

The Crystal Structure of Cobaltpyroborate

SVEN V. BERGER

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

X-ray studies on preparations, belonging to the CoO-rich region of the system CoO—B₂O₃, indicate ortho- and pyroborate as the only compounds formed. In a previous communication from this Institute¹ the crystal structure of the orthoborate is described. The present paper gives an account of the crystallographic arrangement of the pyroborate Co₂B₂O₅. As a result of this study the existence of the composite ion B₂O₅⁴⁻ was proved.

Crystals of this borate have been mentioned by Ebelmen², Mallard³, Burgess and Holt⁴, Ouvrard⁵, Guertler⁶ among others. They are reported to be violet, double refracting, triclinic needles.

The crystals used in the present investigation were prepared by melting together the pure oxides in the molar proportions 2 : 1. They form very hard, reddish-violet prisms and needles. In this case well-shaped, prismatic crystals were picked out and a prism, suitable for taking single crystal photographs, was examined by the rotation and Weissenberg methods. Mo-K-radiation was used.

UNIT CELL AND SPACE GROUP

The external shape of the crystal speaks in favour of the triclinic symmetry, which was also proved by the Weissenberg photographs. Rotation and Weissenberg photographs were taken about the shortest axis, which was chosen as [100], and about [211]. Thereby the layer lines 0—4 and 0—8, respectively, were obtained. The connection between intensities of reflections from different layer lines of the former photographs were brought about by means of the reflections *0kl* of the latter. The intensities were estimated visually, 4 : 2 : 1 being adopted as the intensity ratio of Mo-K α_1 , Mo-K α_2 and Mo-K β radiation. Relative values of F_{hkl}^2 were obtained by multiplying the intensity values with the factor $\cos^2\mu \cdot \sin\gamma / (1 + \cos^2 2\theta)$ utilizing the curves given by Chia-Si Lu⁷. The temperature factor was neglected.

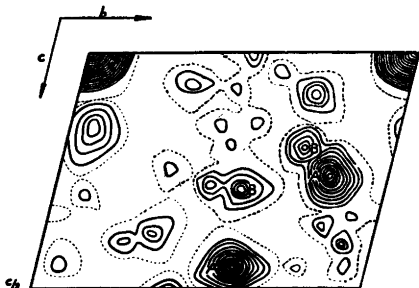


Fig. 1. Projection of the Patterson-function on the bc -plane, $p(yz)$. The dotted line corresponds to the 0-level.

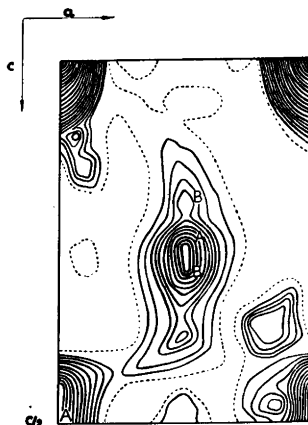


Fig. 2. Projection of the Patterson-function on the ac -plane, $p(xz)$.

The linear and angular constants as calculated from the single crystal photographs are found to be:

$$\begin{array}{ll} a = 3.16 \text{ \AA} & \alpha = 103.9^\circ \\ b = 5.94 \text{ \AA} & \beta = 91.0^\circ \\ c = 8.95 \text{ \AA} & \gamma = 92.0^\circ \end{array}$$

These values correspond to the axial ratios 0.35 : 0.66 : 1. The unit cell containing 2 $\text{Co}_2\text{B}_2\text{O}_5$ has the volume 162.8 \AA^3 and the calculated density 4.48. The observed density is 4.40.

Since there are no regular extinctions observed and no piezoelectric effect detected, $C_i^1 - P \bar{1}$ must be the most probable space group.

