Crystal structure of triclinic chilgardite $Ca_2[B_5O_9]Cl \cdot H_2O = Ca_2[B_3^{\pm}B_2^{\Delta}O_9]Cl \cdot H_2O$

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The crystals studied were obtained by one of the authors from the Mining Museum at the Leningrad Institute of Mining, which received the mineral under the name "chilgardite" from E. I. Nefedov. Studies of single-crystal specimens with a roentgen meter, however, showed that they were not chilgardite[1] but a triclinic modification,[2] probably coinciding with the earlier described tyretskite (Refs. 3, 4).

An interesting crystallographic characteristic of triclinic chilgardite (that is the name we use at present for this mineral) was established with a CAD–4F automatic x-ray diffractometer manufactured by Enraf–Novius[2]: It is possible to select in it two sets of four unit cells which are very much alike. The smallest dimensions of the axes and the unique pseudoorthogonal symmetry axis (for lattice vectors) along the c axis are given in a tabular arrangement in Ref. 2: $a = 6.463$, $b = 6.564$, $c = 6.302$ Å, $\alpha = 61°38'$, $\beta = 118°46'$, $\gamma = 105°47'$, $V = 205.8$ Å^3. The unit cell contains one unit of $Ca_2B_5O_8(OH)_2Cl$ (Refs. 1, 5), and the space group could only be P1.

The parameters of the tyretskite cell, according to the data of V. V. Kondrat'eva,[4] are in the arrangement[2]: $a = 6.44$, $b = 6.45$, $c = 6.41$ Å, $\alpha = 61°46'$, $\beta = 119°45'$, $\gamma = 106°30'$, $V = 203.2$ Å^3. To resolve the question of whether triclinic chilgardite is identical with tyretskite, the cell parameters of the latter must be redetermined precisely and the H_2O and Cl content in them must be refined. Let us add that a paper[6] by P. N. Sokolov on a Soviet find of chilgardite contains information about the results of chemical analysis and optical studies on specimens; the mineral Sokolov found could equally well be triclinic chilgardite because the symmetry of the small crystals was not determined in his paper.[6]

Colorless, flattened and wedge–shaped small crystals were the object of our study. A three–dimensional body of x–ray reflections (3380 nonzero F_{hkl}, taken in the interval $1° \le \theta \le 45°$) was obtained for one of them on a CAD–4F diffractometer. No absorption correction was introduced because of the irregular form of the wedge-
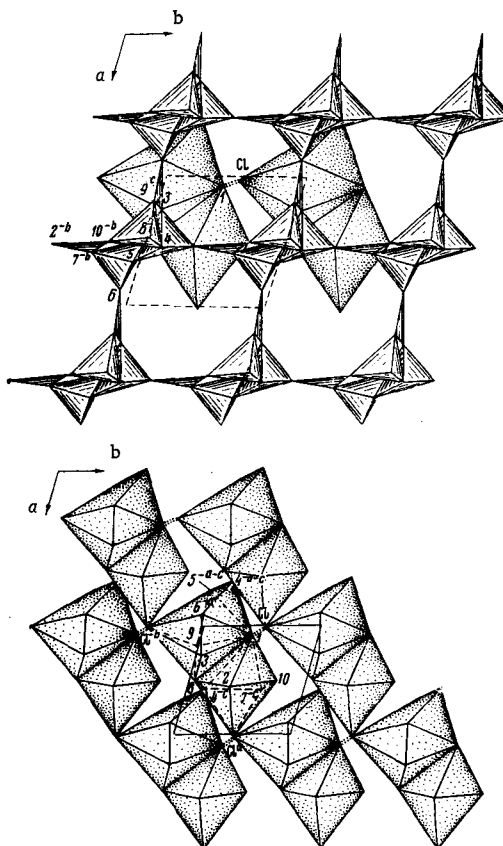

FIG. 1. Projection of structure of triclinic chilgardite along c axis: a) boron–oxide skeleton; b) layer of Ca polyhedra. The numbers are the numbers of oxygen atoms. Dashed lines indicate the hydrogen bonds O— H ... Cl.

