

groups across the ring. The average cross-ring axial methyl carbon distance is 4.21 Å, a distance which is much larger than twice the van der Waals radius, 4.0 Å for methyl groups.

Conclusion

From the present study of $[\text{Si}(\text{CH}_3)_2]_6$ in the solid state, it would seem that the preferred conformation of this molecule is the chair conformation. The fact that $[\text{Si}(\text{CH}_3)_2]_6$ seems to prefer the chair conformation reinforces the idea that in solution the molecule undergoes rapid conformational flips between chair conformations, so that on a time-average basis the methyl protons are equivalent as indicated by both the n.m.r. spectrum of $[\text{Si}(\text{CH}_3)_2]_6$ and the e.s.r. spectrum of its anion radical at low temperatures, as previously noted.

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The Crystal Structure of a Sodium Triborate Modification, $\beta\text{-Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$

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The β -modification of sodium triborate, $\beta\text{-Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$, is monoclinic with the following unit-cell dimensions (at 22°C): $a = 8.990 \pm 0.003$, $b = 11.033 \pm 0.002$, $c = 12.107 \pm 0.004$ Å, $\beta = 90.50 \pm 0.03^\circ$; $Z = 6$, calculated density 2.246 g.cm^{-3} ; space group $P2_1/c$. Three-dimensional X-ray intensity data were measured with a Picker automatic single-crystal diffractometer, using $\text{Cu K}\alpha$ radiation. The structure was determined by direct methods and refined by full-matrix least squares to an R value of 0.065. The weighted R value was 0.043. The borate polyanion in this phase is built up from three different kinds of groups, *viz.* pentaborate groups, triborate groups and BO_4 tetrahedra. The groups share corners with each other and in this way are mutually connected to an infinite double layer. The average B–O bond lengths for the BO_4 tetrahedra and the BO_3 triangles are normal, 1.474 and 1.368 Å respectively, but significant deviations from the averages depending on local surroundings are observed. The three crystallographically different sodium atoms are surrounded by 6, 7 and 8 oxygen atoms at distances ranging from 2.2 Å to 3.1 Å.

Introduction

The only anhydrous triborate for which the structure is known is the caesium compound (Krogh-Moe, 1960). In this compound the anion structure consists of a single infinite three-dimensional network of triborate groups sharing corners. Triborates of a number of different cations are known to exist, however. In the system sodium oxide–boron oxide Tilman & Bouaziz (1968)

reported the presence of three different crystalline triborate phases. The phase labelled β by Tilman & Bouaziz is the subject of the present study. This modification seemed interesting inasmuch as its infrared spectrum was more similar to that of a pentaborate than that of a triborate. Apart from an interest in the main features of this structure, accurate knowledge of boron–oxygen bond lengths and angles is desirable. Thus recent work (Krogh-Moe, 1972) has revealed

platinum crucible. The water was driven off and a glass melt was formed. The glass was heat treated in the temperature interval 730 to 740°C to obtain the β -phase.

A single-crystal fragment of somewhat irregular shape was used. The specimen may be approximately described as a prismatic needle with the dimensions $0.05 \times 0.06 \times 0.14$ mm. The c axis coincides with the needle axis of the specimen. Intensity data were collected with an on-line Picker single-crystal automatic diffractometer. Cu $K\alpha$ radiation was used and the X-ray reflexions were measured at 2374 reciprocal lattice points (of which 2275 were independent).

Unit-cell dimensions and standard errors $a = 8.990 \pm 0.003$, $b = 11.033 \pm 0.002$, $c = 12.107 \pm 0.004$ Å, $\beta = 90.50 \pm 0.03^\circ$ were obtained by the method of least squares from angle data recorded at 22°C for 12 high-angle reflexions (based on the wavelength 1.5405 Å for Cu $K\alpha_1$). For 6 formula units of $\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$ in the cell, the calculated density is 2.246 g.cm^{-3} . A crude experimental test showed the material to have a density of $2.2 \pm 0.1 \text{ g.cm}^{-3}$.

