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The space group and crystal structure of trizinc diorthoborate

By WERNER H. BAUR and EKKEHART TILLMANNS

Department of Geological Sciences, University of Illinois, Chicago, Illinois

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Auszug

Die Struktur des $Zn_3(BO_3)_2$ kristallisiert in der zentrosymmetrischen Raumgruppe $I2/c$, und nicht, wie GARCIA-BLANCO und FAYOS (1968) annehmen, in Ic. Die neue Verfeinerung ergab $R = 0{,}133$ für 787 beobachtete Strukturfaktoren, verglichen mit $R = 0{,}132$, dem Wert, der von GARCIA-BLANCO und FAYOS angegeben wurde. Die Bindungslängen und -winkel in der zentrosymmetrischen Struktur stimmen gut überein mit entsprechenden Werten in sorgfältig bestimmten anderen Strukturen, während die nichtzentrosymmetrische Struktur des $Zn_3(BO_3)_2$ eigentümliche Verzerrungen der Bindungslängen und -winkel aufweist.

Abstract

The structure of trizinc diorthoborate is shown to crystallize in the centrosymmetric space group $I2/c$, and not in Ic as assumed by GARCIA-BLANCO and FAYOS (1968) who determined the structure originally. The new refinement yielded an $R = 0.133$ for 787 F_{obs}, as compared to $R = 0.132$ achieved by the previous authors. The bond lengths and angles in the centrosymmetric structure agree well with values for comparable bonds in well determined structures, while the acentric structure exhibits some unusual distortions from the commonly accepted values.

Introduction

GARCIA-BLANCO and FAYOS (1968) determined recently the crystal structure of $Zn_3(BO_3)_2$. The structure as described by them contains an unusual feature: the range of the values of bond lengths, which should be chemically equivalent, is large. The spread is 1.86 to 2.13 Å for Zn—O, and 1.22 to 1.54 Å for B—O bonds and thus larger than for any known, well refined structure containing such bonds. Such a range can neither be explained by edge-sharing considerations (PAULING, 1960), since only one of the polyhedral edges is shared, nor can it be explained by the extended electrostatic valence rule

(BAUR, 1961) because the charge of all the oxygen atoms is exactly balanced by the electrostatic bond strengths received from the cations.

Refinement of the crystal structure

GARCIA-BLANCO and FAYOS claim that the refinement of their data to an R of 13.2% (excluding the 15 largest F_{obs}) in space group Ic is final proof that the structure is acentric. The only indication they find for a higher symmetry is what they call a "pseudosymmetry in (010) projection with a false center in position $\frac{1}{4}\frac{1}{4}$". More careful inspection of the illustrations of the structure reveals, however, the presence of the following approximate symmetry elements: a two-fold axis in $0y0$, a two-fold screw axis in $\frac{1}{4}y\frac{1}{4}$ and centers of symmetry in $00\frac{1}{4}$ and $\frac{1}{4}\frac{1}{4}0$. That means that all symmetry elements of space group $I2/c$ are present if one allows shifts of a few hundredth of a cell edge in the positional parameters. Consequently we employed the F_{obs} measured by GARCIA-BLANCO and FAYOS in a refinement based on space group $I2/c$. As starting parameters we used the values for the unprimed atoms of their Table 3; however we shifted the origin of the unit cell by 3/4 in the c direction. All atoms are thus in the general eight-fold position of $I2/c$ with $(000; \frac{1}{2}\frac{1}{2}\frac{1}{2}) \pm (x\,y\,z;\ x\,\bar{y}\,\frac{1}{2}+z)$. The unit-cell dimensions determined by GARCIA-BLANCO and FAYOS ($a = 23.406$, $b = 5.048$, $c = 8.381$ Å and $\beta = 97.53°$) were used. All B values were set initially at 1 Å^2. The scattering-factor curves for B^{+1}, O^{-1} and Zn^{+2} from the *International Tables*, vol. III (1962) were employed in the structure-factor calculations. A Hughes-type