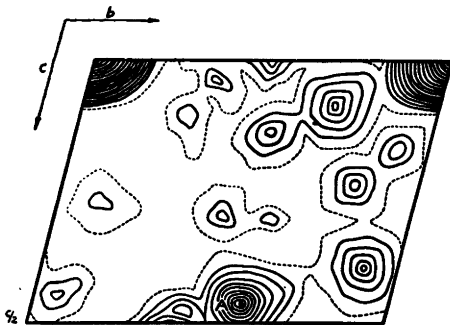


Fig. 3. The Harker-section $P(0yz)$.

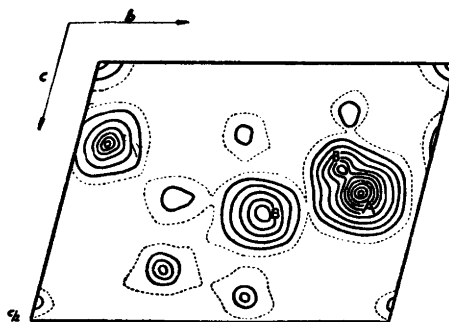


Fig. 4. The Harker-section $P(\frac{1}{2}yz)$.

THE ATOMIC ARRANGEMENT OF COBALT AND OXYGEN

The fact that in the space group $P\bar{1}$ four heavy atoms, the contribution of which to the structure factor is dominating compared with that of the other atoms in the cell, give rise to two main peaks and two of half the size in the projections of the Patterson function on the axial planes, made it possible to determine the present approximate parameters of the Co atoms from $p(yz)$ and $p(xz)$. The map $p(yz)$ — Fig. 1 — shows two strong maxima (*A*) and four, which are about half as large — two of which, belonging to Co—Co vectors, are called (*B*). The projection $p(xz)$ — Fig. 2 — also contains two strong maxima and a few minor peaks, but here vector-overlapping takes place, so that it was impossible to make any distinctions at all between the weaker maxima. After having developed the function $p(xyz)$ into a set of sections, however, the different (*A*) and (*B*) maxima could be determined from $P(0yz)$ and $P(1/2 yz)$ — Figs. 3 and 4. In that way the following arrangement of the Co atoms was obtained:

	<i>x</i>	<i>y</i>	<i>z</i>
2 Co ²⁺ in (2i) = Co I	0.74	0.218	0.351
2 Co ²⁺ in (2i) = Co II	0.25	0.375	0.103

By means of these values the more accurate ones, given below, could be obtained from a few successive calculations of the electron density projections $\rho(xy)$ and $\rho(yz)$:

	<i>x</i>	<i>y</i>	<i>z</i>
Co I	0.744	0.214	0.358
Co II	0.245	0.374	0.100

Simultaneously, the density distribution gave the following approximate parameters of the oxygen atoms:

	<i>x</i>	<i>y</i>	<i>z</i>
2 O ²⁻ in (2i) = O I	0.25	0.706	0.052
2 O ²⁻ in (2i) = O II	0.23	0.092	0.190
2 O ²⁻ in (2i) = O III	0.75	0.483	0.253
2 O ²⁻ in (2i) = O IV	0.58	0.853	0.284
2 O ²⁻ in (2i) = O V	0.75	0.704	0.492

It was then possible to obtain the sign of the structure factor of most reflections with a high degree of certainty, especially as the influence of the oxygen atoms in general being too small to be of any importance compared with the contribution of the metal atoms.

FOURIER-REFINEMENT OF THE PARAMETERS

Instead of using three-dimensional calculations of the electron density function to determine the final Co parameters, the values settled above were refined by means of "differential synthesis" according to Booth⁸. In making the calculations leading to the necessary system of equations, utilizing the about 1 100 reflections, two aids, devised by Hägg⁹, have highly facilitated the work. The corrections were found to be:

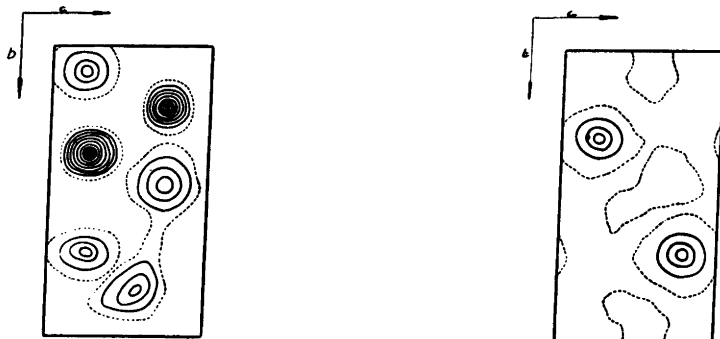
	Co I	Co II
ε_x	- 0.001 Å	0.000 Å
ε_y	- 0.001 Å	0.000 Å
ε_z	+ 0.002 Å	0.000 Å

As a consequence of this result the coordinates of the Co atoms given above may be considered rather satisfactory.

The x -coordinates of the oxygen lattice derived above are not of the same accuracy as are y and z , owing to the fact that $\rho(xy)$ is not free from overlapping, $\rho(yz)$, however, is. To get final parameters the "bounded projection" method, devised by Booth⁸, was applied for the xy -coordinates. The z -parameters were obtained from the Bragg projection $\rho(yz)$, where consideration was taken to the influence on the sign of the structure factor of both the Co and oxygen atoms.

It is clear from $\rho(yz)$ that a section through $z = 0.440$ passes a region with the electron density practically zero. On account of this, two "bounded projections" on the ab -plane were chosen, namely between the limits $z = 0-0.440$ and $z = 0.440-0.560$, respectively. These gave maps without overlapping, as is evident from the Figs. 5 and 6. The final z -parameters settled from $\rho(yz)$ — Fig. 7 — were found to be nearly the same as those given without taking consideration of the influence of the oxygen atoms on the sign of the structure factor. The final oxygen parameters were found to be:

	x	y	z
O I	0.244	0.709	0.054
O II	0.208	0.092	0.190
O III	0.735	0.476	0.249
O IV	0.562	0.842	0.288
O V	0.770	0.698	0.489



The "bounded projections".

Fig. 5. $B_{z_1}^{z_2}$, when $z_1 = 0$ and $z_2 = 0.440$. Fig. 6. $B_{z_1}^{z_2}$, when $z_1 = 0.440$ and $z_2 = 0.560$.

THE ATOMIC ARRANGEMENT OF BORON

Pyroborates have not been investigated by x-ray methods earlier and, consequently, experimental data of the configuration of the pyroborate ion are lacking. Owing to the well known tendency of the boron to acquire a plane, triangular coordination of oxygen, one must expect the pyroborate ion to consist of two such triangles with a corner in common. From earlier investigations¹⁰ on different borates it is known that the oxygen-oxygen distances within the boron-oxygen triangles are of about the length 2.2—2.4 Å. It can therefore be taken as granted that the four boron atoms must be placed in, or very near, the centres of gravity of the four nearly equilateral oxygen triangles with edges of about these dimensions, which exist in the cell. If the boron atoms are placed exactly in the centres of gravity they obtain the following parameters:

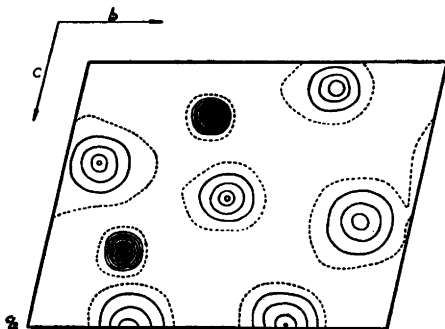


Fig. 7. Projection of the electron density parallel to [100].

	x	y	z
2 B ³⁺ in (2i) = B I	0.67	0.67	0.34 ₅
2 B ³⁺ in (2i) = B II	0.36	0.88	0.17

These parameters give boron positions corresponding to B₂O₅⁴⁻-ions with the expected configuration.