Structure determination

The systematic extinctions corresponds to those of the space group $P2_1/c$. A statistical test of structure fac-

tors indicated a centre of symmetry as expected for $P2_1/c$. The experimental intensities were converted in the usual manner to observed structure factors. No correction for absorption was applied. The linear absorption coefficient is 28 cm^{-1} . With a crystal of the above-mentioned size and shape, the relative absorption correction in the structure factors would be quite small. Signs for the largest structure factors were determined by the symbolic addition method, using the program *Symbol* by Hjortås (1969). An E map revealed the structure quite clearly. The structure was refined by the method of least squares, using a version of the full-matrix program *ORFLS* (Busing, Martin & Levy, 1962) revised by Borgen & Mestvedt (1966). Structure factors corresponding to the four strongest experimental intensities were affected by extinction and were omitted from the refinement as were also the very weak structure factors (weaker than three times the estimated standard error). 1628 independent non-zero reflexions, used in the refinement, are reproduced in Table 1.

The atomic scattering factors for O, B and Na^+ , used for obtaining the calculated structure factors (Table 1), were taken from *International Tables for X-ray Crystallography* (1962). The refinement was carried out with a weighting scheme based on the statistical counting errors compounded with errors as-

Table 2. Final atomic parameters

Positional parameters are expressed as a fraction of the cell edge, and temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. All values are multiplied by 10^4 .

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	1008	3700	4362	61	28	27	-8	1	-1
Na(2)	4406	8390	2859	61	46	33	12	-12	-13
Na(3)	1142	9051	4195	69	52	36	-30	-22	12
O(1)	2727	677	4454	35	27	14	-15	-1	5
O(2)	1807	2147	3163	33	20	18	8	-5	-2
O(3)	2790	198	2528	33	11	22	4	-7	-6
O(4)	4402	1797	3258	35	27	13	-13	0	-4
O(5)	4823	1729	5205	40	43	16	-22	-5	5
O(6)	1523	1555	1291	74	15	22	17	-13	1
O(7)	3265	718	6407	30	28	15	-9	-1	1
O(8)	6157	3087	4008	23	23	20	-14	-5	8
O(9)	831	3528	1837	33	7	31	-4	-6	0
O(10)	1969	9635	674	43	17	19	11	-11	-12
O(11)	1047	5541	1204	34	14	20	2	-4	-2
O(12)	1277	7543	592	43	24	31	-11	-16	15
O(13)	1916	7056	2455	80	15	25	-7	-6	0
O(14)	2027	4991	3031	42	15	15	2	-3	3
O(15)	2769	6664	4197	65	32	10	-25	-2	-6
B(1)	2951	1195	3357	45	11	22	-7	9	-2
B(2)	1786	4601	1885	34	9	17	2	0	-6
B(3)	2512	8423	359	33	13	22	1	4	-1
B(4)	3548	1018	5351	20	10	32	5	3	8
B(5)	5154	2197	4165	25	19	26	8	-1	6
B(6)	1399	2412	2118	15	17	29	-4	-1	-2
B(7)	2140	403	1529	24	20	22	0	-1	0
B(8)	2227	6189	3259	22	28	24	1	10	-2
B(9)	1397	6726	1428	27	19	23	13	5	-1
Standard deviations									
Na	2	2	2	3	2	2	2	2	2
O	3	3	2	4	3	2	3	3	2
B	5	5	4	7	5	4	5	4	4

sumed to be 1% of the observed intensity. With anisotropic temperature factors the structure refined to an R value of 0.065 (or 0.043 for the weighted R value). Final atomic coordinates with standard deviations and the parameters of the anisotropic temperature factors are given in Table 2.

Discussion of the structure

The structure of β -Na₂O · 3B₂O₃ may be described as a double layer structure. To the knowledge of the author no case of a binary anhydrous borate containing infinite borate polymer layers has previously been reported. The double layers in β -Na₂O · 3B₂O₃ run almost perpendicular to the a axis of the crystal. A projection of the structure along the a axis is shown in Fig. 1. In this Figure the upper of the double layers is drawn with thin lines. The unit cell is indicated by a rectangle. At right outside this rectangle the contents of the asymmetric unit are shown. Here the atoms are numbered consistently with Table 2. It is seen that the borate polymer is built up from three different groupings – the double ring pentaborate group, the single ring triborate group and a single BO₄-tetrahedron. The pentaborate groups and the triborate groups have previously been found as building units in other polyborate structures (see for instance Krogh-Moe, 1960, 1972).

