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The Crystal Structure of Caesium Enneaborate, $Cs_2O . 9B_2O_3$

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Caesium enneaborate, $Cs_2O . 9B_2O_3$, is pseudotetragonal with unit-cell dimensions $a=b=8{\cdot}768 \pm 0{\cdot}005$ Å and $c=15{\cdot}790 \pm 0{\cdot}010$ Å and the angles α, β and γ close to 90°. The symmetry closely obeys the requirements of the enantiomorphic pair of space groups $P4_122$ and $P4_322$. The true space group is of lower symmetry, however. A three-dimensional structure analysis was carried out, based on 721 visually estimated structure factors. The structure obtained was refined by the method of least squares, which led to a reliability index of $R=12{\cdot}9$ %. The structure consists of two interpenetrating separate boron-oxygen twin networks. The two basic units of each network are the boroxol group (a six-membered planar boron-oxygen ring) and the triborate group (also containing a six-membered boron-oxygen ring, but with one of the boron atoms coordinated tetrahedrally by oxygen).

Introduction

During the last few years the structures of many anhydrous borates have been determined. No borate structure with a ratio of boron oxide to metal oxide higher than five to one has been worked out previously, however. In a phase diagram study from 1958, Krogh-Moe established the existence of a caesium enneaborate. This is a compound with a ratio of boron oxide to metal oxide equalling nine to one. Because of the high boron oxide content, the enneaborate may exhibit structure elements characteristic of pure boron oxide. The structure of boron oxide glass is still a matter of controversy which has proved extremely difficult to resolve. Circumstantial evidence, such as may be obtained from the structure of caesium enneaborate, is therefore of some interest.

Experimental

Crystalline caesium enneaborate was prepared by fusing caesium carbonate with a small excess of boric acid and annealing the supercooled melt at 580°C.

Unit-cell dimensions for caesium enneaborate have previously been given by Krogh-Moe (1958). For the present work, the unit-cell dimensions were revised. A least-squares adjustment of twelve indexed powder lines from a diffractometer recording gave the following lengths for the cell axes:

$$a=b=8{\cdot}768 \pm 0{\cdot}005 \text{ Å} \quad c=15{\cdot}790 \pm 0{\cdot}010 \text{ Å}$$

The calculated density with 2 formula units of $Cs_2O . 9B_2O_3$ in the cell is 2·485 g.cm³. The observed density is $2{\cdot}47 \pm 0{\cdot}02$ g.cm^{-3}.

Weissenberg exposures show that the cell axes deviate only slightly from orthogonality, the cell angles being estimated to $90{\cdot}2 \pm 0{\cdot}2$°. All crystals investigated did exhibit twinning, as evidenced by some double spots found in the upper level Weissenberg photographs for the rotation about the a axis. The double spots occurred closely spaced, so as to be resolved only in certain regions on one side of the central line of the film. The intensity ratios of the double spots were not always the same for each pair. For the unresolved spots, however, it was found that the conditions $F(h,k,l)=F(h,\bar{k},l)=F(h,k,\bar{l})$ were quite well fulfilled. (Hence negative values of the indices were not taken into account in the subsequent work.) Moreover it was observed that the pair of structure factors, related by the exchange of the indices h and k, generally have the same value within the experimental errors (Table 1). Systematic extinctions occurred only for the $00l$ type of reflexion, which vanished when the index l was not a multiple of 4. From this extinction condition and the intensity relations it was concluded that the enantiomorphic pair of space groups $P4_122$ (no. 91) and $P4_322$ (no. 95) may be used for a description of the structure.

The intensity data were collected with Mo $K\alpha$ radiation; the linear absorption coefficient in this case is 32 cm^{-1}. A crystal of 0·0105 cm length in the direction of the rotation axis (the a axis) and with a quadratic cross-section of $0{\cdot}0085 \times 0{\cdot}0085$ cm was used. Absorption corrections (for visually estimated intensities) were considered unnecessary with a crystal of this size.

Triple film Weissenberg exposures were taken about the a axis for the zero to sixth level. The intensities were estimated visually, utilizing regions of the film where no resolution of double spots occurred. (Since the double spots were only partially resolved, a reasonably complete set of data based on a single of the twins could not be obtained.) The 721 observed structure factors are given in Table 1.

