3)	62.21 (8)
B—Ca(1)	3.347 (3) Å	B—Ca(1 ⁱⁱⁱ)	2.755 (3) Å
B—Ca(2 ⁱⁱ)	2.773 (3)	B—Ca'(1 ⁱⁱ)	3.150 (3)
B—Ca'(2 ⁱⁱ)	3.275 (3)	B—Ca'(2 ⁱⁱⁱ)	3.413 (3)

The interatomic distances and bond angles listed in Tables 2, 3, 4, and 5 were computed with *ORFFE* (Busing, Martin & Levy, 1964). They include the lattice parameter errors and are averaged over the thermal motion on the assumption of an independent movement of the atoms. The equivalent positions are: (i) $\bar{x}, \bar{y}, \bar{z}$; (ii) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$. The atoms marked by a prime are from neighbouring unit cells.

However, the average interatomic distances and angles in the BO_3 group are of the usual order of magnitude. The average B–O distance uncorrected for thermal motion is 1.382 Å, the average O–B–O angle 119.97° , comparable to 1.384 Å and 119.95° found in $\text{Ca}_3(\text{BO}_3)_2$ (Vegas, Cano & Garcia-Blanco, 1974) and to that in $\text{Ni}_3(\text{BO}_3)_2$ (B–O 1.383 Å; Pardo, Martinez-Ripoll & Garcia-Blanco, 1971) and LuBO_3 (B–O 1.370 Å; Abrahams, Bernstein & Keve, 1971). However, in $\text{Ca}_3(\text{BO}_3)_2$ and LuBO_3 , the threefold symmetry of the BO_3 group is preserved by the space group symmetry.

The coordination number of the Ca atom is seven. There are two types of Ca coordination polyhedra: CaCl_2O_5 and CaCl_3O_4 . As indicated in Fig. 3, the coordination polyhedra can be visualized as being formed from tetragonal and trigonal pyramids with approximately parallel bases and the Ca atom at their com-

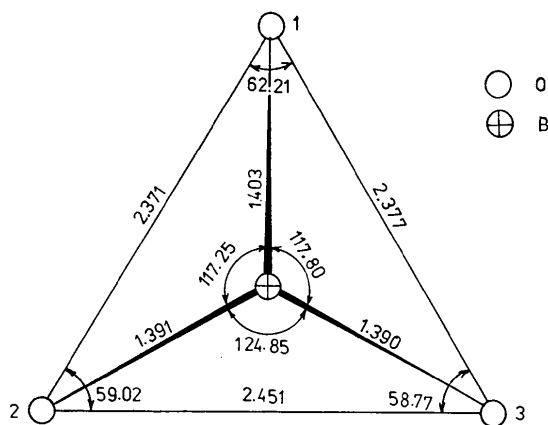


Fig. 1. Bond lengths and angles in the BO_3 group.

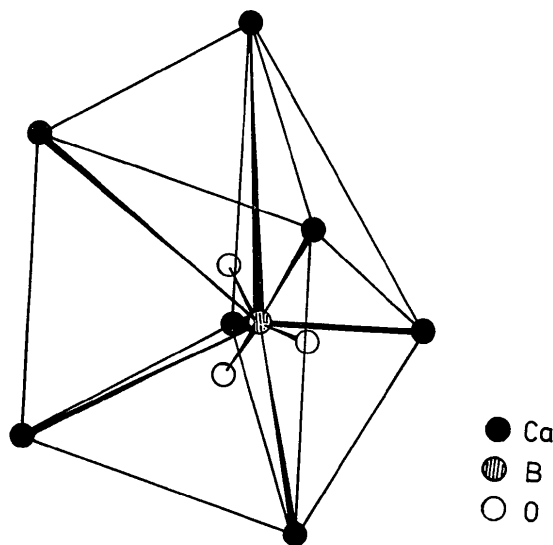


Fig. 2. Packing of Ca atoms about the BO_3 group.