Table 1. *Positional and thermal parameters of* $Zn_3(BO_3)_2$

In parentheses are the estimated standard deviations in units of the last significant digits of the values

Atom	x	y	z	B
Zn(1)	0.0495(1)	0.8291 (4)	0.3746 (2)	0.61(7) Å^2
Zn(2)	0.1275(1)	0.6841 (4)	0.7488 (2)	0.53(7)
Zn(3)	0.2095(1)	0.6921 (4)	0.4992 (3)	0.60(7)
B(1)	0.0660(7)	0.3213(31)	0.5320(18)	− 0.3 (2)
B(2)	0.1870(7)	0.1835(33)	0.6683(19)	− 0.2 (2)
O(1)	0.0363(5)	0.2018(24)	0.6362(13)	0.2 (2)
O(2)	0.0820(4)	0.5885(23)	0.5408(13)	0.1 (2)
O(3)	0.0798(5)	0.1874(24)	0.4001(15)	0.7 (2)
O(4)	0.1843(4)	0.9117(25)	0.6632(12)	0.0 (2)
O(5)	0.2149(5)	0.3132(21)	0.5537(13)	0.2 (2)
O(6)	0.1633(5)	0.6783(21)	0.2847(14)	0.4 (2)

Table 2. *Observed and calculated structure factors*

h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c
-28 0 0	63	-55	0 0 8	311	331	-23 1 4	104	-94	3 1 10	44	46	0 2 4	123	-130	11 3 0	57	-45
-26	143	-117	2	54	-48	-21	51	32	2 2 0	29	37	2	193	240	13	46	43
-24	298	281	4	21	-18	-15	110	-90	6	31	26	4	45	38	15	192	191
-22	73	63	6	83	-77	-13	80	62	8	60	55	6	54	-40	17	108	-91
-18	50	54	8	19	- 1	-11	133	142	10	41	33	8	135	-118	19	44	-35
-16	76	69	12	274	-283	-9	94	85	12	*222	336	10	153	-143	21	250	-269
-14	154	150	14	23	29	-7	68	59	14	89	-113	12	121	106	23	62	52
-12	*362	-483	16	33	35	-5	45	-30	18	71	-55	14	143	-141	-26 3 1	48	-43
-10	45	-39	-14 0 10	121	135	-3	65	52	24	138	-176	16	51	-40	-24	27	18
-8	249	-274	-12	47	46	-1	231	-303	26	95	91	20	137	126	-20	115	-105
-6	88	-75	-10	91	88	1	144	-139	-25 2 1	33	25	22	102	90	-18	71	61
-4	69	-62	-8	163	-159	3	109	93	-23	224	249	24	61	-70	-16	21	15
-28 0 2	150	127	-6	117	-104	7	117	112	-21	67	56	-25 2 5	82	-94	-14	109	90
-26	249	-208	-4	119	107	9	47	-42	-17	38	30	-23	60	55	-12	30	-19
-24	78	-66	-2	128	-123	11	115	95	-15	109	-100	-21	113	-131	-10	81	-81
-22	233	-214	0	35	-46	13	110	95	-13	128	-170	-19	132	-147	-8	120	130
-20	144	116	2	14	-12	15	73	-59	-11	*214	-346	-17	122	117	-6	74	-69
-18	120	139	4	118	122	23	95	-86	-9	119	139	-15	109	96	-4	23	19
-16	130	-137	6	75	80	25	34	-33	-7	132	140	-13	143	145	-2	36	28
-14	264	335	3 1 0	156	189	-24 1 5	150	-163	-5	86	-68	-11	36	-16	0	31	-20
-12	144	154	5	55	47	-22	206	-256	-3	146	144	-9	170	162	2	21	-15
-10	257	280	7	32	-29	-20	150	121	-1	109	115	-7	59	46	4	130	-147
-8	334	-429	9	164	-223	-18	70	-53	1	238	297	-5	208	-196	6	22	19
-6	279	-294	11	29	21	-16	44	45	3	61	-61	-3	124	-125	8	79	67
-4	141	106	13	96	-81	-14	128	115	5	148	-179	-1	169	-155	10	64	66