Table 1. *Observed and calculated structure factors*

h	k	l	F_o	F_c
0	0	4	119	109
0	0	8	172	157
0	0	12	50	39
0	0	16	64	80
0	1	4	125	110
0	1	5	25	24
0	1	6	229	205
0	1	8	62	50
0	1	9	72	66
0	1	10	139	117
0	1	11	31	36
0	1	14	65	71
0	1	18	42	45
0	2	0	104	119
0	2	1	41	54
0	2	2	86	78
0	2	3	141	121
0	2	4	63	80
0	2	5	41	35
0	2	6	13	13
0	2	8	156	145
0	2	12	102	96
0	2	15	47	60
0	3	0	32	29
0	2	1	50	54
0	3	2	200	184
0	3	3	34	31
0	3	4	43	46
0	3	5	25	14
0	3	6	146	129
0	3	7	25	21
0	3	8	22	29
0	3	9	30	35
0	3	10	125	125
0	3	14	44	57
0	4	0	154	128
0	4	1	154	112
0	4	2	49	35
0	4	3	21	6
0	4	4	175	147
0	4	5	70	72
0	4	6	73	67
0	4	8	93	94
0	4	9	45	45
0	4	11	26	24
0	4	12	84	76
0	4	16	41	42
0	5	1	60	45
0	5	2	144	130
0	5	6	111	100
0	5	7	44	42
0	5	8	25	27
0	5	9	18	33
0	5	10	49	63
0	5	14	34	42
0	6	0	102	93
0	6	3	44	45
0	6	4	106	91
0	6	5	17	12
0	6	7	43	51
0	6	8	49	62
0	6	11	34	39
0	6	12	42	53
0	7	2	43	53
0	7	3	48	50
0	7	4	49	33
0	7	5	49	54
0	7	6	50	50
0	7	7	20	30
0	7	10	42	56
0	8	0	36	49
0	8	1	36	35
0	8	4	29	49
0	8	6	29	29
0	8	8	33	48
0	9	2	36	50
1	0	3	47	49
1	0	4	119	111
1	0	5	23	21
1	0	6	227	201
1	0	8	51	50
1	0	9	65	64
1	0	10	126	120
1	0	11	26	35
1	0	14	77	70
1	0	13	39	47
1	1	4	209	233
1	1	5	49	47
1	1	6	45	45
1	1	7	17	18
1	1	8	95	83
1	1	9	23	27
1	1	12	129	124
1	1	15	26	33
1	1	16	50	49
1	2	0	43	36
1	2	1	53	44
1	2	2	203	229
1	2	3	77	74
1	2	4	24	35
1	2	5	17	14
1	2	6	174	149
1	2	7	55	43
1	2	8	19	16
1	2	10	101	97
1	2	14	72	67
1	2	18	35	45
1	3	0	196	190
1	3	1	29	28
1	3	2	20	25
1	3	3	41	38
1	3	4	170	150
1	3	5	24	16
1	3	6	33	38
1	3	7	32	33
1	3	8	147	128
1	3	9	25	28
1	3	12	74	69
1	3	16	52	55
1	4	0	28	25
1	4	1	37	28
1	4	2	139	131
1	4	3	71	57
1	4	4	22	10
1	4	5	107	95
1	4	6	132	105
1	4	7	20	13
1	4	9	26	21
1	4	10	85	75
1	4	11	34	38
1	4	14	70	65
1	4	18	34	37
1	5	0	116	111
1	5	1	54	54
1	5	3	39	36
1	5	4	88	83
1	5	5	41	44
1	5	6	36	29
1	5	7	22	21
1	5	8	108	91
1	5	9	23	23
1	5	10	24	14
1	5	11	25	27
1	5	12	62	67
1	5	15	33	36
1	6	1	47	43
1	6	2	86	80
1	6	3	36	40
1	6	6	92	91
1	6	7	40	48
1	6	8	24	27
1	6	9	25	28
1	6	10	73	73
1	6	11	27	27
1	6	14	32	35
1	7	0	79	92
1	7	1	47	57
1	7	2	24	26
1	7	4	74	74
1	7	5	32	39
1	7	7	25	36
1	7	8	37	45
1	7	12	34	40