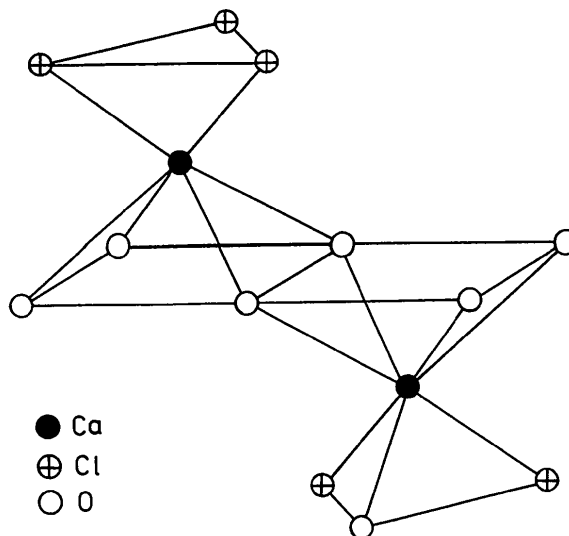


Fig. 3. The Ca coordination polyhedra in $\text{CaCl}_2 \cdot \text{Ca}_3(\text{BO}_3)_2$.

mon apex. The pyramids are rotated around the axis perpendicular to the pyramid bases to make the mutual ligand distances as large as possible. The Cl atoms are always situated at the corners of the trigonal base. The Ca coordination polyhedra are linked by sharing common edges to form a three-dimensional network. The interatomic distances averaged over the thermal motion and corrected for lattice constant errors are listed in Table 3.

Table 3. *Interatomic distances and angles in the Ca(1)O₄Cl₃ and Ca(2)O₅Cl₂ coordination polyhedra*

Ca(1)–O(1 ⁱⁱ)	2.379 (2) Å	O(1 ⁱⁱ)–Ca(1)–O(2 ⁱⁱ)	59.20 (7)°
Ca(1)–O(2 ⁱⁱ)	2.417 (2)	O(2 ⁱⁱ)–Ca(1)–O(3)	81.76 (6)
Ca(1)–O(3)	2.311 (2)	O(3)–Ca(1)–O'(2 ⁱⁱ)	81.67 (7)
Ca(1)–O'(2 ⁱⁱ)	2.291 (2)	O'(2 ⁱⁱ)–Ca(1)–O(1 ⁱⁱ)	90.13 (6)
Ca(1)–Cl ⁱⁱ	2.907 (1)	Cl ⁱⁱ –Ca(1)–Cl ⁱⁱⁱ	83.72 (3)
Ca(1)–Cl ⁱⁱⁱ	3.020 (1)	Cl ⁱⁱⁱ –Ca(1)–Cl ⁱⁱⁱ	67.11 (3)
Ca(1)–Cl ⁱⁱⁱⁱ	2.913 (1)	Cl ⁱⁱⁱⁱ –Ca(1)–Cl ⁱⁱⁱ	90.33 (3)
Ca(2)–O(3 ⁱⁱ)	2.410 (2)	O(3 ⁱⁱ)–Ca(2)–O'(1 ⁱⁱ)	58.55 (7)
Ca(2)–O(2)	2.381 (2)	O'(1 ⁱⁱ)–Ca(2)–O'(3 ⁱⁱ)	85.21 (8)
Ca(2)–O'(3 ⁱⁱ)	2.330 (2)	O'(3 ⁱⁱ)–Ca(2)–O(2)	79.37 (7)
Ca(2)–O(1 ⁱⁱ)	2.445 (2)	O(2)–Ca(2)–O(3 ⁱⁱ)	80.46 (6)
Ca(2)–Cl ⁱⁱ	2.872 (1)	O(1 ⁱⁱⁱ)–Ca(2)–Cl ⁱⁱ	76.74 (5)
Ca(2)–Cl ⁱⁱⁱ	3.100 (1)	Cl ⁱⁱ –Ca(2)–Cl ⁱⁱⁱ	82.87 (3)
Ca(2)–O(1 ⁱⁱⁱ)	2.321 (2)	Cl ⁱⁱⁱ –Ca(2)–O(1 ⁱⁱⁱ)	89.67 (5)

The coordination number of the O atoms is four. Each O atom is surrounded by three Ca atoms and one B atom in the form of a distorted tetrahedron (Table 4).