-2	207	-206	15	106	-98	-12	232	246	7	43	-37	1	138	122	12	78	-56
0	55	41	17	88	83	-10	195	194	9	113	-121	3	174	-163	16	60	47
2	80	-68	21	177	157	-8	251	-267	11	117	-131	5	41	-26	18	87	-68
4	*368	638	27	68	58	-6	105	90	13	150	-140	7	204	226	20	53	43
6	150	-118	29	50	-57	-4	114	-101	15	246	281	9	128	116	24	56	46
8	196	-201	-26 1 1	154	143	-2	91	-73	17	149	126	11	115	101	-25 3 2	54	44
10	186	202	-20	249	302	0	192	-249	19	58	-40	13	131	-125	-23	24	11
12	157	-164	-18	43	-42	2	184	-223	21	65	41	15	87	72	-19	167	171
14	108	103	-16	155	-152	4	*226	338	23	16	-27	17	105	-87	-17	213	-238
16	326	-381	-14	180	-258	6	32	-35	25	51	46	19	167	-173	-15	90	-84
18	61	-53	-12	21	-12	8	140	100	27	104	-122	-24 2 6	58	-54	-13	117	-104
20	210	178	-10	83	-74	10	87	65	-28 2 2	65	-78	-22	48	37	-9	63	53
22	79	-72	-8	*179	-371	12	167	160	-26	123	124	-20	114	-117	-7	195	-242
24	132	101	-6	*156	263	16	262	-275	-24	64	56	-16	144	155	-5	*281	454
26	96	77	-4	166	198	18	101	90	-22	134	127	-14	45	35	-3	176	177
28	190	188	-2	190	244	20	77	-61	-20	108	-109	-12	94	83	-1	23	-13
-28 0 4	15	- 9	0	17	13	-25 1 6	41	38	-18	77	-68	-10	101	-88	1	144	-123
-26	157	-112	2	39	-29	-23	68	63	-16	106	91	-8	134	129	3	125	-118
-24	186	166	4	*217	374	-21	59	60	-14	149	-161	-6	78	-66	5	84	70
-22	228	-217	6	169	-218	-19	112	-105	-10	159	-216	-4	210	-225	7	*234	-375
-20	132	-116	8	183	-238	-17	51	15	-8	174	225	-2	49	36	9	38	27
-18	124	-116	10	172	-215	-15	70	-62	-6	112	104	2	129	113	11	122	105
-16	28	22	12	88	91	-13	99	-92	-4	144	-140	4	99	-91	13	179	168
-14	272	343	14	57	52	-11	53	-37	-2	210	226	6	83	72	15	112	79
-12	235	-238	16	178	-156	-9	34	26	0	18	-14	8	135	125	17	82	-65
-10	275	295	18	292	304	-7	182	164	2	72	57	10	82	-70	19	205	192
-8	249	241	20	131	105	-1	65	45	4	258	-339	12	37	-28	21	71	-57
-6	79	58	24	141	-138	3	98	-74	6	19	- 8	14	120	-111	23	112	-106
-4	210	-175	26	98	-89	5	97	-84	8	140	153	16	58	66	-26 3 3	32	29
-2	336	-361	28	57	57	9	78	-53	10	73	-75	18	37	-34	-24	48	-45
0	175	163	-29 1 2	47	-44	15	86	72	12	94	93	20	61	-71	-20	31	19
2	309	-390	-27	83	-80	17	131	118	14	71	-56	-21 2 7	36	-29	-18	57	50
4	193	-197	-25	32	-45	19	66	-65	16	198	193	-17	96	-101	-16	72	-54
6	61	50	-19	70	-52	-24 1 7	117	132	18	28	-23	-15	151	-190	-14	36	33
8	240	289	-17	158	146	-22	49	-47	20	117	-96	-13	149	149	-10	41	-28
10	202	252	-13	67	63	-20	65	-63	22	63	56	-11	44	41	-6	88	-80
12	59	-78	-9	37	-29	-18	181	-196	24	56	-42	-9	82	72	-4	151	146