DESCRIPTION OF THE STRUCTURE

The following structure is thus arrived at:

Cell content: 2 Co₂B₂O₅

Space group: C_i¹-P $\bar{1}$

	x	y	z
2 Co ²⁺ in (2i) = Co I	0.743	0.213	0.360
2 Co ²⁺ in (2i) = Co II	0.245	0.374	0.100
2 O ²⁻ in (2i) = O I	0.244	0.709	0.054
2 O ²⁻ in (2i) = O II	0.208	0.092	0.190
2 O ²⁻ in (2i) = O III	0.735	0.476	0.249
2 O ²⁻ in (2i) = O IV	0.562	0.842	0.288
2 O ²⁻ in (2i) = O V	0.770	0.698	0.489
2 B ³⁺ in (2i) = B I	0.67	0.67	0.34 ₅
2 B ³⁺ in (2i) = B II	0.36	0.88	0.17

Projections of the structure on ($\bar{3}24$) and parallel to [021] and [2 $\bar{1}1$] are given in the Figs. 8, 9 and 10.

By using the above parameters and atomic scattering factors according to *International tables*, the following agreement between calculated and observed $|F|$ -values was obtained:

DISCUSSION OF THE STRUCTURE

The structure of Co₂B₂O₅ is built up by B₂O₅⁴⁻-groups and Co²⁺-ions, the latter surrounded by six oxygen atoms forming a deformed octahedron. The average space available per oxygen atom, given by the quotient between the volume of the unit cell and the number per cell of oxygen atoms, is 16.3 Å³. Within the composite ion B₂O₅⁴⁻, formed by two BO₃²⁻-triangles, linked by sharing one oxygen atom, there exist very short interatomic distances. When calculated from the above parameters they are found to be:

<i>hkl</i>	<i> F </i> /Calc.	<i> F </i> /Obs.	<i>hkl</i>	<i> F </i> /Calc.	<i> F </i> /Obs.	<i>hkl</i>	<i> F </i> /Calc.	<i> F </i> /Obs.
100	64	58	240	27	26	202	75	76
200	513	412	250	103	84	204	269	294
			260	24	24	207	230	200
010	122	102	270	140	112	208	145	190
020	243	252	280	74	48	20 11	147	172
040	76	66	320	199	184	302	328	316
050	108	92	330	215	202	303	154	134
070	159	142	340	171	148	305	165	145
0 12 0	128	105	350	140	143	306	148	102
			320	218	200	307	91	52
002	73	40	330	247	218	309	208	170
003	73	56	340	132	90	30 11	121	88
004	206	218	350	145	106	30 13	96	36
005	162	162	370	89	46	302	366	352
007	227	224	3 10 0	97	56	303	48	24
008	108	120	440	30	28	305	114	70
00 11	188	172	470	170	142	306	192	164
00 13	110	108	420	202	193	309	228	178
00 15	140	125	450	145	106	30 10	101	82
00 17	63	56				30 13	91	48
			101	76	86	402	54	32
110	18	28	102	440	504	403	106	84
120	248	268	103	222	252	404	181	114
130	214	216	105	110	144	405	158	120
140	145	164	106	126	158	407	202	146
150	169	160	109	260	260	409	96	72
170	56	40	10 11	116	111	40 11	110	82
180	81	48	10 13	131	160	403	25	26
190	68	46	102	567	536	404	172	116
1 10 0	135	105	103	118	92	408	181	124
1 11 0	53	68	105	156	162			
110	33	40	106	145	196	011	69	52
120	204	243	109	223	204	021	70	76
130	306	372	10 11	86	40	031	174	196
140	182	192	10 13	131	114	041	279	304
150	185	168	10 15	84	46	061	158	184
170	81	92	10 17	119	92	0 11 1	178	106
180	76	48	201	135	166	0 12 1	31	28
1 10 0	106	60	202	18	44	011	317	328
220	155	192	203	21	24	021	194	252
230	83	60	204	179	236	031	146	176
250	130	148	205	102	126	041	93	120
270	209	216	207	251	324	051	64	44
210	163	192	208	98	80	061	179	156
220	179	176	20 11	164	180	081	223	194
230	37	16	20 12	63	32	091	76	56
			20 13	127	98			

