As a result of this sharing, thick anionic sheets $(B_5O_9)_n^{3n-}$ are produced. All O atoms in the polyanion except O(1), which is part of the triangular unit about B(1), are bonded to two B atoms: O(1) is bonded to one B. The separate anion sheets corresponding to contiguous glide planes, which are symmetry-related by the operation of the centre of symmetry lying between sheets, do not share any O atoms. This anion unit appears to be a new type. The basic unit shown in Fig. 1, (I), is, however, similar to the borate anions in $Ca_2B_5O_9Br$ (Lloyd, Levasseur & Fouassier, 1973) and in $Na_2B_4O_7$ (Krogh-Moe, 1974), shown in Fig. 1 as units (II) and (III) respectively.

The structure contains two sets of cation sites for *M* ions (Fig. 3). Those of one type (*A*) lie in the middle of sheets, while those of the other (*B*) lie between sheets, close to centres of symmetry. Positions *A* can be regarded, together with associated O atoms, as forming channels parallel to the *c* axis: each cation is coordinated to seven O atoms, five belonging to the sheet which nearly envelops it and two underbonded O(1) atoms of adjacent sheets. These cations are separated in the **c** direction by 3·94 Å (~*c*/2), sharing the atoms O(1) and O(4) between two *M* atoms and so forming polyhedral chains sharing edges $(MO_5)_n$. The distances *M*(*A*)—O range from 2·43 to 2·75 Å, averaging 2·53 Å. The occupancy of position *A* is $Ca^{2+}{}_{0.83}Na^{+}{}_{0.17}$ while that of position *B* is complementary: $Na^{+}_{0.83}Ca^{2+}_{0.17}$. Positions *B* form centrosymmetric dimers, $M_2O_{14}$, where $M—M' = 3{\cdot}67$ Å in which each cation is coordinated to eight O atoms, two of which [O(5) and O(5′)] are shared. The *M*(*B*)—O distances range from 2·38 to 2·70 Å, with an average of 2·53 Å. The mean sizes of the holes at *A* and *B* are virtually identical, in accord with the similar sizes of Na and Ca (Vainshtein, Fridlein & Indentov, 1982).

JF acknowledges the financial assistance of the Royal Society which made it possible to visit Aberdeen.

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*Acta Cryst.* (1985). C**41**, 1396–1398

# Structure of Calcium Trisodium Pentaborate

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(*Received* 1 *May* 1985; *accepted* 21 *June* 1985)

**Abstract.** $CaNa_3B_5O_{10}$, $M_r = 323{\cdot}1$, triclinic, $P\bar{1}$, $a = 7{\cdot}460\,(3)$, $b = 7{\cdot}445\,(4)$, $c = 11{\cdot}124\,(6)$ Å, $\alpha = 120{\cdot}58\,(4)$, $\beta = 61{\cdot}94\,(3)$, $\gamma = 120{\cdot}17\,(3)°$, $V = 440{\cdot}3$ Å$^3$, $Z = 2$, $D_x = 2{\cdot}437$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}879$ mm$^{-1}$, $F(000) = 316$, room temperature, final $R = 0{\cdot}069$ for 2487 unique observed reflections; crystal selected from synthetic material. The structure contains discrete $(B_5O_{10})^{5-}$ anions in the form of a pair of six-membered rings. Each ring contains two triangular $BO_3$ units. The rings are connected by a shared tetrahedral $BO_4$ unit.

**Introduction.** In the course of phase equilibrium studies of the system $Na_2O—CaO—B_2O_3$, three ternary phases were encountered (Lawson, 1981). The synthesis of two of these phases, $CaNaB_5O_9$ and $CaNaBO_3$, had been reported in the literature and the structure of one, $CaNaB_5O_9$, has been determined (Fayos, Howie & Glasser, 1985). However, the composition of a third phase was not definitely established as a result of the phase studies: the mole ratio $3Na_2O.6CaO.11B_2O_3$ was suggested. In order to resolve these doubts as well as to understand the principles of borate polyanion formation

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in the presence of alkali and alkaline earths, a crystal-structure determination has been undertaken.