14	193	210	-7	182	213	-16	134	128	-25 2 3	114	-119	-5	29	36	-2	60	-52
18	47	-30	-5	211	-286	-12	128	-113	-23	49	-37	-3	176	169	0	113	-93
20	255	-234	-3	142	-136	-10	145	141	-21	70	67	-1	162	-164	2	28	25
22	169	-130	-1	28	-14	-8	43	43	-19	160	194	1	87	-82	4	77	-65
24	135	146	3	141	127	-6	217	220	-17	73	62	3	112	-96	6	103	103
26	120	-142	5	37	23	-4	194	-184	-15	108	-112	7	77	-73	8	58	-60
-26 0 6	36	41	7	176	205	0	95	78	-13	136	149	9	49	-46	10	53	41
-24	64	58	11	108	-106	2	168	-164	-11	61	-55	11	214	257	12	120	94
-22	56	-44	13	116	-117	4	113	-100	-9	125	-129	13	66	58	14	76	-54
-20	166	144	19	102	-79	6	178	-180	-7	177	-211	15	50	44	18	11	-16
-16	206	-198	23	43	28	8	227	244	-5	45	-46	17	58	-69	20	52	44
-14	99	-93	25	94	83	14	175	176	-3	166	175	-16 2 8	48	-28	22	40	-33
-12	124	-131	-28 1 3	130	-144	16	54	47	-1	137	-126	-14	70	-56	-25 3 4	56	50
-10	127	129	-26	101	-95	18	52	53	1	164	161	-12	159	194	-23	144	159
-8	244	-271	-24	64	36	-21 1 8	48	49	3	156	163	-10	25	31	-21	58	-42
-6	178	178	-18	54	-35	-19	37	35	5	185	208	0	192	-218	-19	108	103
-4	*364	444	-16	*248	366	-15	97	-97	7	29	-23	6	47	37	-17	29	8
-2	26	-24	-14	41	33	-9	113	-104	9	207	-268	8	37	18	-15	165	169
0	26	23	-12	192	-276	-3	109	86	11	112	87	12	126	149	-13	153	-153
2	212	-259	-10	31	-31	3	126	119	13	158	-134	-15 2 9	62	-66	-11	231	-284
4	43	55	-8	115	-125	7	59	-55	15	155	-139	-13	39	-38	-9	38	-30
6	115	-116	-6	93	72	9	92	-89	17	93	-76	-11	131	-170	-7	108	-94
8	212	-222	-4	211	-263	11	48	-32	19	104	87	-9	53	44	-5	67	55
10	167	152	-2	100	87	15	32	-24	21	142	140	-7	49	41	-3	117	-112
12	81	88	0	239	306	-18 1 9	68	-60	23	27	-20	-3	78	84	-1	*233	402
14	164	136	2	89	69	-16	68	-65	25	95	115	-1	47	44	1	201	271
16	75	-79	4	138	133	-14	112	-128	-26 2 4	105	112	1	162	191	3	116	-118
18	63	54	6	93	-87	-8	180	-196	-24	109	-104	3	98	-104	5	44	29
20	127	121	8	234	315	-6	123	117	-22	97	98	5	89	-96	7	169	-151
22	105	-94	10	188	-229	-4	68	65	-20	63	53	9	57	-64	9	49	43
-20 0 8	12	21	12	342	-396	-2	158	176	-18	42	33	-8 2 10	72	104	11	211	-231
-18	69	74	14	45	-36	4	181	188	-14	148	-155	-6	48	53	13	151	-140
-16	80	69	16	82	-53	6	165	-190	-12	145	151	-4	41	-51	15	134	117
-14	111	88	18	138	126	8	107	-107	-10	173	-175	-2	63	75	17	41	16
-12	293	-309	20	77	-67	10	107	-117	-8	129	-141	3 3 0	*221	-393	19	88	60
-10	154	-147	22	196	189	-5 1 10	107	-119	-6	89	-79	5	81	63	21	23	-26
-6	38	20	24	139	159	-3	40	-38	-4	141	144	7	88	78	-22 3 5	81	75
-2	137	115	26	44	-44	1	46	52	-2	201	241	9	282	355	-20	75	-67