TABLE I. Coordinates of Basal Atoms of the Structure of Triclinic Chilgardite $Ca_2[B_5O_9]Cl \cdot H_2O$

Atom	x/a	y/b	z/c	B_i	Atom	x/a	y/b	z/c	B_i
Ca$_1$	0	0	0	1.2$_8$	O$_3$	0.277$_3$	0.037$_2$	0.416$_0$	1.2$_0$
Ca$_2$	0.5462	0.4527	−0.1125	1.3$_1$	O$_4$	0.578$_5$	0.145$_6$	0.775$_0$	1.0$_0$
B$_1$	0.525$_3$	0.128$_0$	0.531$_3$	0.7$_8$	O$_5$	0.694$_3$	−0.029$_2$	0.598$_7$	1.0$_8$
B$_2$	0.667$_8$	−0.089$_3$	0.396$_4$	0.9$_1$	O$_6$	0.891$_4$	−0.051$_3$	0.363$_9$	1.3$_0$
B$_3$	0.445$_9$	−0.023$_3$	−0.071$_4$	0.9$_7$	O$_7$	0.607$_3$	0.648$_9$	0.482$_3$	1.2$_2$
B$_4$	0.118$_3$	−0.004$_8$	0.519$_8$	0.9$_4$	O$_8$	0.491$_4$	0.032$_9$	0.141$_8$	1.1$_1$
B$_5$	0.552$_4$	0.577$_7$	0.289$_6$	0.9$_2$	O$_9$	0.190$_4$	−0.013$_1$	−0.236$_4$	1.2$_3$
O$_1$ **	0.110$_7$	0.416$_9$	−0.221$_2$	2.0$_2$	O$_{10}$	0.515$_n$	0.736$_1$	0.030$_6$	1.2$_1$
O$_2$	0.552$_3$	0.356$_7$	0.325$_9$	1.2$_2$	Cl	0.0214	0.5265	0.1924	1.6$_8$

Note: Two asterisks denote O atoms in H_2O groups.

B tetrahedra

B_1—O_4	1.460 (Ca_1^{a+c}, Ca_2^c, B_3^c)	B_2—O_8	1.425 (Ca_2, B_3, Ca_1)	B_3—O_8	1.435 (Ca_1, Ca_2, B_2)
O_5	1.461 (Ca_1^{a+c}, B_2)	O_5	1.436 (Ca_1^{a+c}, B_1)	O_9	1.468 (Ca_1, B_4^{-c})
O_2	1.478 (Ca_2, B_5)	O_6	1.494 (Ca_1^a, B_4^a)	O_4^{-c}	1.470 (Ca_1^a, Ca_2, B_1^{-c})
O_3	1.493 (Ca_1, B_4)	O_7^{-b}	1.534 (Ca_2^{c-b}, B_5^{-b})	O_{10}^{-b}	1.500 (Ca_2^{-b}, B_5^{-b})
Average	1.473	Average	1.472	Average	1.468
O_4—O_5	2.351 [Ca_1^{a+c}]	O_6—O_8	2.347	O_8—O_9	2.336 [Ca_1]
O_2—O_3	2.385	O_5—O_8	2.391	O_4^{-c}—O_8	2.368 [Ca_2]
O_2—O_5	2.406	O_6—O_7^{-b}	2.399	O_9—O_{10}^{-b}	2.406
O_3—O_5	2.422	O_5—O_7^{-b}	2.400	O_4^{-c}—O_9	2.420
O_2—O_4	2.429	O_7^{-b}—O_8	2.420	O_8—O_{10}^{-b}	2.423
O_3—O_4	2.439	O_5—O_6	2.456	O_4^{-c}—O_{10}^{-b}	2.431
Average	2.405	Average	2.401	Average	2.397

Ca polyhedra				**B triangles**	
Ca_1—Cl^{-b}	2.764 (Ca_2^{-a-b})	Ca_2—Cl^a	2.784 (Ca_1^{a+b})	B_4—O_9^c	1.351 (Ca_1^c, B_3^c)
O_9	2.384 (B_3, B_4^{-c})	O_7^{-c}	2.430 (B_2^{b-c}, B_5^{-c})	B_4—O_6^{-a}	1.365 (Ca_1, B_2^{-a})
O_5^{-a-c}	2.410 (B_1^{-a-c}, B_2^{-a-c})	O_8	2.471 (Ca_1, B_2, B_3)	B_4—O_3	1.372 (Ca_1, B_1)
O_3	2.418 (B_1, B_4)	O_2	2.507 (B_1, B_5)	O_3—O_6^{-a}	2.296 [Ca_1]
O_1^{**}	2.492 (Ca_2)	O_{10}	2.507 (B_3^b, B_5)	O_3—O_9^c	2.370
O_6^{-a}	2.560 (B_2^{-a}, B_4)	O_4^{-c}	2.517 (Ca_1^a, B_1^{-c}, B_3)	O_6^{-a}—O_9^c	2.407
O_4^{-a-c}	2.599 (Ca_2^{-a}, B_1^{-a-c}, B_3^{-a})	O_1^{**}	2.527 (Ca_1)		
O_8	2.830 (Ca_2, B_2, B_3)	Ca_2—O_5^{b-c}	3.13	B_5—O_2	1.357 (Ca_2, B_1)
Ca_1—O_{10}^{-a-b}	3.19			B_5—O_7	1.361 (Ca_2^c, B_2^b)
The remaining Ca—O exceed 3.4 Å				B_5—O_{10}	1.396 (Ca_2, B_3^b)
				O_2—O_{10}	2.283 [Ca_2]
				O_7—O_{10}	2.406
				O_2—O_7	2.421