COBALTPYROBORATE

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<i>hkl</i>	<i>F</i> /Calc.	<i>F</i> /Obs.	<i>hkl</i>	<i>F</i> /Calc.	<i>F</i> /Obs.	<i>hkl</i>	<i>F</i> /Calc.	<i>F</i> /Obs.
0 $\bar{1}$ 2	140	128	0 $\bar{4}$ 5	213	188	0 $\bar{2}$ 9	115	126
0 $\bar{2}$ 2	325	328	0 $\bar{5}$ 5	119	100	0 $\bar{3}$ 9	65	56
0 $\bar{3}$ 2	399	496	0 $\bar{6}$ 5	154	156	0 $\bar{4}$ 9	196	184
0 $\bar{4}$ 2	100	140	0 $\bar{7}$ 5	27	32	0 $\bar{5}$ 9	210	195
0 $\bar{5}$ 2	177	164	0 $\bar{8}$ 5	32	50	019	132	140
0 $\bar{1}$ 0 2	123	106	0 $\bar{9}$ 5	166	128	029	114	94
012	28	45	015	355	348	039	190	174
022	142	124	025	101	88	079	157	90
032	79	92	035	286	242	0 $\bar{1}$ 10	82	100
042	153	152	045	59	26	0 $\bar{3}$ 10	155	156
052	164	172	055	6	vw	0 $\bar{4}$ 10	146	160
072	81	32	065	51	44	0 $\bar{8}$ 10	145	164
092	132	98	085	113	108	02 10	92	77
0 10 2	146	86	0 $\bar{1}$ 6	219	232	03 10	90	64
0 $\bar{1}$ 3	234	200	0 $\bar{2}$ 6	57	81	04 10	220	184
0 $\bar{2}$ 3	252	208	0 $\bar{3}$ 6	201	208	0 $\bar{2}$ 11	138	152
0 $\bar{3}$ 3	87	96	0 $\bar{5}$ 6	51	40	0 $\bar{3}$ 11	42	20
0 $\bar{4}$ 3	60	36	0 $\bar{7}$ 6	46	24	0 $\bar{7}$ 11	193	165
0 $\bar{5}$ 3	34	32	0 $\bar{8}$ 6	161	140	03 11	104	78
0 $\bar{6}$ 3	205	224	0 $\bar{1}$ 0 6	121	104	05 11	184	134
073	142	116	016	84	99	0 $\bar{1}$ 12	122	128
083	80	76	026	299	316	04 12	69	56
093	106	84	046	204	192	0 $\bar{5}$ 12	44	24
013	136	156	056	104	88	0 $\bar{6}$ 12	139	118
023	88	72	066	51	32	01 12	224	204
033	187	180	096	158	81	06 12	114	75
043	236	208	017	114	124	0 $\bar{3}$ 13	100	67
053	221	196	0 $\bar{2}$ 7	305	324	0 $\bar{5}$ 13	101	80
063	176	143	0 $\bar{3}$ 7	78	44	0 $\bar{1}$ 0 13	110	92
0 $\bar{1}$ 4	80	52	047	59	52	02 13	172	142
0 $\bar{2}$ 4	44	28	077	142	126	03 13	122	98
034	21	12	087	21	20	0 $\bar{1}$ 14	132	108
0 $\bar{5}$ 4	224	224	097	141	134	0 $\bar{2}$ 14	196	163
0 $\bar{6}$ 4	162	144	017	171	152	0 $\bar{3}$ 14	87	56
0 $\bar{7}$ 4	113	116	037	53	36	0 $\bar{4}$ 14	122	104
024	238	252	047	53	52	0 $\bar{2}$ 15	69	56
034	34	48	057	154	144	0 $\bar{3}$ 15	70	40
044	137	144	0 $\bar{1}$ 8	259	276	0 $\bar{4}$ 16	75	52
054	174	168	0 $\bar{4}$ 8	138	120	0 $\bar{6}$ 16	96	88
064	90	64	0 $\bar{5}$ 8	142	164	01 16	94	70
074	224	196	0 $\bar{8}$ 8	133	136	02 17	151	86
094	89	46	018	132	122			
0 $\bar{2}$ 5	52	60	028	87	104			
0 $\bar{3}$ 5	7	vw	068	165	96			
			078	158	94			