Table 2. *(Continued)*

h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c	h k l	$\|F_o\|$	F_c
-18 3 5	51	46	15 3 6	97	-99	-2 3 9	77	-71	19 4 1	89	79	9 4 3	192	182	7 4 5	228	-271
-16	23	17	17	147	-187	0	14	- 8	21	79	-75	11	122	-103	9	121	-110
-14	47	-41	-18 3 7	81	83	2	34	30	-18 4 2	47	-34	13	193	185	11	68	-51
-12	76	-54	-16	78	-84	4	69	-79	-16	46	-41	15	122	108	13	139	132
-10	88	-66	-12	44	29	4 4 0	19	20	-14	48	-40	17	104	101	15	61	-65
-8	91	77	-10	62	-56	6	19	16	-12	68	-64	19	114	-111	17	54	67
-4	29	19	-8	68	65	8	59	53	-10	40	32	-22 4 4	38	38	-18 4 6	25	24
-2	38	-31	-6	55	-34	10	56	50	-8	54	52	-20	38	43	-14	46	49
0	78	54	-4	86	76	12	17	9	-6	79	76	-18	37	44	-6	68	-55
2	34	20	0	99	-82	14	32	21	-4	68	64	-14	35	-26	-4	72	-63
4	92	-75	2	43	27	16	45	-41	-2	16	-12	-12	31	-27	-2	41	-37
6	105	97	4	28	22	18	21	-19	0	24	23	-10	25	-22	2	42	34
8	33	-23	6	62	49	22	53	-46	2	63	-51	-8	55	-47	4	63	60
10	40	25	8	66	-63	-23 4 1	173	-213	4	72	-65	-4	26	10	6	45	39
12	83	-70	12	24	-22	-21	52	-45	6	18	-22	0	51	42	8	33	31
14	64	-50	14	32	-28	-19	53	47	8	46	-39	2	35	19	12	36	-43
16	101	95	-17 3 8	66	-79	-17	93	-77	10	29	-15	4	64	56	14	13	-11
18	58	-59	-15	119	145	-15	38	26	14	36	36	8	65	-57	-15 4 7	125	183
20	29	26	-13	27	-22	-13	173	166	16	65	53	10	29	-26	-13	95	-101
-21 3 6	64	-68	-11	32	-21	-11	250	322	18	60	49	12	65	-53	-11	26	-28
-19	166	189	-9	167	205	-9	119	-92	-23 4 3	30	30	18	26	24	-9	71	-73
-17	66	-46	-7	63	64	-7	82	-71	-19	169	-189	-19 4 5	91	89	-5	80	-80
-15	83	83	-5	23	10	-5	22	-17	-17	119	-111	-17	112	-120	-3	140	-146
-13	117	119	-3	177	-195	-3	107	-128	-15	153	156	-15	98	-95	-1	181	216
-11	134	121	-1	29	-22	-1	69	-80	-13	169	-160	-13	129	-128	1	54	51
-7	254	-297	1	30	-23	1	*171	-290	-11	105	82	-11	132	123	3	116	113
-5	76	59	3	156	-184	3	154	206	-9	179	163	-9	179	-189	5	60	-66
-3	82	-59	5	31	13	5	121	127	-7	146	119	-7	87	-77	7	29	27
-1	107	-88	7	45	51	7	53	-52	-3	187	-200	-5	182	167	9	82	96
3	140	124	9	141	173	9	123	98	-1	122	110	-3	42	37	-10 4 8	51	67
5	188	205	11	41	38	11	45	32	1	56	-42	-1	209	202	-2	51	-52
7	107	-96	-8 3 9	86	89	13	210	194	3	101	-97	1	112	-96	0	22	-17
9	50	39	-6	44	-41	15	219	-209	5	216	-214	3	168	156			
13	27	27	-4	24	21	17	142	-123	7	47	35	5	66	56			

