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The Crystal Structure of Cadmium Diborate, $CdO . 2B_2O_3$

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The crystal structure of cadmium diborate has been determined by a three-dimensional Fourier synthesis. The atomic position parameters have been refined by a least-squares analysis including 519 reciprocal-lattice points. A residual index R equal to 8·5 % was obtained. The structure consists of two interlocking, identical networks. The networks are built up from a single type of borate unit, composed of four borate polyhedra. A boron–oxygen arrangement of this type has first been found in the isolated polyanion unit of borax. 50 % of the boron atoms are fourfold coordinated in the structure. The cadmium atoms are surrounded by four close oxygens, arranged in a distorted tetrahedron.

Introduction

The structures of several compounds with a ratio of metal oxide to boron oxide of 1 to 2 are known. The hydrated compounds $Na_2O . 2B_2O_3 . 10H_2O$ (Morimoto, 1956) and $K_2O . 2B_2O_3 . 4H_2O$ (Marezio, Plettinger & Zachariasen, 1963) contain a characteristic double ring polyion as an isolated unit. In the anhydrous lithium diborate, $Li_2O . 2B_2O_3$, these double ring polyions are condensed to two interlocking three-dimensional networks (Krogh-Moe, 1962). 50% of the boron atoms are fourfold coordinated in all these phases, conforming to the rule that the number of borons in fourfold coordination is equal to the total number of charge units carried by foreign cations (excluding H^+).

Recently the structure of strontium diborate, $SrO . 2B_2O_3$, has been determined (Krogh-Moe, 1964). Here a completely different type of network is found, having *all* the boron atoms in fourfold coordination. As a consequence some of the oxygen atoms are coordinated by three boron atoms. This is contrary to prevailing ideas about oxygen always acting as a bridge between *two* network-forming cations in the so called network structures. An inquiry into the condition for abnormal coordination numbers of oxygen is thus of some interest.

The difference in coordination behaviour of the lithium and strontium diborates obviously must originate in properties of the cation. Simple empirical correlations between boron coordination behaviour and parameters of the cation, such as radius, charge, electronegativity or polarizability are conceivable. On the other hand the dependence of boron coordination on the cation could also be of a more complex nature. To elucidate this question, structural data about other diborates are highly desirable, and an investigation of the structure of cadmium diborate was therefore undertaken.

Experimental

Crystalline cadmium diborate was prepared by fusing boric acid with a small excess of cadmium oxide, and annealing the supercooled melt at 800 °C.

Unit-cell dimensions for cadmium diborate have previously been given by Hand & Krogh-Moe (1962). For the present work the unit-cell dimensions were refined by a least-squares adjustment, using nine indexed powder lines from a diffractometer recording. The following dimensions were found:

$$a = 8·21 \pm 0·01 , \quad b = 8·70 \pm 0·01 , \quad c = 14·18 \pm 0·02 \text{ Å}$$

Space group *Pbca*. The calculated and observed densities with 8 formula units in the unit cell are 3·51 and 3·52 $g.cm^{-3}$ respectively.

A single crystal of the sample was ground to a nearly perfect sphere of radius $R = 0·005$ cm. With Mo $K\alpha$-radiation the linear absorption coefficient is 44 cm^{-1}, making absorption errors quite small for a sphere of this size ($\mu R = 0·22$).

Integrated multiple-film Weissenberg exposures were obtained for the zero to seventh layers, rotating the crystal around the a axis and using Mo $K\alpha$-radiation. The intensities were measured photometrically in 519 points in the reciprocal lattice and corrected for the Lorentz and polarization factors in the usual manner.

Determination of the structure

The unit cell contains 8 cadmium atoms, occupying, as it turns out, a single general position. The three positional parameters of the cadmium atom were determined from Patterson projections along two of the axes. Signs derived from this heavy atom position together with the experimental structure factors were employed for calculating a complete three-dimensional Fourier synthesis. From the electron density sections thus obtained, a crude model of the structure was constructed settling the positions of the 4 boron and 7 oxygen atoms of the asymmetric unit. The structure was subsequently refined by the method of least squares,

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using the program written by S. Aleby for the SAAB D21 computer of the crystallographic group at the Insitute of Medical Biochemistry in Göteborg. A final reliability index of $R=8{\cdot}5\%$ was obtained.