O I — O II ₁	2.31 Å
O I — O IV	2.25 Å
O II ₁ — O IV	2.22 Å
O III — O IV	2.20 Å
O III — O V	2.21 Å
O IV — O V	2.26 Å
B I — O III	1.28 Å
B I — O IV	1.30 Å
B I — O V	1.28 ₅ Å
B II — O I	1.30 Å
B II — O II'	1.33 Å
B II — O IV	1.29 Å

In the deformed octahedron, formed by the oxygen atoms, surrounding the Co²⁺-ions, the interatomic distances calculated are:

Co I — O II	2.22 Å	Co II — O I	2.12 Å
Co I — O II ₂	2.13 Å	Co II — O I'	2.02 Å
Co I — O III	2.02 Å	Co II — O I' ₂	2.13 Å
Co I — O IV ₁	2.20 Å	Co II — O II	2.02 Å
Co I — O V'	2.14 Å	Co II — O III	2.00 Å
Co I — O V' ₂	2.01 Å	Co II — O III ₂	2.12 Å
O II — O III	2.71 Å	O I — O I'	2.98 Å
O II — O II ₂	3.16 Å	O I — O I' ₂	2.82 Å
O II ₂ — O IV ₁	2.75 Å	O II — O I'	3.19 Å
O II — O V'	2.84 Å	O II — O I' ₂	3.18 Å
O III — O II ₂	2.68 Å	O II — O III	2.71 Å
O III — O V' ₂	3.18 Å	O II — O III ₂	2.68 Å
O III — O V'	3.19 Å	O III — O I	2.92 Å
O V' — O IV ₁	3.18 Å	O III — O I'	2.67 Å
O V' ₂ — O IV ₁	3.01 Å	O III — O I' ₂	2.95 Å
		O III — O III ₂	3.16 Å

The denomination of the oxygen atoms in the one half-cell is OI—OV and in the other OI'—OV'. The subscripts 1 and 2 refer to equivalent positions in the surrounding cells in horizontal and vertical direction, respectively.

From the interatomic distances given above it is seen that the connecting forces within the B₂O₅⁴⁻-groups undoubtedly must be much stronger than the other bonds. Accordingly, there is direct evidence for the existence of these groups in the lattice, and for the chemical formula Co₂(B₂O₅).

Formally the structure may be described as constructed of two-dimensional layers formed by the B₂O₅⁴⁻-groups, as is illustrated by the Figs. 8, 9 and 10. These layers are extended in (111) — Fig. 10 — and are a little rough because of the fact that the separate groups included are not parallel to (111) but

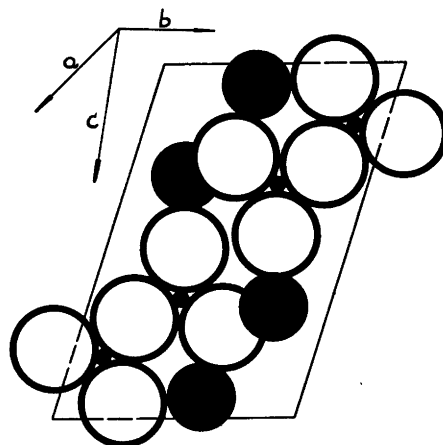


Fig. 8. Projection of the structure on $(\bar{3}24)$.