The groups are mutually connected by a sharing of oxygen atoms. Thus the BO₄-tetrahedron shares two of its oxygen atoms, O(8) and O(10), with pentaborate

groups and the other two, O(12) and O(15), with triborate groups. Likewise the triborate group shares two of its oxygen atoms [O(12), O(15)] with single BO₄ tetrahedra and two [O(7), O(9)] with pentaborate groups. Finally the pentaborate group shares two of its oxygens [O(7), O(9)] with triborate groups and two [O(8), O(10)] with the single tetrahedra. In this way the borate groups are connected to an infinite double layer. Within each of the two layers constituting the double layer, the borate groups form 5-membered rings, consisting of two triborate groups, a pentaborate group, a single BO₄ group and in addition either a pentaborate group or a single BO₄ group. The two layers are connected by a bridge between pentaborate groups and single BO₄ groups. (The bridge comprises atoms B(3)–O(8)–B(5).) The arrangement of groups is such that no two boron atoms in fourfold coordination are directly bonded to each other by a B–O–B link.

Boron–oxygen bond lengths are given in Table 3. The average boron–oxygen distance of the fourfold coordinated borons, B(1), B(2) and B(3), is 1.474 Å as compared with 1.368 Å for the average of the threefold coordinated borons. These values differ no more than 0.001 Å from the corresponding averages reported by Hyman, Perloff, Mauer & Block (1967) for sodium tetraborate. The individual boron–oxygen distances of the threefold coordinated boron atoms differ, depending on the surroundings of the oxygen atom involved in the bond. In order to conveniently describe this circumstance, the coordination number of an atom

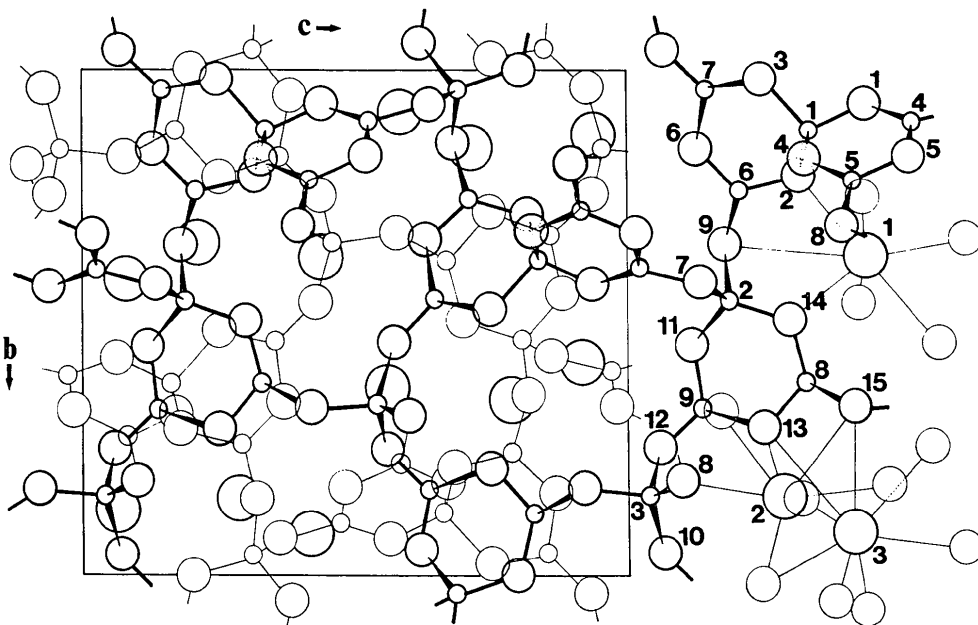


Fig. 1. Projection of the structure of β -Na₂O · 3B₂O₃ along the a axis. The small circles represent boron atoms, the intermediate circles represent oxygen atoms and the large circles represent sodium atoms. Unit-cell dimensions are indicated by a rectangle. At the right of the Figure, outside the rectangle, the atoms of the asymmetric unit are numbered consistently with Table 2. The coordination of the cations is also indicated in this part of the Figure. The upper layer of the double layer within the rectangle is drawn with thin lines.