A list of final positional parameters and temperature factors, together with standard deviations, is given in Table 1. Table 2 gives the observed and calculated structure factors.

Description and discussion of the structure

The structure consists of two infinite three-dimensional networks of boron–oxygen linkages. This is shown in Fig. 1, which gives a projection of the structure along the *a* axis. The connexions of the networks perpendicular to the plane of the paper are easily recognized by considering the operation of the twofold screw axes normal to the paper plane. (These screw axes have the following y, z values: $0, \frac{1}{4}; 0, \frac{3}{4}; \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{3}{4}$).

Each of the twin networks can be derived from the other by the symmetry operations of the space group, and is thus separate and interlocking. (For clarity one of the networks is shown dashed in Fig. 1.) This phenomenon of two interlocking, but separate, borate networks has been found in several other anhydrous borate structures (Krogh-Moe, 1962, 1965).

Table 1. *Atomic position parameters, with standard deviations*

Values are given as fractions multiplied by 10^4, of the unit cell edge. The last two columns give the parameter B (together with its standard deviation) of the temperature factor $\exp[-B(\sin\theta/\lambda)^2]$. Temperature factors of atoms O(4), O(5), B(3) and B(4) were arbitrarily fixed at 0·1 to avoid (small) negative values during refinement.

Atom	x/a	$\sigma_{x/a}$	y/b	$\sigma_{y/b}$	z/c	$\sigma_{z/c}$	B	σ_B
Cd	1210	2	1105	2	1125	1	0·94 Å^2	0·02
O(1)	543	17	4103	17	1875	10	0·58	0·03
O(2)	3853	15	1325	13	980	8	0·40	0·03
O(3)	3544	22	3759	17	21	9	1·18	0·03
O(4)	4733	14	3837	15	1489	8	0·10	—
C(5)	5335	17	1642	16	2433	8	0·10	—
O(6)	6094	18	2561	19	201	10	0·94	0·03
O(7)	6595	16	428	17	1147	10	0·94	0·02
B(1)	4473	28	2864	30	679	18	1·04	0·04
B(2)	5140	27	3285	26	2346	15	0·44	0·03
B(3)	5061	23	640	23	1624	14	0·10	—
B(4)	7019	25	1374	22	425	14	0·10	—