The large black spheres represent the cobalt atoms,
 » small » » » boron »
 » large white » » » oxygen »

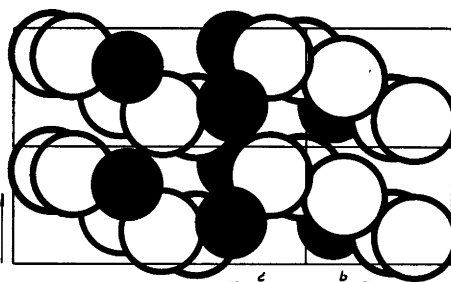


Fig. 9. Projection of the structure parallel to $[02\bar{1}]$.

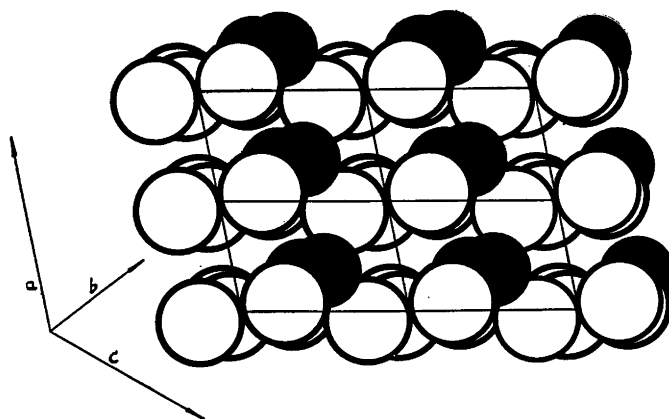


Fig. 10. Projection of the structure parallel to $[2\bar{1}1]$.

nearly to $(\bar{3}24)$ — Fig. 8. The connection between the groups within one layer and the binding between the different layers is maintained by the Co^{2+} -ions. From the figures it is also visible that a line through the centres of gravity of the two triangles in a group and the corner in common, is not a straight one. The angle is measured to be about 153° . The planes of these triangles are furthermore slightly screwed in opposite directions to each other related to (324) — Figs. 9, 10 and 11.

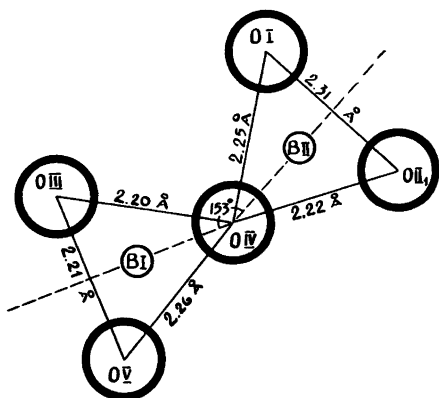


Fig. 11. $\text{B}_2\text{O}_4^{4-}$ -ion projected on $(\bar{3}24)$. This plane contains the two boron atoms and the central oxygen atom. The planes of the two triangles are screwed about the indicated axial lines in opposed directions about 7 degrees from the plane of projection.

SUMMARY

The crystal structure of cobaltpyroborate is triclinic (space group $C_2^1 - P \bar{1}$) with $2 \text{Co}_2(\text{B}_2\text{O}_5)$ in the unit cell. Dimensions and atomic positions have been determined. The structure contains pyroborate groups $\text{B}_2\text{O}_5^{4-}$, formed by two BO_3^{3-} -triangles with one oxygen atom in common — Fig. 11.

The present study was carried out at the Institute of Inorganic Chemistry of the University of Uppsala. To the Head of this Institute, Professor G. Hägg, I wish to express my sincere gratitude for valuable discussions and never failing support. I am also very grateful to his co-workers, especially Dr I. Lindqvist, for many valuable conversations.

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