weighting scheme was applied in the refinement. The conventional R value for the first structure-factor calculation was 0.24. This dropped after four cycles of full-matrix least-squares refinement to 0.151. If the 15 strongest reflections, which were given zero weight in the refinement, are left out, R equals 0.133. The final parameters are listed in Table 1. The F_{obs}'s given by GARCIA-BLANCO and FAYOS

Table 3. *Interatomic distances and angles with their estimated standard deviations*

Tetrahedron I	distance	angle around Zn	Tetrahedron II	distance	angle around Zn
Zn(1)–O(2)	1.93(1) Å		Zn(2)–O(3)	1.91(1) Å	
Zn(1)–O(3)	1.95(1)		Zn(2)–O(4)	1.96(1)	
Zn(1)–O(1)	1.99(1)		Zn(2)–O(2)	1.98(1)	
Zn(1)–O(1)	2.00(1)		Zn(2)–O(6)	2.02(1)	
O(2)–O(3)	3.24(2)	113.8°(5)	O(3)–O(4)	3.38(2)	121.8 (5)
O(2)–O(1)	3.58(2)	132.2 (5)	O(3)–O(2)	3.22(2)	112.0 (5)
O(2)–O(1)	3.15(2)	106.4 (4)	O(3)–O(6)	3.38(2)	118.4 (5)
O(3)–O(1)	3.03(2)	101.0 (5)	O(4)–O(2)	2.97(2)	97.6 (4)
O(3)–O(1)	3.33(2)	115.2 (5)	O(4)–O(6)	3.21(2)	107.3 (5)
O(1)–O(1)	2.72(3)	85.7 (8)	O(2)–O(6)	2.93(2)	94.3 (5)
averaged values			averaged values		
Zn(1)–O	1.97		Zn(2)–O	1.97	
O –O	3.18		O –O	3.18	

Table 3. *(Continued)*

Tetrahedron III	distance	angle around Zn
Zn(3)–O(4)	1.92(1) Å	
Zn(3)–O(5)	1.97(1)	
Zn(3)–O(6)	1.97(1)	
Zn(3)–O(5)	1.98(1)	
O(4)–O(5)	3.27(2)	114.3°(5)
O(4)–O(6)	3.36(2)	119.3 (4)
O(4)–O(5)	3.20(2)	110.6 (4)
O(5)–O(6)	3.04(2)	100.9 (5)
O(5)–O(5)	3.20(3)	108.7 (7)
O(5)–O(6)	3.07(2)	101.9 (5)
averaged values		
Zn(3)–O	1.96	
O –O	3.19	

Triangle I	distance	angle around B
B(1)–O(1)	1.33(2) Å	
B(1)–O(2)	1.40(2)	
B(1)–O(3)	1.37(2)	
O(1)–O(3)	2.34(2)	120°(1)
O(1)–O(2)	2.41(2)	124 (1)
O(3)–O(2)	2.34(2)	116 (1)
averaged values		
B – O	1.37	
O – O	2.36	

Triangle II	distance	angle around B
B(2)–O(4)	1.37(2) Å	
B(2)–O(5)	1.39(2)	
B(2)–O(6)	1.37(2)	
O(4)–O(5)	2.37(2)	118°(1)
O(4)–O(6)	2.39(2)	121 (1)
O(5)–O(6)	2.41(2)	121 (1)
averaged values		
B – O	1.38	
O – O	2.39	

are compared with the calculated structure factors in Table 2. The fact that the crystal structure could be refined in the centric space group (with half as many parameters as in the acentric one) to essentially the same R value as in the acentric case shows that the centric space group is to be preferred. It is striking that all B values are either small or negative (however not significantly negative if one considers the large estimated standard deviations); most likely this is correlated with the fact that the data were not corrected for absorption.