1	8	2	47	53
1	8	3	28	34
1	8	6	41	60
1	8	7	27	33
1	9	0	32	43
1	9	4	31	32
2	0	3	121	124
2	0	4	83	75
2	0	5	36	36
2	0	6	14	11
2	0	8	170	148
2	0	10	22	23
2	0	12	107	94
2	0	16	54	61
2	1	2	193	228
2	1	3	71	72
2	1	4	34	34
2	1	5	17	13
2	1	6	162	151
2	1	7	52	42
2	1	8	18	17
2	1	10	106	95
2	1	14	70	68
2	1	18	35	44
2	2	0	145	163
2	2	1	34	32
2	2	2	27	29
2	2	3	64	62
2	2	4	194	204
2	2	5	26	28
2	2	7	27	31
2	2	8	137	117
2	2	9	33	38
2	2	12	92	81
2	2	13	24	34
2	2	15	17	20
2	2	16	78	52
2	2	20	32	36
2	3	0	49	41
2	3	1	49	48
2	3	2	130	123
2	3	3	26	27
2	3	4	19	16
2	3	5	11	10
2	3	6	101	98
2	3	7	69	65
2	3	8	43	43
2	3	9	27	41
2	3	10	113	96
2	3	13	25	30
2	3	14	73	70
2	3	18	33	35
2	4	0	104	105
2	4	1	29	24
2	4	2	26	29
2	4	3	50	35
2	4	4	158	139
2	4	5	22	19
2	4	7	52	45
2	4	8	109	95
2	4	9	26	23
2	4	10	21	12
2	4	11	15	19
2	4	12	76	71
2	4	16	31	34
2	5	0	59	37
2	5	1	70	69
2	5	2	109	97
2	5	3	23	26
2	5	4	22	22
2	5	5	35	39
2	5	6	119	103
2	5	7	40	40
2	5	8	21	21
2	5	9	25	25
2	5	10	75	59
2	5	11	25	27
2	5	13	17	25
2	5	14	51	59
2	6	0	100	95
2	6	1	32	38
2	6	2	39	34
2	6	3	47	47
2	6	4	80	76
2	6	5	56	59
2	6	7	15	17
2	6	8	34	48
2	6	10	28	27
2	6	12	39	46
2	6	16	33	32
2	7	1	30	25
2	7	2	72	69
2	7	3	33	38
2	7	5	44	39
2	7	6	70	71
2	7	7	36	36
2	7	8	26	29
2	7	9	29	29
2	7	10	46	49
2	8	0	39	43
2	8	2	27	17
2	8	3	39	54
2	8	4	47	56
2	8	5	26	28
2	8	7	27	26
2	8	8	33	34
2	8	9	30	26
2	9	0	25	33
2	9	2	30	34
3	0	3	25	30
3	0	4	37	42
3	0	5	19	17
3	0	6	140	129
3	0	7	19	23
3	0	8	29	32
3	0	9	24	33
3	0	10	131	116
3	0	11	10	10
3	0	14	67	57
3	0	18	48	45
3	1	2	20	23
3	1	3	31	37
3	1	4	130	155
3	1	5	25	15
3	1	6	39	39
3	1	7	33	34
3	1	8	117	124
3	1	9	26	26
3	1	10	10	11
3	1	11	15	22
3	1	12	80	70
3	1	13	18	21
3	1	16	62	55
3	1	20	33	31
3	2	0	35	38
3	2	1	39	44
3	2	2	116	123
3	2	3	28	31
3	2	4	15	16
3	2	5	15	15
3	2	6	99	98
3	2	7	68	63
3	2	8	43	43
3	2	9	46	38
3	2	10	114	96
3	2	11	16	12
3	2	13	26	31
3	2	14	89	70
3	2	18	40	35
3	3	0	111	126
3	3	1	43	53
3	3	2	75	66
3	3	3	55	51
3	3	4	96	88
3	3	5	55	52
3	3	7	24	18
3	3	8	115	115
3	3	9	17	15
3	3	12	64	48
3	3	16	54	48
3	3	20	26	27
3	4	0	12	11
3	4	1	50	42
3	4	2	122	144
3	4	3	37	37
3	4	4	35	30
3	4	5	26	29
3	4	6	104	94
3	4	7	15	8
3	4	9	28	27
