Refined crystal structure of solongoite $Ca_2[B_3O_4(OH)_4]Cl$

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(Submitted December 14, 1976)

Kristallografiya **22**, 624–626 (May–June 1977)

PACS numbers: 61.60.+m, 61.10.Fr

A detailed x-ray structural analysis of the new Cl-containing Ca-borate solongoite $Ca_2[B_3O_4(OH)_4]Cl$ discovered[1] in 1974 was carried out that same year on the basis of diffractometric material (1369 independent nonzero reflections, automatic Syntex P$\bar{1}$ diffractometer, R_{hkl} = 6.0%).

Our present refinement of the structure of solongoite was aimed at locating the H atoms and revealing possible hydrogen bonds on the basis of precision experimental material (Syntex P$\bar{1}$ automatic diffractometer, $2\theta-\theta$ method, variable scanning rate 6-24 deg/min, graphite monochromator, λ Mo Kα max $(\sin\theta/\lambda)$ = 1.08 Å^{-1}, 3212 independent nonzero ($I \geq 1.96\sigma I$) reflections]. The parameters of the monoclinic solongoite cell refined in the same automatic diffractometer were a = 7.975(2), b = 12.571(5), c = 7.237(2) Å, γ = 86.14(3)°, V = 723.87 Å^3, d_{exp} = 2.514, d_{calc} = 2.58 g/cm^3, Z = 4, space group C_{2h}^5 = $P2_1/b$, in good agreement with those given in Ref. 2. The initial analysis of the experimental data and all subsequent calculations were carried out in the specialized Syntex XTL computing system.

The coordinates of the basic atoms taken from Ref. 2 as a starting point were refined on the complete-matrix isotropic and anisotropic approximations to be R_{hkl} = 7.6 and 5.3% respectively.

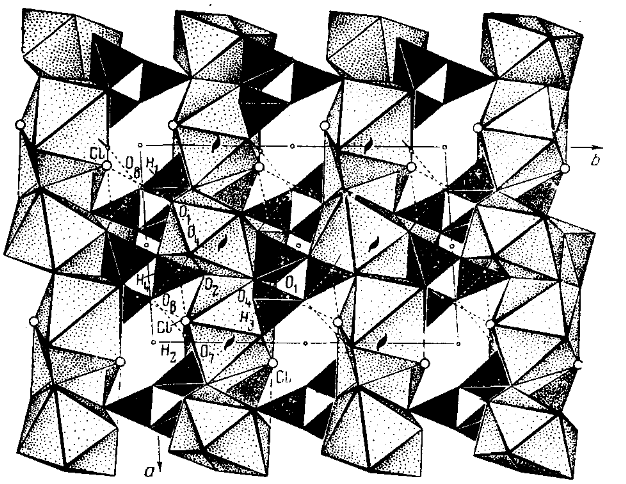

FIG. 1. Solongoite $Ca_2[B_3O_4(OH)_4]Cl$, xy projection. The small spheres represent H atoms, the continuous line a donor bond, the dashed line an acceptor bond.

TABLE I. Solongoite $Ca_2[B_3O_4(OH)_4]Cl$. Coordinates of the Basic Atoms and Individual Isotropic and Anisotropic Temperature Factors (standard deviations in parentheses)

Atoms	x/a	y/b	z/c	B, Å²
Ca_1	0.09054(8)	0.23788(5)	0.15660(9)	0.75(1)
Ca_2	0.51673(8)	0.29785(4)	0.35715(9)	0.68(1)
B_1	0.7950(4)	0.3901(2)	−0.0006(5)	0.61(5)
B_2	0.4002(4)	0.0851(2)	0.2253(5)	0.63(5)
B_3	0.3300(4)	0.4280(2)	0.0873(5)	0.64(5)
H_1	0.239(5)	0.054(3)	0.042(5)	6(1)
H_2	0.971(5)	0.100(3)	0.431(6)	4(1)
H_3	0.822(5)	0.359(3)	0.258(6)	3(1)
H_4	0.642(5)	0.106(3)	0.203(6)	5(1)
O_1	0.2902(3)	0.0957(2)	0.0567(3)	0.81(4)
O_2	0.3374(3)	0.3207(2)	0.0738(3)	0.71(4)
O_3	0.3577(3)	0.1327(2)	0.1692(3)	0.78(4)
O_4	0.7812(3)	0.3372(2)	0.1823(3)	0.85(4)
O_5	0.4274(3)	0.4736(2)	0.2227(3)	0.68(4)
O_6	0.3236(3)	0.1518(2)	0.3726(3)	0.65(4)
O_7	0.0301(3)	0.1385(2)	0.4264(3)	0.76(4)
O_8	0.7753(3)	0.5067(2)	0.0223(3)	0.79(4)
Cl	0.1006(1)	0.38567(7)	0.4360(1)	1.50(2)

$$T=\exp\left[-1/4\left(B_{11}h^2a^{*2}+B_{22}k^2b^{*2}+B_{33}l^2c^{*2}+2B_{12}hka^*b^*+2B_{13}hla^*c^*+2B_{23}klb^*c^*\right)\right]$$