Further proof that the structure is more properly described in the centric space group comes from the fact that the bond lengths and angles (Table 3) now conform better with commonly accepted

values. The reason that the bond-length values diverge so pronouncedly in GARCIA-BLANCO and FAYOS acentric refinement is that the parameters of the atom pairs which should be related by a center of symmetry, but are not, are very highly correlated. Consequently they can be adjusted by large amounts in opposing, mutually compensating, directions.

We proved this point by refining by full-matrix least-squares methods GARCIA-BLANCO and FAYOS's acentric model. It refined to an R of 0.120, but at the same time the correlations of most of the x and z parameters of the corresponding pairs of atoms became large. The shifts in parameters through four cycles of least-squares calculations remained large; on the average the shifts were bigger than one half the estimated standard deviations. And, what is even worse, many parameters tended to oscillate around a mean value. The bond distances were not improved by this further refinement in space group *Ic*. The spread of Zn—O bond-length values was 1.85 to 2.07 Å, while those of the B—O bond lengths was 1.18 to 1.55 Å. Some of the bond lengths which were the longest ones in GARCIA-BLANCO and FAYOS's refinement of the structure became the shortest ones in our refinement in space group *Ic*.

Discussion of the crystal structure

The topological connections of the coordination polyhedra remain unaltered by the refinement in the more highly symmetric space group. Therefore, Fig. 4, 5 and 6 in GARCIA-BLANCO and FAYOS's paper are still a correct description of the crystal structure. However, individual bond lengths were changed by the refinement in extreme cases by 0.1 Å or more.

The triangular coordinations around the boron atoms are now much more regular. Even the shortest bond length, B(1)—O(1), is at best probably significantly shorter than the mean of the B—O bond-lengths values in the two borate groups in $Zn_3(BO_3)_2$. The averaged value of all six B—O bond lengths is 1.37_4 Å which is remarkably close to the average value found in many well refined borates with boron in three-coordination. In D_3BO_3 (CRAVEN and SABINE, 1966) the average of six different B—O bond lengths is 1.367 ± 0.007 Å.

The Zn—O distances in the tetrahedral coordination around the Zn atoms now range from 1.91 to 2.02 Å, while the mean Zn—O bond length is 1.96_4 Å. This average value agrees with other well determined bond distances: the average Zn—O bond length is 1.972 Å in hodg-

Table 4. *Coordination polyhedra sharing edges or corners in zinc compounds*
Coordination numbers for the zinc atoms are given in brackets

	Oxygen polyhedra around		Common element	Zn–Zn	O–O	O–Zn–O	
$Zn_3(BO_3)_2$ (this work)	$Zn(1)^{[4]}$	$Zn(1)^{[4]}$	edge	2.909(5) Å	2.72(3) Å	85.7°(8)	
	$Zn(2)^{[4]}$	$Zn(3)^{[4]}$	corner	3.019(3)			
	$Zn(2)^{[4]}$	$Zn(3)^{[4]}$	corner	3.262(3)			
α $Zn_3(PO_4)_2$ (CALVO, 1965)	$Zn(2)^{[4]}$	$Zn(2)^{[4]}$	edge	2.955(9)	2.73 (5)	85 (1)	
	$Zn(2)^{[4]}$	$Zn(1)^{[4]}$	corner	3.383(4)			
β $Zn_3(PO_4)_2$ (STEPHENS and CALVO, 1967)	$Zn(1)^{[4+1]}$	$Zn(1)^{[4+1]}$	edge	3.106(2)	2.615(10)	80.2(4)	
	$Zn(2)^{[6]}$	$Zn(3)^{[5]}$	edge	3.120(1)	2.666(8)	80.9(2)	76.9(2)
γ $Zn_3(PO_4)_2$ (CALVO, 1963)	$Zn(2)^{[5]}$	$Zn(2)^{[5]}$	edge	2.975(4)	2.88 (8)	88 (2)	
	$Zn(2)^{[5]}$	$Zn(1)^{[6]}$	edge	3.234(2)	2.70 (2)	82 (1)	77 (1)