3	4	10	96	83
3	4	11	32	35
3	4	12	17	11
3	4	13	18	15
3	4	14	62	52
3	4	15	19	18
3	4	16	33	30
3	5	0	104	112
3	5	1	37	33
3	5	2	14	14
3	5	3	41	41
3	5	4	92	95
3	5	5	47	42
3	5	6	16	11
3	5	7	50	47
3	5	8	87	80
3	5	9	54	41
3	5	10	19	11
3	5	11	44	39
3	5	12	65	50
3	5	13	20	19
3	5	16	37	38
3	5	20	30	26
3	6	0	19	15
3	6	1	63	54
3	6	2	69	72
3	6	3	27	28
3	6	4	15	9
3	6	5	24	26
3	6	6	57	56
3	6	7	23	22
3	6	8	23	21
3	6	9	24	27
3	6	10	54	48
3	6	11	20	17
3	6	13	23	22
3	6	14	31	27
3	6	15	24	17
3	6	17	24	21
3	6	18	26	28
3	7	0	49	51
3	7	1	35	37
3	7	2	23	18
3	7	3	18	16
3	7	4	33	39
3	7	5	28	30
3	7	6	17	8
3	7	7	41	38
3	7	8	59	62
3	7	9	39	36
3	7	11	22	19
3	7	12	30	39
3	7	16	26	24
3	8	1	53	47
3	8	2	49	55
3	8	3	32	42
3	8	4	29	25
3	8	5	21	26
3	8	6	33	42
3	8	7	18	20
3	8	8	13	13
3	8	9	19	20
3	8	10	28	30
3	8	11	20	18
3	8	14	22	23
3	9	0	29	42
3	9	1	13	19
3	9	2	20	21
3	9	3	21	27
3	9	4	27	35
3	9	5	19	23
3	9	6	19	15
3	9	7	22	19
3	9	8	22	32
3	9	9	20	27
3	9	10	21	11
4	0	3	24	0
4	0	4	146	140
4	0	5	58	69
4	0	6	64	68
4	0	8	96	98
4	0	9	47	43
4	0	10	11	11
4	0	11	20	25
4	0	12	93	74
4	0	16	47	42
4	1	2	120	131
4	1	3	52	57
4	1	4	16	12
4	1	5	92	94
4	1	6	119	104
4	1	7	19	14
4	1	8	17	16
4	1	9	22	21
4	1	10	92	75
4	1	11	32	39
4	1	12	20	19
4	1	13	21	22
4	1	14	80	65
4	1	18	43	37
4	2	0	89	110
4	2	1	23	24
4	2	2	19	27
4	2	3	51	33
4	2	4	131	135
4	2	5	19	18
4	2	6	13	13
4	2	7	44	44
4	2	8	93	97
4	2	9	29	25
4	2	10	18	12
4	2	11	18	20
4	2	12	80	70
4	2	13	14	19
4	2	16	40	34
4	2	20	33	29
4	3	0	15	10
4	3	1	39	46
4	3	2	135	144
4	3	3	38	33
4	3	4	25	29
4	3	5	25	26
4	3	6	115	94
4	3	7	18	11
4	3	9	31	28
4	3	10	98	83
4	3	11	34	34
4	3	14	64	52
4	3	18	34	30
4	4	0	54	56
4	4	1	46	56
4	4	2	33	30
4	4	3	43	49
4	4	4	82	90
4	4	5	39	41
4	4	7	65	57
4	4	8	88	71
4	4	9	19	18
4	4	10	18	14
4	4	11	19	15
4	4	12	52	46
4	4	15	26	25
4	4	16	42	42
4	5	0	22	20
4	5	1	24	35
4	5	2	80	82
4	5	3	47	51
4	5	4	19	16
4	5	5	25	26
4	5	6	57	58
4	5	7	35	39
4	5	9	22	22
4	5	10	59	53
4	5	11	28	29
4	5	12	21	10
4	5	13	25	26
4	5	14	41	38
4	6	0	96	83
4	6	1	34	35
4	6	3	20	18
4	6	4	54	67
4	6	5	33	35
4	6	6	24	26
4	6	7	38	39
4	6	8	59	66
4	6	9	37	30
4	6	11	23	22
4	6	12	40	40
4	6	13	25	26
4	6	16	25	26
4	7	0	44	27