Table 2. *Observed and calculated structure factors*

h	k	l	F_o	F_c
0	0	4	249	-292
0	0	6	112	-101
0	0	8	268	282
0	0	10	168	156
0	0	12	80	-63
0	0	14	174	-175
0	0	18	136	120
0	0	22	100	-90
0	2	1	173	-227
0	2	2	53	-40
0	2	3	280	-315
0	2	4	178	-172
0	2	5	42	37
0	2	7	299	335
0	2	11	203	-203
0	2	12	42	-36
0	2	13	70	-72
0	2	15	159	163
0	2	17	92	100
0	2	21	69	-73
0	4	0	329	-385
0	4	1	50	-44
0	4	3	143	-138
0	4	4	233	234
0	4	5	60	51
0	4	6	91	90
0	4	7	95	92
0	4	8	176	-177
0	4	10	127	-117
0	4	11	68	-66
0	4	12	55	63
0	4	14	127	129
0	4	18	110	-97
0	6	0	139	-134
0	6	1	103	99
0	6	3	174	169
0	6	4	130	132
0	6	7	152	-162
0	6	10	99	-87
0	6	11	138	136
0	6	12	60	49
0	6	15	112	-104
0	6	16	49	-11
C	8	0	163	164
0	8	2	82	82
0	8	3	77	77
0	8	4	119	-112
0	8	7	100	-101
0	8	8	106	103
0	8	10	92	90
0	8	11	87	86
0	8	12	80	-58
0	10	0	88	79
0	10	4	107	-112
0	10	7	80	85
0	10	11	108	-98
0	12	3	87	-74
1	0	4	33	-38
1	0	6	167	184
1	0	8	128	128
1	0	10	51	-57
1	0	12	104	-100
1	0	16	77	76
1	1	5	131	-135
1	1	6	113	116
1	1	7	80	78
1	1	8	78	76
1	1	9	125	123
1	1	12	92	-96
1	1	13	79	-55
1	1	14	86	82
1	2	1	80	-115
1	2	3	131	135
1	2	5	214	238
1	2	9	143	-149
1	2	13	105	107
1	2	17	68	-57
1	3	1	117	-118
1	3	2	139	-148
1	3	3	62	58
1	3	4	59	-54
1	3	5	66	69
1	3	6	62	63
1	3	7	61	-59
1	3	8	98	89
1	3	9	75	-68
1	3	10	83	-82
1	3	12	113	-118
1	3	14	65	65
1	4	2	198	219
1	4	4	53	55
1	4	6	152	-154
1	4	8	90	-90
1	4	10	94	95
1	4	12	115	117
1	5	1	115	-119
1	5	2	54	46
1	5	3	76	73
1	5	5	149	146
1	5	6	54	-48
1	5	7	77	-81
1	5	9	135	-137
1	5	13	94	79
1	6	1	90	93
1	6	2	74	79
1	6	3	110	-102
1	6	5	157	-164
1	6	9	113	116
1	6	13	98	-89
1	6	14	88	-32
1	7	2	133	133
1	7	6	103	-97
1	7	8	88	-103
1	7	10	84	74
1	7	12	74	75
1	8	1	63	69
1	8	2	90	-100
1	8	6	105	101
1	8	8	70	68
1	8	9	72	72
1	8	13	76	-62
1	9	1	121	115
1	9	5	88	-96
1	9	9	84	78
1	10	2	85	-89
1	11	2	79	-75
2	1	3	168	-223
2	1	4	118	128
2	1	5	92	89
2	1	6	57	62
2	1	7	201	207
2	1	8	133	-123
2	1	9	61	-56
2	1	10	79	-71
2	1	11	146	-145
2	1	12	89	89
2	1	13	44	-16
2	1	14	113	118
2	1	15	110	110
2	1	17	46	53
2	1	18	61	-58
2	3	0	193	-214
2	3	1	72	78
2	3	2	45	40
2	3	3	62	65
2	3	4	253	273
2	3	6	128	127
2	3	7	79	-76
2	3	8	107	-108
2	3	9	46	32
2	3	10	105	-104
2	3	11	62	56
2	3	12	119	113
2	3	14	131	132
2	3	15	74	-62
2	3	16	73	-56
2	3	18	93	-99
2	5	1	114	118
2	5	2	56	-41
2	5	3	167	176
2	5	4	63	-47
2	5	5	89	-81
2	5	6	56	-56
2	5	7	169	-168
2	5	11	151	150