Table 3. *Interatomic distances and bond angles*

Boron-oxygen bond lengths (standard deviation 0.006 Å), sodium-oxygen bond lengths (standard deviation 0.004 Å) below 3.526 Å and oxygen-boron-oxygen and boron-oxygen-boron bond angles (standard deviations 0.4°).

B(1)-O(1)	1.462 Å	B(9)-O(11)	1.371 Å
B(1)-O(2)	1.487	B(9)-O(12)	1.359
B(1)-O(3)	1.495	B(9)-O(13)	1.373
B(1)-O(4)	1.470		
B(2)-O(7')	1.497	Na(1)-O(14)	2.343
B(2)-O(9)	1.463	Na(1)-O(2)	2.361
B(2)-O(11)	1.479	Na(1)-O(6')	2.394
B(2)-O(14)	1.467	Na(1)-O(12)	2.419
B(3)-O(8')	1.463	Na(1)-O(10')	2.573
B(3)-O(10)	1.475	Na(1)-O(10'')	2.868
B(3)-O(12)	1.504	Na(1)-O(9)	3.065
B(3)-O(15')	1.431	Na(2)-O(8')	2.336
B(4)-O(1)	1.360	Na(2)-O(5')	2.442
B(4)-O(5)	1.402	Na(2)-O(4')	2.467
B(4)-O(7)	1.348	Na(2)-O(3)	2.499
B(5)-O(4)	1.358	Na(2)-O(13)	2.720
B(5)-O(5)	1.394	Na(2)-O(15)	2.908
B(5)-O(8)	1.347	Na(3)-O(9')	2.237
B(6)-O(2)	1.347	Na(3)-O(1)	2.311
B(6)-O(6)	1.382	Na(3)-O(12')	2.442
B(6)-O(9)	1.375	Na(3)-O(11')	2.476
B(7)-O(3)	1.358	Na(3)-O(11'')	2.606
B(7)-O(6)	1.416	Na(3)-O(3)	2.814
B(7)-O(10)	1.345	Na(3)-O(15)	3.013
B(8)-O(13)	1.392	Na(3)-O(13)	3.130
B(8)-O(14)	1.362		
B(8)-O(15)	1.338		
O(1)-B(1)-O(2)	108.6°	O(6)-B(6)-O(9)	117.7°
O(1)-B(1)-O(3)	108.0	O(3)-B(7)-O(6)	119.7
O(1)-B(1)-O(4)	112.3	O(3)-B(7)-O(10)	128.8
O(2)-B(1)-O(3)	110.6	O(6)-B(7)-O(10)	111.5
O(2)-B(1)-O(4)	106.3	O(13)-B(8)-O(14)	120.0
O(3)-B(1)-O(4)	111.0	O(13)-B(8)-O(15)	113.3
O(7)-B(2)-O(9)	108.5	O(14)-B(8)-O(15)	126.8
O(7)-B(2)-O(11)	110.2	O(11)-B(9)-O(12)	118.0
O(7)-B(2)-O(14)	108.1	O(11)-B(9)-O(13)	120.5
O(9)-B(2)-O(11)	106.6	O(12)-B(9)-O(13)	121.5
O(9)-B(2)-O(14)	110.9		
O(11)-B(2)-O(14)	112.6	B(1)-O(1)-B(4)	122.6
O(8)-B(3)-O(10)	111.5	B(1)-O(4)-B(5)	121.1
O(8)-B(3)-O(12)	109.8	B(1)-O(2)-B(6)	118.9
O(8)-B(3)-O(15)	111.1	B(1)-O(3)-B(7)	121.0
O(10)-B(3)-O(12)	106.9	B(2)-O(7)-B(4)	126.8
O(10)-B(3)-O(15)	111.8	B(2)-O(9)-B(6)	119.9
O(12)-B(3)-O(15)	105.5	B(2)-O(14)-B(8)	119.6
O(1)-B(4)-O(5)	119.6	B(2)-O(11)-B(9)	117.2
O(1)-B(4)-O(7)	125.7	B(3)-O(8)-B(5)	131.1
O(5)-B(4)-O(7)	114.7	B(3)-O(10)-B(7)	137.2
O(4)-B(5)-O(5)	120.1	B(3)-O(15)-B(8)	138.3
O(4)-B(5)-O(8)	116.9	B(3)-O(12)-B(9)	120.9
O(5)-B(5)-O(8)	123.1	B(4)-O(5)-B(5)	120.1
O(2)-B(6)-O(6)	120.6	B(6)-O(6)-B(7)	120.1
O(2)-B(6)-O(9)	121.6	B(8)-O(13)-B(9)	121.0