Note: 1. The rest of the cations bound to a given anion are given in parentheses and bound to two anions, in brackets. 2. Indices $\pm a$, $\pm b$, and $\pm c$ indicate atoms displaced with respect to the basal atom by the corresponding translation. 3. Two asterisks denote O atoms in H_2O groups.

TABLE III. B—B, B—Ca, and Ca—Ca Distances Participating in Formation of Cation Polyhedra around Anions

B_2—B_3	2.447	(O_8)	B_3—Ca_2	2.921	(O_8, O_4^{-c})	B_2—Ca_1^{a+c}	3.605	(O_5)
B_1—B_3^c	2.474	(O_4)	B_4—Ca_1	2.970	(O_6^{-a}, O_3)	B_1—Ca_2	3.628	(O_2)
B_1—B_2	2.493	(O_5)	B_5—Ca_2	2.993	(O_2, O_{10})	B_1—Ca_1	3.692	(O_3)
B_3—B_4^{-c}	2.393	(O_9)	B_1—Ca_1^{a+c}	3.025	(O_4, O_5)	B_1—Ca_2^c	3.702	(O_4)
B_2—B_5^{-b}	2.411	(O_7^{-b})	B_3—Ca_1	3.175	(O_8, O_9)	B_2—Ca_1^a	3.779	(O_6)
B_3—B_5^{-b}	2.513	(O_{10}^{-b})	B_3—Ca_1^a	3.357	(O_4^{-c})	B_3—Ca_2^{-b}	3.812	(O_{10}^{-b})
B_1—B_4	2.516	(O_3)	B_2—Ca_2^{-b+c}	3.383	(O_7)	B_2—Ca_1	3.849	(O_8)
B_2—B_4^a	2.596	(O_6)	B_2—Ca_2	3.436	(O_8)	Ca_1—Ca_2	4.060	(O_1^{**}, O_8)
B_1—B_5	2.601	(O_2)	B_5—Ca_2^c	3.473	(O_7)	Ca_1—Ca_2^{-a-b}	4.085	(Cl^{-b})
			B_4—Ca_1^c	3.475	(O_9^c)	Ca_1—Ca_2^{-a}	4.321	(O_4^{-a-c})

Note: Anions coordinated by the given pair of cations are given in parentheses.
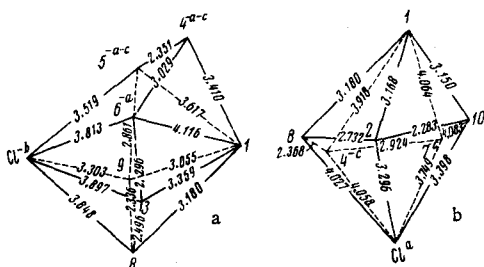

FIG. 2. Coordination polyhedra around Ca atoms: a) Ca_1 eight-cornered figures; b) Ca_2 seven-cornered figures.

shaped crystals. The structure was found on the basis of analysis of the three-dimensional Patterson function with a subsequent series of syntheses of the electron density and was refined by the least-squares method according to the "Kristall" program. Taking account of the individual anisotropic thermal constants we have from all reflections R_{hkl} = 7.47%, and with allowance for the isotropic constants, R_{hkl} = 10.50%. The atomic parameters of the chilgardite structure are given in Table I, and the principal interatomic distances, calculated on the basis of these coordinates, are given in Tables II and III.

The details of the structure of triclinic chilgardite are illustrated in Fig. 1. The boron and oxygen atoms form a three-dimensional boron—oxide skeleton whose elementary link consists of three BO_4— tetrahedra and two BO_3— triangles. The boron—oxide tetrahedra are linked by their vertices to form infinite chains extending along the c axis and joined by boron—oxide triangles.