2	5	15	98	-95
2	7	0	153	161
2	7	2	50	35
2	7	4	144	-148
2	7	8	97	95
2	7	10	97	98
2	7	12	81	-86
2	7	14	106	-105
2	9	1	82	-86
2	9	3	117	-125
2	9	5	65	56
2	9	7	124	117
2	9	11	96	-100
2	11	0	90	-82
2	11	4	111	120
2	11	6	49	54
2	11	8	58	-69
3	0	4	56	-51
3	0	6	165	182
3	0	8	123	125
3	0	10	61	-61
3	0	12	101	-112
3	0	14	73	74
3	0	16	105	96
3	0	20	79	-63
3	1	5	40	36
3	1	6	97	-102
3	1	7	33	-30
3	1	8	57	-55
3	1	9	96	-89
3	1	10	56	52
3	1	11	57	-41
3	1	13	59	59
3	1	16	49	-57
3	1	17	61	-63
3	2	1	133	-155
3	2	2	37	-44
3	2	3	73	73
3	2	5	221	232
3	2	9	156	-166
3	2	10	52	-40
3	2	12	50	-39
3	2	13	125	131
3	2	15	70	65
3	2	17	80	-64
3	2	19	72	-61
3	3	1	66	67
3	3	2	124	132
3	3	5	50	-56
3	3	6	120	-120
3	3	9	95	99
3	3	10	73	72
3	3	12	69	48
3	3	13	53	-58
3	4	1	35	-35
3	4	2	207	225
3	4	5	74	72
3	4	8	72	-62
3	4	9	50	-50
3	4	10	97	100
3	4	12	116	124
3	4	16	76	-76
3	5	1	114	114
3	5	2	62	-59
3	5	3	56	-57
3	5	5	90	-90
3	5	6	50	47
3	5	9	115	117
3	5	10	66	-60
3	5	13	81	-82
3	5	17	71	81
3	6	1	106	112
3	6	2	83	85
3	6	3	73	-62
3	6	5	137	-147
3	6	6	64	-60
3	6	9	99	102
3	6	13	100	-94
3	7	2	126	-127
3	7	6	128	136
3	7	8	61	49
3	7	10	69	-62
3	7	12	60	-62
3	8	5	82	-73
3	8	6	89	89
3	8	9	79	83
3	9	3	85	-70
3	9	5	81	76
3	9	9	121	-111
3	9	13	78	82
3	10	2	85	-87
3	10	9	85	-54
3	11	2	87	72
3	11	6	85	-64
4	0	4	203	237
4	0	6	88	97
4	0	8	188	-197
4	0	10	220	-227
4	0	12	99	109
4	0	14	132	132
4	0	18	122	-116
4	0	22	96	69
4	2	1	104	108
4	2	2	31	28
4	2	3	212	255
4	2	4	52	53
4	2	5	110	-118
4	2	6	72	68
4	2	7	211	-229
4	2	11	179	179
4	2	15	107	-107
4	2	17	63	-67
4	2	19	74	63
4	4	0	169	182
4	4	1	56	56
4	4	2	53	60
4	4	3	65	-47
4	4	4	184	-198
4	4	6	99	-102
4	4	7	81	-79
4	4	8	133	130
4	4	10	147	156
4	4	11	76	73
4	4	12	79	-67
4	4	14	104	-103
4	4	15	70	-55
4	4	18	111	108
4	6	0	115	119
4	6	1	122	-123
4	6	3	139	-146
4	6	5	90	82
4	6	6	68	-62
4	6	7	130	131
4	6	8	91	96
4	6	11	109	-104
4	8	0	149	-157
4	8	1	74	-70
4	8	3	78	-74
4	8	4	76	78
4	8	7	87	79
4	8	8	100	-95
4	8	10	90	-83
4	8	11	68	-59
4	8	14	88	76
4	8	15	70	60
4	10	0	89	-85
4	10	1	70	69
4	10	3	79	79
4	10	4	80	77
4	10	5	62	-48
4	10	6	58	45
4	10	7	83	-76
4	10	8	76	-63
4	12	0	69	64
4	12	1	80	70
4	12	3	80	66
5	0	4	48	60
5	0	6	101	-105
5	0	8	85	-91
5	0	10	95	89
5	0	12	71	65
5	0	16	92	-88
5	1	3	54	58
5	1	5	100	105
5	1	6	88	-90
5	1	7	46	-34
5	1	8	57	-47
5	1	9	98	-94
5	1	10	66	61
5	1	13	100	93
5	1	16	79	-79
5	1	17	55	-67
5	2	1	91	110