Table 1 (*cont.*)

h	k	l	F_o	F_c
4	7	1	41	40
4	7	2	49	51
4	7	3	38	33
4	7	4	23	16
4	7	5	30	32
4	7	6	43	48
4	7	7	31	24
4	7	9	25	21
4	7	10	31	32
4	7	11	29	27
4	7	14	26	29
4	8	0	31	35
4	8	1	22	23
4	8	2	22	13
4	8	3	27	27
4	8	4	35	43
4	8	5	32	26
4	8	6	15	6
4	8	7	24	27
4	8	8	26	27
4	8	9	16	17
4	9	1	28	32
4	9	2	26	32
4	9	6	23	28
5	0	2	116	135
5	0	3	23	6
5	0	6	112	102
5	0	7	51	46
5	0	8	20	26
5	0	9	24	34
5	0	10	81	62
5	0	11	18	18
5	0	12	41	37
5	0	14	54	43
5	0	18	41	35
5	1	0	85	106
5	1	1	30	52
5	1	2	20	8
5	1	3	30	37
5	1	4	60	86
5	1	5	40	46
5	1	6	31	27
5	1	7	20	21
5	1	8	100	88
5	1	9	21	22
5	1	10	17	13
5	1	11	26	27
5	1	12	83	68
5	1	13	20	23
5	1	16	38	36
5	1	20	24	22
5	2	0	36	35
5	2	1	52	69
5	2	2	92	96
5	2	3	16	25
5	2	4	18	24
5	2	5	37	39
5	2	6	110	103
5	2	7	42	41
5	2	8	24	21
5	2	9	24	25
5	2	10	91	58
5	2	11	28	26
5	2	12	25	17
5	2	13	24	25
5	2	14	77	59
5	2	15	24	24
5	2	18	30	23
5	3	0	106	110
5	3	1	27	34
5	3	2	11	15
5	3	3	40	41
5	3	4	109	97
5	3	5	40	43
5	3	6	10	10
5	3	7	49	47
5	3	8	85	79
5	3	9	54	40
5	3	10	18	13
5	3	11	42	38
5	3	12	67	50
5	3	13	23	19
5	3	15	47	38
5	3	20	32	26
5	4	0	24	21
5	4	1	22	32
5	4	2	75	62
5	4	3	54	55
5	4	4	15	16
5	4	5	24	29
5	4	6	65	58
5	4	7	40	36
5	4	9	24	22
5	4	10	70	53
5	4	11	28	30
5	4	13	26	26
5	4	14	38	38
5	4	18	26	20
5	5	0	23	28
5	5	1	24	29
5	5	3	42	34
5	5	4	67	67
5	5	5	38	31
5	5	6	27	30
5	5	8	49	41
5	5	11	32	29
5	5	12	56	47
5	5	13	22	20
5	5	16	25	20
5	6	0	42	28
5	6	1	32	37
5	6	2	71	61
5	6	3	26	22
5	6	4	22	19
5	6	5	69	53
5	6	6	64	55
5	6	7	28	33
5	6	8	20	9
5	6	9	25	25
5	6	10	39	45
5	6	11	22	19
5	6	13	15	16
5	6	14	29	30
5	7	0	55	56
5	7	1	46	44
5	7	3	43	40
5	7	4	62	55
5	7	5	37	38
5	7	6	20	11
5	7	7	23	28
5	7	8	23	20
5	7	11	15	24
5	7	12	24	26
5	7	13	16	19
5	7	14	16	11
5	8	1	19	20
5	8	2	19	26
5	8	3	20	21
5	8	5	20	21
5	8	6	22	32
5	8	7	23	28
5	8	10	24	31
6	0	3	35	43
6	0	4	68	91
6	0	5	23	10
6	0	7	42	52
6	0	8	75	63
6	0	11	32	38
6	0	12	79	53
6	0	13	30	31
6	0	16	44	46
6	1	1	26	40
6	1	2	66	81
6	1	3	35	42
6	1	4	16	18
6	1	5	23	28
6	1	6	111	90
6	1	7	42	45
6	1	8	25	27
6	1	9	26	27
6	1	10	86	74
6	1	11	32	28
6	1	14	37	34
6	1	18	40	29
6	2	0	76	97
6	2	1	25	39
6	2	2	32	33
6	2	3	44	46
6	2	4	86	75
6	2	5	55	58
6	2	8	61	49
6	2	9	23	19
6	2	10	28	26
6	2	11	30	24
6	2	12	53	45
6	2	16	37	32
6	3	0	24	14
6	3	1	51	54
6	3	2	75	72
6	3	3	23	27
6	3	5	23	27
6	3	6	63	56
6	3	7	15	23
6	3	8	23	22
6	3	9	24	27
6	3	10	46	48
6	3	14	32	27
6	4	0	84	84
6	4	1	36	35
6	4	3	14	18
6	4	4	70	65
6	4	5	30	35
6	4	6	26	28
6	4	7	43	39
6	4	8	75	67
6	4	9	30	30
6	4	11	19	22
6	4	12	40	39
6	4	13	29	26
6	5	0	28	29
6	5	1	44	40
6	5	2	68	61
6	5	3	23	20
6	5	4	25	19
6	5	5	56	51
6	5	6	58	55
6	5	7	35	35
6	5	9	19	26
6	5	10	46	44
6	5	14	35	30
6	6	0	75	64
6	6	1	63	51
6	6	2	17	14
6	6	5	18	20
6	6	7	27	21
6	6	8	36	47
6	8	0	38	37