**Experimental.** Single crystals were prepared by slow cooling of a ternary melt, known from the liquidus phase diagram to lie within the region of primary crystallization of the desired ternary phase. Since the phase melts incongruently, the compositions chosen for growth contained a substantial excess of both Na and B. Thus the crystals were always obtained surrounded by a liquid matrix which, upon quenching, yielded a glass. The identity of the crystals could be confirmed by powder X-ray diffraction and single crystals suitable for crystal-structure work were hand-picked from partially crystallized melts under a polarizing microscope.

More or less equant crystal 0·5 mm diameter; Nicolet *P*3 diffractometer with Mo $K\alpha$ radiation and $\omega/2\theta$ scan method; cell refined from 14 reflections in range $10 < \theta < 15°$; no absorption correction; $\sin\theta/\lambda \le 0{\cdot}704$ Å$^{-1}$; indices in ranges $0 \le h \le 10$, $0 \le |k| \le 10$, $0 \le |l| \le 15$; no significant variation of intensities of standard reflections 311 and $2\bar{3}\bar{1}$; 2534 unique reflections measured, 47 with $I < 2\sigma(I)$ classed as unobserved and excluded from all calculations. Structure solved using *MULTAN*80 (Main *et al.*, 1980) and refined by block-diagonal least squares to minimize $\sum w(|F_o| - |F_c|)^2$ where $w$ was 1 for reflections with $|F_o| < 15$ and $15/|F_o|$ otherwise. In final stages of refinement anisotropic thermal vibration assumed for all atoms except B. $R = 0{\cdot}069$, $wR = 0{\cdot}090$. When the shifts on atomic parameters were essentially zero (max. $\Delta/\sigma$ 0·02) refinement was stopped and $|\Delta\rho|$ on the difference map was then generally $< 0{\cdot}9$ e Å$^{-3}$ except in the vicinity of O(2) which displays a degree of disorder (see below). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations performed on the Honeywell 66/80 of the Computing Centre of the University of Aberdeen using for the most part *NRC* programs (Ahmed, Hall, Pippy & Huber, 1966). Atomic parameters and selected bond lengths and angles are given in Tables 1 and 2.*

**Discussion.** The completed structure reveals clearly that the compound is chemically formulated as $CaNa_3B_5O_{10}$. The polyanion unit consists of two six-membered rings joined through a $BO_4$ group, as shown in Fig. 1. Each ring consists of two $BO_3$ triangular units and one $BO_4$ tetrahedral unit. The pentaborate $B_5O_{10}CaNa_3$ is composed of polyanion units $(B_5O_{10})^{5-}$ having a structure in which every O atom coordinates between one and four cations. There

Table 1. *Atomic parameters of* $CaNa_3B_5O_{10}$

| | *x* | *y* | *z* | $B_{eq}/B_{iso}$(Å$^2$) |
|---|---|---|---|---|
| Ca | 0·7772 (1) | 0·3711 (1) | −0·8800 (1) | 1·07 |
| Na(1) | 0·2743 (3) | −0·0147 (3) | 0·2501 (2) | 2·14 |
| Na(2) | 0·0108 (3) | −0·3135 (3) | −0·5466 (2) | 2·49 |
| Na(3) | 0·8261 (3) | −0·0207 (3) | 0·1748 (2) | 2·28 |
| O(12) | 0·5998 (4) | 0·6781 (4) | −0·1908 (3) | 1·53 |
| O(13) | 0·6747 (4) | 0·3583 (4) | −0·2417 (3) | 1·41 |
| O(14) | 0·3579 (4) | 0·3148 (4) | −0·2753 (3) | 1·12 |
| O(15) | 0·7137 (4) | 0·4361 (5) | −0·4362 (3) | 1·79 |
| O(23) | 0·7882 (6) | 0·7054 (5) | −0·0559 (3) | 2·29 |
| O(45) | 0·4103 (5) | 0·1835 (5) | −0·5312 (3) | 1·80 |
| O(2) | 0·7250 (14) | 1·0107 (6) | −0·0026 (8) | 9·12 |
| O(3) | 0·8572 (4) | 0·3993 (5) | −0·0989 (3) | 1·54 |
| O(4) | 0·0781 (6) | 0·0184 (6) | −0·3735 (4) | 4·08 |
| O(5) | 0·7583 (5) | 0·3310 (6) | −0·6847 (3) | 2·27 |
| B(1) | 0·5876 (6) | 0·4449 (6) | −0·2877 (4) | 1·09 (5) |
| B(2) | 0·6999 (7) | 0·8046 (7) | −0·0805 (5) | 1·71 (6) |
| B(3) | 0·7713 (6) | 0·4818 (6) | −0·1318 (4) | 1·26 (5) |
| B(4) | 0·2734 (6) | 0·1657 (7) | −0·3931 (4) | 1·32 (5) |
| B(5) | 0·6308 (6) | 0·3182 (7) | −0·5546 (4) | 1·37 (5) |