5	2	3	115	-132
5	2	4	35	29
5	2	5	110	-120
5	2	9	71	71
5	2	13	84	-83
5	2	15	51	-39
5	2	17	50	40
5	3	1	58	53
5	3	2	151	176
5	3	4	43	34
5	3	5	54	-50
5	3	6	101	-104
5	3	8	38	-22
5	3	9	54	51
5	3	10	86	89
5	3	12	85	77
5	3	13	75	-68
5	3	16	73	-69
5	4	2	111	-116
5	4	3	46	-38
5	4	4	76	-74
5	4	6	89	92
5	4	10	73	-79
5	4	12	64	-72
5	4	16	79	71
5	5	2	39	-36
5	5	3	59	-60
5	5	5	108	-109
5	5	9	112	110
5	5	10	68	-58
5	5	13	89	-92
5	5	17	80	73
5	6	1	63	-72
5	6	2	39	-31
5	6	3	92	92
5	6	6	64	63
5	6	9	89	-80
5	6	12	40	-30
5	6	13	79	77
5	7	2	109	-116
5	7	5	103	112
5	7	8	57	49
5	7	10	56	-52
5	7	12	80	-60
5	7	14	51	56
5	8	1	69	-67
5	8	2	72	67
5	8	3	51	50
5	8	5	65	51
5	8	6	76	-56
5	8	12	57	59
5	9	1	78	-68
5	9	5	84	82
5	9	9	103	-98
5	10	2	42	45
5	10	5	65	-56
5	10	6	56	-58
5	11	2	85	75
5	11	6	75	-68
6	1	2	41	51
6	1	3	89	111
61	1	4	123	-144
6	1	5	62	-66
6	1	7	115	-119
6	1	8	75	76
6	1	10	77	63
6	1	11	133	134
6	1	12	71	-64
6	1	14	46	-36
6	1	15	101	-93
6	1	18	85	58
6	1	19	74	69
6	3	0	100	112
6	3	3	51	-57
6	3	4	163	-183
6	3	5	56	55
6	3	6	77	-76
6	3	7	70	63
6	3	8	127	130
6	3	10	74	64
6	3	11	82	-81
6	3	12	68	-76
6	3	14	94	-75
6	3	18	78	78
6	5	1	103	-107
6	5	3	115	-117
6	5	4	80	87
6	5	5	44	40
6	5	7	123	128
6	5	11	120	-121
6	5	15	106	105
6	7	0	160	-158
6	7	4	109	117
6	7	6	57	64
6	7	8	120	-124
6	7	10	58	-46
6	7	12	72	49
6	7	14	97	77
6	9	1	87	76
6	9	3	75	73
6	9	7	109	-109
6	9	11	98	89
6	11	0	116	112
6	11	4	101	-89
6	11	8	80	69
7	0	4	54	64
7	0	6	126	-141
7	0	8	117	-124
7	0	10	92	100
7	0	12	89	88
7	0	14	50	-35
7	0	16	123	-125
7	1	2	38	-50
7	1	3	21	-23
7	1	4	39	-47
7	1	5	41	-34
7	1	6	47	46
7	1	9	72	66
7	1	10	37	-31
7	1	13	57	-51
7	1	14	45	37
7	2	1	115	161
7	2	2	35	39
7	2	3	82	-105
7	2	4	39	31
7	2	5	116	-134
7	2	9	106	116
7	2	13	95	-92
7	2	17	82	56
7	3	2	52	-47
7	3	4	45	-46
7	3	6	65	61
7	3	8	35	47
7	3	9	59	-48
7	3	10	65	-64
7	3	12	61	-45
7	3	14	57	30
7	4	1	48	39
7	4	2	111	-125
7	4	3	50	-49
7	4	4	70	-77
7	4	5	37	-38
7	4	6	75	81
7	4	8	82	80
7	4	9	44	41
7	4	10	84	-84
7	4	12	89	-89
7	4	13	57	-41
7	4	16	73	79
7	5	1	80	-87
7	5	2	47	44
7	5	3	51	39
7	5	5	57	61
7	5	9	71	-66
7	5	13	62	61
7	6	1	81	-89
7	6	2	41	-40
7	6	3	67	65
7	6	5	93	90
7	6	6	63	71
7	6	9	95	-82
7	6	13	65	61
7	7	2	75	76
7	7	6	67	-65
7	7	8	50	-47
7	7	10	58	55
7	8	1	61	-54
7	8	2	65	67
7	8	4	54	38
7	8	5	59	45
7	8	6	68	-60
7	8	8	67	-59
7	8	9	54	-41
7	8	12	69	59
7	9	1	69	62
7	9	5	54	-48
7	9	9	68	48