Determination of the structure

A crude structure was determined with three-dimensional Patterson and Fourier maps, using the Fourier program written by Dr T. Ashida of Osaka University for the HITAC 5020 computer in Tokyo University. The structure was refined with the Busing, Martin & Levy full-matrix least-squares program. The calculated structure factors are based on the atomic form factors of the neutral atoms as given in *International Tables for X-ray Crystallography*.

The initial refinement was based on the set of positions of space group $P4_122$. (This group was arbitrarily chosen from the enantiomorphic pair.) In this space group the caesium atoms, the boron atom denoted B(5) and the oxygen atoms denoted O(7) and O(8) must occupy special positions. The crude structure refined to an R index of 13·1% counting only observed reflexions. The positional $x\ (=y)$ parameter of the O(7) and O(8) atoms, however, did not converge in a satisfactory manner, but oscillated back and forth with each cycle of refinement. The requirement that $x=y$ for the special positions of these two oxygen atoms was then relaxed by continuing the refinement of these two atoms in a general position of the orthorhombic space group $P222_1$ (and keeping all other atoms fixed). The refinement now proceeded satisfactorily, R becoming 12·9%. The data thus obtained are reproduced in Table 2.

The temperature factors of the oxygen atoms O(7) and O(8) are still conspicously high (Table 2). A refinement based on a lower symmetry, say space group $P1$, may have improved on this, but was precluded by the capacity of the available computing facilities. The overlap of twin crystals may also be responsible for an apparently high value of these temperature factors. A calculation, excluding atoms O(7) and O(8), raised R from 12·9 to 14·9%, however. The presence of these atoms is therefore well supported by the intensity data.

Table 2. *Atomic position parameters, with standard deviations*

The second column gives space group number and Wyckoff notation for the set of equivalent positions assumed for that atom. Columns three to eight give position parameters and standard deviations as fractions ($\times 10^4$) of the unit cell edge. The last two columns give the parameter B of the isotropic temperature factor and the standard deviation of B.

	Space group no. and Wyckoff notation	x/a	$\sigma_{x/a}$	y/b	$\sigma_{y/b}$	z/c	$\sigma_{z/c}$	B	σ_B
Cs	91, (*a*)	0		4797	3	0		2·62	0·07
O(1)	91, (*d*)	2240	24	1633	22	9900	15	2·19	0·42
O(2)	91, (*d*)	2923	24	7122	24	482	12	1·87	0·37
O(3)	91, (*d*)	3231	21	4857	25	1165	11	1·66	0·33
O(4)	91, (*d*)	4072	27	2278	29	1008	15	2·84	0·48
O(5)	91, (*d*)	3504	23	9757	27	754	13	2·65	0·44
O(6)	91, (*d*)	2014	26	9077	29	9564	13	2·53	0·45
O(7)	17, (*e*) [91, (*c*)]	737	50	786	48	8782	28	5·16	0·93
O(8)	17, (*e*) [91, (*c*)]	5731	54	5909	53	3749	31	5·99	1·06
B(1)	91, (*d*)	3274	45	1241	45	565	21	2·24	0·59
B(2)	91, (*d*)	4364	50	3884	54	1120	24	2·37	0·76
B(3)	91, (*d*)	2706	47	8580	48	320	25	2·27	0·67
B(4)	91, (*d*)	1705	53	483	55	9437	29	3·35	0·83
B(5)	91, (*c*)	3554	80	3554	80	3750		2·57	1·14