with respect to its nearest neighbours will be indicated by a subscript in Roman numerals to the atomic symbol. Thus B_{III} and B_{IV} represent boron in three- and fourfold coordinations, and O_{II} indicates that the oxygen atom is coordinated by two boron atoms. Our description, however, requires a statement about the next nearest neighbours, in the borate polymer. Thus the coordination of a threefold coordinated boron in the present structure may be written B_{III}(O_{II}-B_{III})

(O_{II}-B_{IV})₂, (where (O_{II}-B_{III})[†] and ‡ (O_{II}-B_{IV}) signifies oxygen ligands in turn bonded to a second three- or fourfold coordinated boron atom). The B_{III}-O_{II} bond to the (O_{II}-B_{III}) ligand of the above configuration is on average 1.393 Å whereas the distance B_{III}-O_{II} to the two (O_{II}-B_{IV}) ligands is 1.356 Å. In the α potassium pentaborate structure studied by Krogh-Moe (1972) the threefold coordinated borons have the configuration B_{III}(O_{II}-B_{III})₂ (O_{II}-B_{IV}). There are now two (O_{II}-B_{III}) ligands and only one (O_{II}-B_{IV}) ligand. The B_{III} distance to the oxygen atom in the (O_{II}-B_{IV}) unit in the pentaborate structure is 1.323 Å. This is significantly shorter than the B_{III} to (O_{II}-B_{IV}) distance of 1.356 Å in the present structure, which suggests a dependence of this bond length on the number of next nearest B_{IV} atoms. Apparently the B_{III} to (O_{II}-B_{III}) distances do not depend equally strongly on the presence of next nearest B_{IV} atoms. In the potassium pentaborate structure it is on average 1.386 Å (with considerable scatter) as compared with the value 1.393 Å reported here.

In the structure of sodium tetraborate (Hyman, Perloff, Mauer & Block, 1967) both the B_{III}(O_{II}-B_{III})₂ (O_{II}-B_{IV}) and B_{III}(O_{II}-B_{III}) (O_{II}-B_{IV})₂ configurations are present simultaneously. The B_{III}-O_{II} distance to the (O_{II}-B_{IV}) ligand is seen to be 1.338 Å in the former configuration and 1.357 Å for the latter configuration, in fair agreement with the present results. No analogous dependence on the presence of next nearest B_{IV} atoms is observed for the B_{III} to (O_{II}-B_{III}) distance in the sodium tetraborate, as with the present structure.

Table 3 also presents the interatomic O-B-O and B-O-B angles. The three O-B_{III}-O angles for each B_{III} atom sums up to 360° as required for a planar triangle. Likewise the O-B_{IV}-O angles are for each B_{IV} atom on average 109.4°, consistent with the tetrahedral arrangement. The individual bond angles for both the B_{III} and B_{IV} atoms, however, differ considerably from the average (ideal) value. Thus O-B_{IV}-O angles within the six-membered rings of the pentaborate and triborate groups tend to be above average, as one might expect. Some of the distortions in bond angles appear to reflect strains in the packing of the groups. Thus there are three short oxygen-oxygen distances between oxygens belonging to different groups, *viz* O(1)-O(11'), O(5)-O(15') and O(8)-O(13') at 2.938, 2.885 and 2.736 Å respectively. The indirect O-B-O-B-O link between the first two of these oxygen pairs have larger than average values for the bond angles. The third and shortest intergroup oxygen-oxygen distance, however, exhibits close to normal bond angles in this indirect link. In particular the B-O-B intergroup bond angle is surprisingly small, 120.9°. Apart from this intergroup B-O-B angle and one at 119.9°, the remaining B-O-B intergroup bond angles range from 126.8 to 138.3°. For comparison, in α potassium pentaborate an intergroup B-O-B angle around 129° was found.)