The large voids in the boron–oxide skeleton contain Ca polyhedra of two kinds: Ca_2 seven-cornered figures and Ca_1 eight-cornered figures (Fig. 2). They are connected in pairs by the O_1–O_8 edge (Fig. 1b). Individual pairs are connected by common vertices (O_4 and Cl) into layers parallel to xy. One of the common vertices of the Ca_2 polyhedron is not bound to the boron–oxide skeleton (O_1^{**}) and on the basis[2] of the valence balance was identified as an H_2O molecule. Its H atoms effect hydrogen bonds of the type O–H ... Cl (O_1–H ... Cl = 3.186 Å and O_1–H ... Cl = 3.332 Å), which combine the discrete Ca layers together with the boron–oxide skeleton into a single structure.

As a result of the structural determination $Ca_2 \cdot [B_3^t B_2^\Delta O_9]Cl \cdot H_2O$ should be considered to be the expanded chemical formula for triclinic chilgardite as distinct from $Ca_2[B_5O_8(OH)_2]Cl$ for monoclinic chilgardite.[1,5]

The mean interatomic B–O distances in boron–oxide triangles and tetrahedra are 1.36_3, 1.37_1 Å and, respectively, 1.47_3, 1.47_2, and 1.46_8 Å, and the O–O distances in the triangles are 2.35_8 and 2.37_0. In the elementary link $[B_3^t B_2^\Delta O_9]^{3-}$ of the boron–oxide skeleton the B–B distances lie within the limits 2.39-2.60 Å and average 2.47_1 Å for the tetrahedron–tetrahedron distances and 2.50_5 Å for the tetrahedron–triangle distances. The Ca cations are each bound to one Cl atom and by means of quite short bonds to six O atoms (within the limits 2.38-2.60 Å), which corresponds to seven-fold coordination. The coordination sphere for Ca_1 has one more weakly bound atom O_8 (Ca–O_8 = 2.83 Å), which complements the seven-fold coordination of Ca_1 to eight-fold coordination. The O–O distances in the Ca polyhedra are indicated in Fig. 2.

Six of the nine oxygen atoms are coordinated by three cations, B^t, B^Δ, and Ca; the four-fold neighborhoods of $2B^t$ and 2Ca have only O_4 and O_8; moreover, the group O_5 could be conditionally incorporated into this group if the eighth distance Ca_2–O_5^{b-c} = 3.13 Å is taken into account for it. The B–Ca distances are divided into two groups. The first (within the limits 2.92-3.17 with an average of 3.02 Å) comprises Ca–B vectors each coordinating two anions; the second group comprises (within the limits 3.36-3.85 Å with an average of 3.60 Å) Ca–B vectors entering the cation polyhedron around one anion. The Ca–Ca vectors forming the coordination cation polyhedra lie within the narrow limits 4.06-4.32 Å, with the remaining Ca–Ca vectors exceeding 5 Å. The structure has no OH groups since all the atoms around B^t and B^Δ are divided between the two B.

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On the morphology of potassium bichromate crystals

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According to repeatedly verified data of x-ray structural analysis[2] potassium bichromate crystals fall into the pinacoidal class. A manifestation of a "real" influence of the asymmetry of these crystals (Fig. 1), the existence of a fast-growing smooth small (001) face along with a slow-growing structure – large (001) face, has hitherto been inadequately explained. It is acknowledged[5] that the asymmetric growth of triclinic α-$K_2Cr_2O_7$ is caused by interference from another metastable modification, monoclinic β-$K_2Cr_2O_7$. Structural stacks of triclinic potassium bichromate, in contrast to the monoclinic modification, are rotated about the c axis by 90° with respect to each other. One or more stacking faults consolidate a block of β form on the face of the third pinacoid and the polarity of the α-$K_2Cr_2O_7$ thus becomes undetectable by x-ray analysis.[1] It is appropriate to note that crystals of the compounds (isostructural β-$K_2Cr_2O_7$) $(NH_4)_2Cr_2O_7$

and $K_2S_2O_7$ also fall into the centrally-symmetric class 2/m (Refs. 3, 4).

If both modifications of potassium bichromate are centrosymmetric, then what causes the actual polar growth of α-K_2CrO_7 crystals? The causes should be sought not in the nature of the crystal[1] but in the conditions of its growth.

The present authors formulated the problem: 1) by morphological methods verify the categorical assertion that symmetry centers exist in α-$K_2Cr_2O_7$ crystals and at the same time obtain $(NH_4)_2Cr_2O_7$ and $K_2S_2O_7$ crystals under similar conditions and verify the data of x-ray structural analysis on their centrosymmetric character; 2) choose conditions for growing potassium bichromate crystals with a distinct symmetry center.

Etch figures appear when α-$K_2Cr_2O_7$ crystals are immersed for several seconds first in distilled water and

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