With the presence of a heavy atom, it is conceivable that such an atom will account for most of the agreement between the observed and calculated structure factors. In the present case, the R index with caesium only amounts to 28·6%. A considerable fraction of the observed reflexions actually have little or no contribution from caesium.

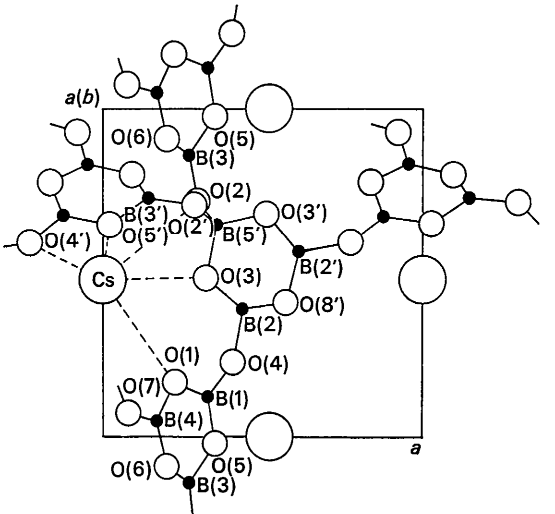

Fig. 1. Projection along the pseudo-tetragonal axis of a section of one of the networks between the levels $z/c=0\cdot875$ and $z/c=1\cdot375$. The unit cell is indicated. Small black circles represent boron, small open circles represent oxygen and large open circles represent caesium. The numbering of the atoms corresponds to the designations in Tables 2 and 3. Five of the ten caesium–oxygen distances from the first coordination sphere of caesium are indicated by dashed lines. The remaining five can be generated from these by the transform $x,y,z \rightarrow -x,y,-z$.

Description and discussion of the structure

The structure consists of two infinite, interlocking three-dimensional networks of boron–oxygen linkages. A projection of a part of one of these networks (between the levels $z/c=0\cdot875$ and $z/c=1\cdot375$) along the pseudo-tetragonal axis is shown in Fig. 1. The network is composed of two different kinds of borate unit, the boroxol group and the triborate group, in the ratio two to one. In the more frequent boroxol group all three boron atoms of the group are threefold coordinated by oxygen. The group is described as a six-membered boron–oxygen ring. The less frequent triborate group also has a six-membered boron–oxygen ring. In this case one boron atom in the ring is fourfold coordinated by oxygen (*cf.* the central group in Fig. 1).

The overall fraction of boron atoms in fourfold coordination, one ninth of the total number, equals that expected from the rule suggested by Krogh-Moe (1962) for anhydrous alkali borates.

Table 3 gives the calculated interatomic distances for the boron–oxygen bond and the caesium–oxygen bond. It should be realized that in addition to the standard deviations given in this table, there is also a systematic error due to the use of the pseudo-symmetry. This error is of unknown magnitude, but presumably small.

All boron–oxygen bond distances fall within the normal values plus or minus twice the standard deviation. The average bond distance is for triangularly coordinated boron 1·35 Å and for tetrahedrally coordinated boron 1·44 Å, close to the 'normal' values.