kinsonite (RENTZEPERIS, 1963) and 1.95 Å in larsenite (PREWITT *et al.*, 1967). The deviations of the individual distances from the mean are in some cases statistically significant. However, it is difficult to decide whether or not the accuracy of the structure determination is sufficient to accept these deviations as proved, because the intensity data have not been corrected for absorption.

A remarkable feature of the crystal structure is the common edge between the two Zn(1) tetrahedra connected by the two-fold axis. A shared edge between two coordination tetrahedra around multivalent cations usually should not occur according to PAULING's (1960) third rule for ionic crystals. The occurrence in $Zn_3(BO_3)_2$ adds another example to the short list of exceptions. Our search of the literature produced only one example of a crystal structure with a comparable arrangement involving Zn atoms, namely $\alpha\,Zn_3(PO_4)_2$ (CALVO, 1965), where the geometry around the shared edge is virtually the same as in $Zn_3(BO_3)_2$. The geometry is already different in $\beta\,Zn_3(PO_4)_2$ (STEPHENS and CALVO, 1967) where the coordination around Zn(1) would be more properly described as $4+1$ since a fifth oxygen atom at a distance of 2.55 Å from the Zn atom is present. These coordinations and a few other ones involving common edges between Zn coordination polyhedra are listed in Table 4. The geometry of the shared edges is somewhat similar in all cases irrespective of the coordination around the Zn atoms. For comparison we have listed

Table 5. *Angles around the oxygen atoms*
(with estimated standard deviations)

B(1)–O(1)–Zn(1)		132°(1)	B(1)–O(2)–Zn(1)		119°(1)
B(1)	–Zn(1)	128 (1)	B(1)	–Zn(2)	113 (1)
Zn(1)	–Zn(1)	93.6(5)	Zn(1)	–Zn(2)	126.8(6)
	Sum	354		Sum	359
B(1)–O(3)–Zn(2)		126°(1)	B(2)–O(4)–Zn(3)		126 (1)
B(1)	–Zn(1)	115 (1)	B(2)	–Zn(2)	127 (1)
Zn(1)	–Zn(2)	118.7(6)	Zn(2)	–Zn(3)	102.2(6)
	Sum	360		Sum	355
B(2)–O(5)–Zn(3)		127°(1)	B(2)–O(6)–Zn(3)		114°(1)
B(2)	–Zn(3)	122 (1)	B(2)	–Zn(2)	124 (1)
Zn(3)	–Zn(3)	106.3(5)	Zn(3)	–Zn(2)	109.6(5)
	Sum	355		Sum	348

three of the Zn—Zn distances between corner-sharing coordination tetrahedra. These Zn—Zn distances are of similar length to those involving shared edges. This is made possible by the distortion around the common edge: the O—O distances are relatively short, the angles O–Zn—O are small, and the distances ZnO— are usually longer than the average.

The sums of the bond angles around the oxygen atoms are all close to 360° (Table 5). Therefore, the cation coordination around the oxygen atoms is, to a first approximation, planar.

Conclusion

Despite the fact that the crystal structure of $Zn_3(BO_3)_2$ can be refined to a lower R value in space group Ic, than it can be in $I2/c$, we prefer the latter one because in the centrosymmetric space group the resulting crystal structure is more reasonable on crystal-chemical grounds and because the refinement process is free from oscillations and correlations.

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