For all atoms other than B, $B_{eq}$ values are calculated from anisotropic thermal vibration parameters where the correction is of the form $\exp|-(h^2B_{11} + k^2B_{22} + l^2B_{33} + hkB_{12} + hlB_{13} + klB_{23})|$ as $\frac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma\, B_{12} + ac\cos\beta\, B_{13} + bc\cos\alpha\, B_{23})$.

Table 2. *Bond distances* (Å) *and angles* (°) *for the* $B_5O_{10}^{5-}$ *anions in* $CaNa_3B_5O_{10}$

Average e.s.d.'s for distances and angles are 0·006 Å and 0·4°.

| | | | |
|---|---|---|---|
| B(1)–O(12) | 1·488 | O(12)–B(1)–O(13) | 111·2 |
| O(13) | 1·473 | O(14) | 106·1 |
| O(14) | 1·463 | O(15) | 109·6 |
| O(15) | 1·453 | O(13)–B(1)–O(14) | 109·8 |
| | | O(15) | 108·2 |
| | | O(14)–B(1)–O(15) | 111·8 |
| B(2)–O(2) | 1·285 | O(2)–B(2)–O(12) | 124·9 |
| O(12) | 1·389 | O(23) | 117·0 |
| O(23) | 1·385 | O(12)–B(2)–O(23) | 118·0 |
| B(3)–O(3) | 1·330 | O(3)–B(3)–O(13) | 122·4 |
| O(13) | 1·370 | O(23) | 118·9 |
| O(23) | 1·400 | O(13)–B(3)–O(23) | 118·7 |
| B(4)–O(4) | 1·308 | O(4)–B(4)–O(14) | 120·2 |
| O(14) | 1·393 | O(45) | 123·4 |
| O(45) | 1·420 | O(14)–B(4)–O(45) | 116·4 |
| B(5)–O(5) | 1·327 | O(5)–B(5)–O(15) | 120·3 |
| O(15) | 1·390 | O(45) | 122·1 |
| O(45) | 1·409 | O(15)–B(5)–O(45) | 117·5 |
| B(1)–O(15)–B(5) | 125·2 | B(1)–O(12)–B(2) | 124·2 |
| B(2)–O(23)–B(3) | 123·0 | B(1)–O(13)–B(3) | 124·5 |
| B(4)–O(45)–B(5) | 122·6 | B(1)–O(14)–B(4) | 124·7 |

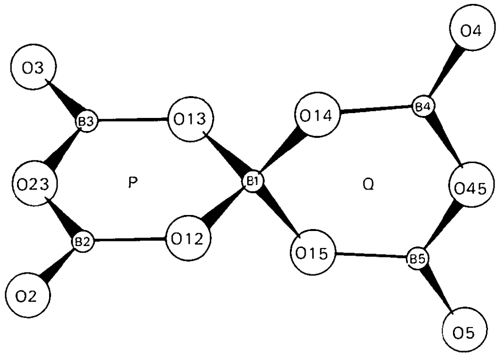

Fig. 1. The borate polyanion in $CaNa_3B_5O_{10}$.