The caesium atom is coordinated by 10 oxygen atoms with distances ranging from 3·14 Å to 3·40 Å. The next oxygen atom comes 4·06 Å away. The average caesium–oxygen bond distance is 3·30 Å. This compares well

Table 3. *Interatomic distances*

Caesium–oxygen distances (standard deviation ±0·02 Å)

Cs–O(1), Cs–O(1′)	3·40 Å
Cs–O(2), Cs–O(2′)	3·36
Cs–O(3), Cs–O(3″)	3·38
Cs–O(4′), Cs–O(4″)	3·24
Cs–O(5′), Cs–O(5″)	3·14

Boron–oxygen bond lengths (standard deviation ± 0·05Å) in triangles

B(1)–O(1)	1·43 Å	B(3)–O(2)	1·32 Å
B(1)–O(4)	1·35	B(3)–O(5)	1·42
B(1)–O(5)	1·35	B(3)–O(6)	1·41
B(2)–O(3)	1·31	B(4)–O(1)	1·33
B(2)–O(4)	1·44	B(4)–O(6)	1·28
B(2)–O(8′)	1·23	B(4)–O(7)	1·37

Boron–oxygen bond lengths in the tetrahedron

B(5′)–O(2), B(5′)–O(2′)	1·46 Å
B(5′)–O(3), B(5′)–O(3′)	1·43

with the average values 3·27 and 3·37 Å reported in *International Tables for X-ray Crystallography* (1962) for caesium coordinated by 8 and 12 oxygen atoms respectively.

The presence of boroxol groups in caesium enneaborate is interesting. It has been suggested from spectroscopic data (Krogh-Moe, 1965) that boron oxide glass consists largely of boroxol groups. This would seem to be supported by the here established tendency to form such groups in borates of very low alkali content.

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The Crystal Structure of *cis*-2-Butene Episulfone

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The crystal structure of *cis*-2-butene episulfone has been determined by X-ray diffraction techniques. The crystals are orthorhombic, space group $Pna2_1$ (C_{2v}^9), with four molecules per unit cell. The unit cell constants are $a=9{\cdot}790\pm0{\cdot}006$, $b=11{\cdot}04\pm0{\cdot}005$ and $c=5{\cdot}53\pm0{\cdot}01$ Å. Atomic and thermal coordinates were refined by isotropic least-squares methods. A unique feature of this molecule is the unusually long observed ring carbon–carbon bond length of 1·60 Å.

Introduction

We have determined the crystal structure of *cis*-2-butene episulfone as part of a program of research on the effect of the sulfone group on the geometry of small ring systems.

Experimental

Crystals of *cis*-2-butene episulfone prepared by the method of Hesse, Reichold & Majmudar (1957) were obtained from Dr S. Hastings of the Humble Oil Company Research Laboratories, Baytown, Texas. These crystals were long, white needles averaging about 0·2–0·3 mm in diameter. Several crystals were mounted along the needle axis and a series of rotation, precession and Weissenberg photographs were taken. Because the compound slowly decomposed at room temperature, all X-ray data were obtained with the crystals enclosed in glass capillaries under an equilibrium pressure of SO_2 and butene.

On the basis of Weissenberg (Cu $K\alpha$ radiation, $\lambda=1{\cdot}5418$ Å) and precession (Mo $K\alpha$ radiation, $\lambda=0{\cdot}707$ Å) photographs, the Laue symmetry was found to be orthorhombic. The observed systematic absences are

$$0kl \text{ absent when } k+l=2n+1$$
$$h0l \text{ absent when } h=2n+1 .$$

The two space groups corresponding to this set of absences are $Pnam$ (D_{2h}^{16}) and $Pna2_1$ (C_{2v}^9). The unit-cell constants, determined from sodium chloride calibrated rotation and zero layer Weissenberg photographs, are

$$a=9{\cdot}790\pm0{\cdot}006 \text{ Å}$$
$$b=11{\cdot}040\pm0{\cdot}005$$
$$c=5{\cdot}53\pm0{\cdot}01$$
$$[a_0(\mathrm{NaCl})=5{\cdot}637 \text{ Å}]$$

Density measurements showed that the unit cell contains four molecules. If the centric space group $Pnam$ (D_{2h}^{16}) were the correct one, the molecules must lie on the mirror planes located at $z=\pm\frac{1}{4}$. However, this type of structure was considered highly unlikely because the short repeat distance in the **c** direction would place successive molecules too close together. For this reason, $Pnam$ was discarded and $Pna2_1$ was assumed to be the correct space group. This assumption was later proven to be correct.

Multiple-film equi-inclination Weissenberg photographs of the $l=0$, 1, 2 and 3 layers were taken with filtered Cu $K\alpha$ radiation. The intensities of the various reflections were estimated visually by comparison with a standard intensity strip. Interlayer correlation of intensities was made with data from $h0l$ and $0kl$ per-