The three crystallographically non-equivalent so-

dium atoms have different coordinations. These are indicated in Fig. 1. Table 3 gives the sodium–oxygen distances below 3·52 Å. Since there are no distances in the range 3·13 to 3·52 Å, the number of oxygen atom neighbours at 3·13 Å or less are taken to be the coordination number of sodium. This number is 7, 6 and 8 for Na(1), Na(2) and Na(3) respectively. The coordinating oxygen atoms do not surround the cations in a symmetrical fashion. The sodium–oxygen distances of the coordinating oxygens range from 2·237 to 3·130 Å. In comparison *International Tables for X-ray Crystallography* (1962) gives for sixfold coordinated sodium, the range 2·25 to 2·78 Å derived from 16 determinations (The sodium–oxygen distances listed by Hyman, Perloff, Mauer & Block (1967) for sodium tetraborate cannot be reconciled with their parameter list.)

The present results reinforce the general impression that the cation sites in borate polymer networks depend strongly on the requirements of the polymer anion.

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The Conformation of Non-Aromatic Ring Compounds. LXXIV.* The Crystal and Molecular Structure of *cis*-2-Chloro-4-*t*-butylcyclohexanone

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Crystals of *cis*-2-chloro-4-*t*-butylcyclohexanone are triclinic. The space group is $P\bar{1}$ and $Z=2$. The unit-cell dimensions are $a=8\cdot294$, $b=10\cdot563$, $c=6\cdot366$ Å, $\alpha=100\cdot8$, $\beta=97\cdot4$ and $\gamma=79\cdot5^\circ$. The structure has been solved by Patterson methods and direct methods and refined with a least-squares procedure using Mo $K\alpha$ data measured with a three-circle diffractometer. The final conventional R value is 3·7%. The cyclohexane ring has a chair conformation with the chlorine atom and the *t*-Bu group in the equatorial positions. The staggering of the latter group with respect to the ring atoms is $-1\cdot5^\circ$. The thermal motion has been analysed in terms of a rigid body. Statistical tests indicate that the rigid body model without methyl groups cannot be rejected on a 5% significance level and suggest a librational motion of the *t*-Bu group.

Introduction

This investigation forms part of the studies in this laboratory concerning the geometry of *t*-Bu groups. Fraterman & Romers (1971) (hereafter referred to as FR) showed that the C(CH₃)₃ groups in the aromatic compound 2,6-di-*t*-butyl-4-(*p*-bromophenyl)imino-2,5-cyclohexadien-1-one have conspicuously high temperature factors and presumably suffer from restricted rotation (libration) about the central C–C bonds, or possibly show conformational disorder. This phenomenon has not been encountered in other aromatic compounds with *t*-Bu groups (consult FR for liter-

ature) but might be present in analogous cyclohexane derivatives. Altona & Sundaralingam (1970) carried out empirical force-field calculations of a number of substituted cyclohexane compounds. Their calculations indicate that the C(CH₃)₃ groups do not occupy staggered positions relative to the ring bonds. The angle of twist with respect to the ideally staggered position ($\pm 17^\circ$) is concomitant with an asymmetrical distortion of the cyclohexane ring. A very low barrier (300 cal.mole⁻¹) separates the two equivalent forms and the authors suggest that in diffraction analysis the twisting phenomenon would reveal itself by unusual large temperature factors (disorder) of atoms of the *t*-Bu group and, to a less degree, of the ring atoms.

So far no published experimental evidence is avail-

* Part LXXIII: Koer, de Kok & Romers (1972)