It is apparent from Fig. 1 that the network may be described as composed of borate units having 4 boron atoms and 5 oxygen atoms within the unit as well as 4 oxygen atoms shared with 4 adjacent units. This double ring structure was first discovered as the isolated polyion, $B_4O_5(OH)_4^{2-}$, in the mineral borax by Morimoto (1956). Later, the group was found as part of a network structure in $Li_2O.2B_2O_3$ (Krogh-Moe, 1962). The twin networks in the lithium compound are arranged somewhat differently from those reported here, however.

Interatomic bond distances are given in Table 3. The average of the boron–oxygen bond distances in the BO_4 tetrahedra is 1·47 Å as opposed to 1·37 Å for the BO_3 triangles. This compares well with the corresponding mean bond lengths observed in potassium diborate tetrahydrate, *viz.* 1.480 Å and 1.368 Å for tetrahedra and triangles respectively (Marezio, Plettinger & Zachariasen, 1963). What appear to be significant variations from the average values in the individual bond lengths (up to 6 times the standard deviation of 0·008 Å) were found by these authors. The boron–oxygen bond lengths obtained by us [excepting the B(2)–O(5) distance] vary within 3 times the standard deviations of 0·02 Å, and too much emphasis should therefore not be placed on these variations. A real effect as large as that obtained would not be unexpected, however.

The cation coordination is noteworthy. Cadmium is surrounded by four close oxygen atoms at distances 2·18, 2·19, 2·21 and 2·22 ± 0·01 Å. Then follow oxygen atoms at 2·59 Å and farther away (*cf.* Table 3). The four close oxygen atoms are arranged in a distorted tetrahedron. (The six O–Cd–O angles of this coordination polyhedron are 81·9, 85·2, 112·9, 116·9, 131·1 and 131·4 ± 0·6°.) The bond distance within the tetrahedron is closer to that obtained from the tetrahedral covalent radii of cadmium and oxygen, *i.e.* 2·14 Å, than to the bond distance, 2·37 Å, calculated from the (octahedral) ionic radii (Pauling, 1960). The cadmium atom therefore seems to be essentially covalent tetrahedrally bonded, though other oxygens probably take some smaller part in the bonding.

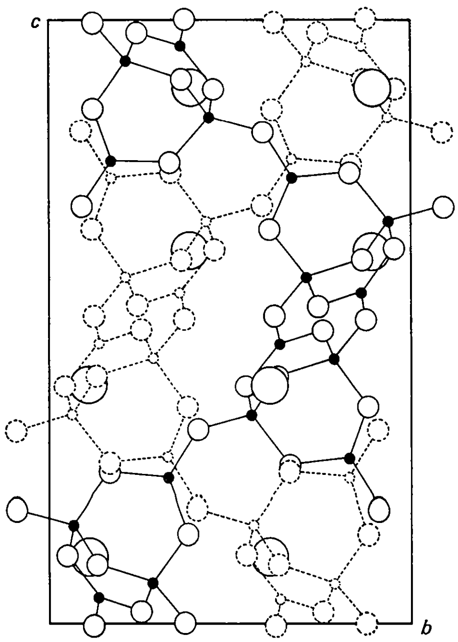

Fig. 1. A projection of the structure along the *a* axis, showing how the structural units are interlinked to a three-dimensional network. Black circles: boron; open circles: oxygen; large open circles: cadmium. The network indicated by dashed lines is a separate interlocking twin of the first network. The unit-cell dimensions are indicated by the rectangle.

Table 3. *Interatomic distances*

Boron–oxygen bond lengths (standard deviation ± 0·02 Å) of the boron coordination polyhedra.

Tetrahedra

B(1)–O(2)	1·50 Å	B(3)–O(1)	1·47 Å
B(1)–O(3)	1·43	B(3)–O(2)	1·47
B(1)–O(4)	1·44	B(3)–O(5)	1·46
B(1)–O(6)	1·52	B(3)–O(7)	1·44

Triangles

B(2)–O(1)	1·35 Å	B(4)–O(3)	1·41
B(2)–O(4)	1·35	B(4)–O(6)	1·32
B(2)–O(5)	1·45	B(4)–O(7)	1·36

Cadmium–oxygen distances (standard deviation ± 0·01 Å)

Cd–O(4)	2·18 Å
Cd–O(2)	2·19
Cd–O(6)	2·21
Cd–O(5)	2·22
Cd–O(3)	2·58
Cd–O(3^1)	2·73
Cd–O(1)	2·87

The cadmium diborate and the lithium diborate are both characterized by a somewhat shorter metal–oxygen bond than found in the strontium compound. It is still imprudent to single out a short metal–oxygen bond as a decisive factor in the formation of the 'normal' $B_4O_5(O)_4$ group in anhydrous diborates. Too few structures are yet known to guide an empirical approach. Moreover the energy associated with a change to the structure type of the strontium compound is probably quite small, so that several factors may come into play. Further structure studies in this field are thus needed before empirical rules for the boron coordination behaviour can be given.

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