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* Lists of structure factors and vibrational parameters for all the atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42322 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are three kinds of B—O bond distances in this group: B(tetrahedral)—O, B(triangular)—O(bridge) and B(triangular)—O(terminal). Their averaged bond lengths are 1·47 (1), 1·39 (1) and 1·32 (1) Å, respectively. The shortest B—O(terminal) are those with O(2) and O(4); these atoms present large anisotropy with r.m.s. for their major ellipsoid axes of 0·32 and 0·12 Å respectively directed almost perpendicular to the B—O bonds. This is also confirmed for O(2) in the last difference map, where a minimum of $-1\cdot5$ e Å$^{-3}$ appears at its position with two maxima of 1·8 e Å$^{-3}$ on each side, these three peaks being the largest on the map. These observations help to explain the short B—O distances, especially of O(2), which may be statistically disordered as a result of its complex coordination to the other cations. Neither six-membered ring with attached O terminals is exactly planar (see Fig. 1), with the largest atom deviations and $\sum\sigma^2$ of 0·04 Å, 0·004 Å$^2$ for ring *P* and 0·14 Å, 0·05 Å$^2$ for ring *Q*. The two best planes, one for each ring, lie at an angle of 85·9° to each other, which corresponds to a rotation around the axis O(23)B(1)O(45) allowing O(12) to approach O(14), and O(13) to approach O(15). All O(bridge) coordinate to two cations other than B except for O(45) which coordinates to only one. The O(terminal) coordinate to three cations, excluding the long distance O(2)—Na(3), of 2·96 Å. A hydroxylated version of this anion occurs in the crystal structure of $[B_5O_6(OH)_4]^-K^+.2H_2O$ (Zachariasen & Plettinger, 1980).

The cation coordination of $CaNa_3B_5O_{10}$ affords Ca six O atoms at distances from 2·22 to 2·47 (1) Å, the averaged value being 2·34 Å. Two of the three $Na^+$ are also coordinated by six O atoms, while the remaining one is coordinated by five. Na—O distances range between 2·21 and 2·89 (1) Å, with an averaged value of 2·52 Å. These averaged values agree well with those reported in other structures for Ca—O and Na—O of 2·41 and 2·53 Å respectively.

With the exception of Na(1), the rest of the cations form small clusters, $X_2O_{10}$, around crystallographic centres of symmetry. The cation polyhedra packing around Ca and Na(3) can be described as distorted octahedra, which build zigzag chains sharing edges of the form CaCaNaNa......., cation–cation distances being Ca–Ca = 3·51, Ca–Na = 3·48 and Na–Na = 3·59 (1) Å. These chains are interconnected through Na(1) and Na(2) polyhedra which share only their corners, the only exception being the edge-shared pairs of centrosymmetric-related Na(2) atoms, which form $Na_2O_8$ groups with Na–Na = 3·34 (1) Å.

JF acknowledges the financial assistance of the Royal Society which made it possible to visit Aberdeen.

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*Acta Cryst.* (1985). C**41**, 1398–1400

# Synthèse et Structure d'un Nouveau Siliciure: Octasiliciure de Lithium et d'Heptapotassium

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(*Reçu le* 13 *décembre* 1984, *accepté le* 10 *juin* 1985)

**Abstract.** $K_7LiSi_8$, $M_r = 505\cdot34$, cubic, $Pa3$, $a = 12\cdot492$ (2) Å, $V = 1949$ Å$^3$, $Z = 4$, $D_x = 1\cdot72$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 Å, $\mu$(Mo $K\alpha$) = 1·9 mm$^{-1}$, $F(000) = 992$, room temperature, $R(F) = 0\cdot025$, $wR(F) = 0\cdot037$ for 239 independent reflections. The compound $K_7LiSi_8$ has been found in the ternary system K–Li–Si and its structure is isotypical with those of the ternary compounds $Rb_7NaGe_8$ and $K_7NaGe_8$. The structure contains tetrahedral $Si_4^{4-}$ anions which are surrounded by $K^+$ and $Li^+$ cations. The Li atom sits between two faces of two neighbouring tetrahedra forming a sandwich arrangement.

0108-2701/85/101398-03$01.50