Table 4. *Interatomic distances (Å) and angles (°) in the OBca₃ polyhedra*

O(1)–B	1.403 (3)	B—O(1)–Ca(1 ⁱⁱ)	90.1 (1)
O(1)–Ca(1 ⁱⁱ)	2.379 (2)	B—O(1)–Ca(2 ⁱⁱ)	88.2 (1)
O(1)–Ca(2 ⁱⁱ)	2.445 (2)	B—O(1)–Ca'(2 ⁱⁱⁱ)	132.5 (2)
O(1)–Ca'(2 ⁱⁱⁱ)	2.321 (2)	Ca(1 ⁱⁱ)–O(1)–Ca(2 ⁱⁱ)	131.87 (9)
		Ca(2 ⁱⁱ)–O(1)–Ca'(2 ⁱⁱⁱ)	99.80 (7)
		Ca'(2 ⁱⁱⁱ)–O(1)–Ca(1 ⁱⁱ)	115.87 (8)
O(2)–B	1.391 (3)	B—O(2)–Ca(2)	137.8 (2)
O(2)–Ca(2)	2.381 (2)	B—O(2)–Ca(1 ⁱⁱ)	88.7 (2)
O(2)–Ca(1 ⁱⁱ)	2.417 (2)	B—O(2)–Ca'(1 ⁱⁱ)	116.1 (2)
O(2)–Ca'(1 ⁱⁱ)	2.291 (2)	Ca(2)–O(2)–Ca(1 ⁱⁱ)	97.82 (6)
		Ca(1 ⁱⁱ)–O(2)–Ca'(1 ⁱⁱ)	114.45 (8)
		Ca'(1 ⁱⁱ)–O(2)–Ca(2)	99.01 (7)
O(3)–B	1.390 (3)	B—O(3)–Ca(1)	128.6 (2)
O(3)–Ca(1)	2.311 (2)	B—O(3)–Ca(2 ⁱⁱ)	89.9 (1)
O(3)–Ca(2 ⁱⁱ)	2.410 (2)	B—O(3)–Ca'(2 ⁱⁱ)	122.1 (2)
O(3)–Ca'(2 ⁱⁱ)	2.330 (2)	Ca(1)–O(3)–Ca(2 ⁱⁱ)	99.97 (7)
		Ca(2 ⁱⁱ)–O(3)–Ca'(2 ⁱⁱ)	113.25 (8)
		Ca'(2 ⁱⁱ)–O(3)–Ca(1)	99.95 (6)

Coordination polyhedra around the Cl atoms can be described as distorted tetragonal pyramids with the Cl atom close to the centre of the base (Table 5).

Table 5. *Interatomic distances and angles in the ClCa₄ polyhedron*

Cl–Ca(2 ⁱⁱ)	2.872 (1) Å	Ca(2 ⁱⁱ)–Cl–Ca(1 ⁱⁱ)	97.01 (3)°
Cl–Ca(1 ⁱⁱ)	2.907 (1)	Ca(1 ⁱⁱ)–Cl–Ca'(1 ⁱⁱ)	83.73 (2)
Cl–Ca'(1 ⁱⁱ)	3.020 (1)	Ca'(1 ⁱⁱ)–Cl–Ca'(2 ⁱⁱ)	90.00 (3)
Cl–Ca'(2 ⁱⁱ)	3.100 (1)	Ca'(2 ⁱⁱ)–Cl–Ca(2 ⁱⁱ)	82.87 (2)

The calculations were performed on a TESLA 200 computer at the Laboratory of Computing Machines, Faculty of Mechanical Engineering, Technical University, Brno and on a GIER computer at the Computing Centre of the Slovak Academy of Sciences, Bratislava. The authors are indebted to both institutions for putting computer time at their disposal. We are grateful to Dr I. Sklenář, Institute of Solid State Physics, Czechoslovak Academy of Sciences in Prague, for his help with the programs for the TESLA 200 computer.

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