Atoms	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca_1	0.76(2)	0.63(2)	0.90(2)	0.04(1)	0.00(2)	0.17(2)
Ca_2	1.09(2)	0.46(2)	0.60(2)	−0.01(1)	−0.14(2)	0.02(1)
B_1	0.82(10)	0.35(8)	0.76(10)	0.03(7)	−0.13(8)	−0.04(7)
B_2	0.85(10)	0.40(8)	0.70(10)	0.00(7)	0.03(8)	0.06(7)
B_3	0.79(10)	0.53(9)	0.75(10)	0.06(7)	0.07(8)	−0.04(8)
O_1	1.05(7)	0.67(6)	0.76(7)	0.01(5)	−0.18(6)	0.06(6)
O_2	1.01(7)	0.36(6)	0.86(7)	0.02(5)	0.08(6)	−0.03(5)
O_3	0.82(7)	0.73(6)	0.90(8)	−0.17(5)	0.25(6)	0.03(6)
O_4	1.38(2)	0.71(6)	0.55(7)	0.05(6)	−0.04(6)	0.15(5)
O_5	1.04(7)	0.34(6)	0.85(7)	0.16(5)	−0.14(6)	−0.16(5)
O_6	0.91(7)	0.36(5)	0.76(7)	−0.01(5)	0.24(6)	−0.10(5)
O_7	0.70(7)	0.65(6)	0.98(7)	−0.01(5)	−0.00(6)	0.02(6)
O_8	1.11(8)	0.42(6)	0.96(7)	0.04(5)	−0.29(6)	−0.00(5)
Cl	1.88(3)	1.12(3)	1.70(3)	−0.31(2)	0.39(3)	−0.11(2)

TABLE II. Solongoite $Ca_2[B_3O_4(OH)_4]Cl$. Interatomic Distances (Å)

	Ca₁-polyhedron	
$Ca_1–Cl$ = 2.751(1)	$O_1–O_2$ = 2.881(3) **	$O_4–Cl$ = 3.231(3)
Cl' = 2.757(1)	O_6 = 2.413(3) *	Cl' = 3.400(3)
O_1 = 2.422(2)	O_7 = 3.406(3)	$O_6–O_7$ = 2.390(3) *
O_2 = 2.365(2)	Cl'' = 3.229(3)	Cl = 3.364(3)
O_4 = 2.696(2)	$O_2–O_6$ = 3.038(3) **	$O_7–Cl$ = 3.195(3) **
O_6 = 2.607(2)	O_7' = 3.128(3)	Cl' = 3.717(3)
O_7 = 2.384(2)	Cl = 3.301(3)	$O_7'–Cl$ = 3.850(3)
O_7' = 2.432(2)	$O_4–O_7$ = 3.554(3)	Cl' = 3.195(3) **
Av. 2.552	O_7' = 2.419(3) *	O_1 = 4.174(3)
		Av. 3.126
	Ca_2-polyhedron	
$Ca_2–O_1'$ = 2.554(2)	$O_1'–O_2'$ = 2.881(3) **	$O_2'–O_3$ = 3.112(3)
O_2 = 2.506(2)	O_3' = 2.358(3) *	O_3' = 2.931(3) **
O_2' = 2.408(2)	O_4 = 2.883(3)	O_4 = 3.621(3)
O_3 = 2.486(2)	O_5 = 3.378(3)	O_6 = 3.111(3)
O_3' = 2.478(2)	$O_2–O_3$ = 2.931(3) **	$O_3–O_4$ = 3.228(3)
O_5 = 2.474(2)	O_4 = 3.645(3)	O_6 = 2.377(3) *
O_4 = 2.537(2)	O_5 = 2.357(3) *	$O_3'–O_5$ = 3.495(3)
O_6 = 2.477(2)	O_6 = 3.038(3) **	O_6 = 3.632(3)
Av. 2.490	O_3' = 4.436(3)	$O_4–O_5$ = 3.215(3)
		Av. 3.146
B_1-tetrahedron	**B_2-tetrahedron**	**B_3-triangle**
$B_1–O_4$ = 1.489(1)	$B_2–O_4$ = 1.504(4)	$B_3–O_2$ = 1.350(4)
O_6' = 1.443(4)	O_3 = 1.483(4)	O_5 = 1.397(4)
O_7' = 1.512(4)	O_5' = 1.454(4)	O_8' = 1.383(4)
O_8 = 1.473(4)	O_6 = 1.464(4)	Av. 1.377
Av. 1.479	Av. 1.476	$O_2–O_5$ = 2.357(3) *
$O_4–O_6'$ = 2.393(3)	$O_1–O_3$ = 2.358(3)	O_8' = 2.395(3)
O_7' = 2.419(3) *	O_5' = 2.424(3)	$O_5–O_8'$ = 2.400(3)
O_8 = 2.423(3)	O_6 = 2.413(3)	Av. 2.384
$O_6'–O_7'$ = 2.390(3) *	$O_3–O_5'$ = 2.443(3)	
O_8 = 2.445(3)	O_6 = 2.377(3) *	
$O_7'–O_8$ = 2.417(3)	$O_5'–O_6$ = 2.435(5)	
Av. 2.41_5	Av. 2.408	

Note: 1) The standard deviations are shown in parentheses. 2) One asterisk denotes common edges of B and Ca polyhedra; two denote common edges of Ca polyhedra.

TABLE III. Hydrogen Bonds in the Structure of Solongoite $Ca_2[B_3O_4(OH)_4]Cl$, Å

D–H ...	D–H	H ... A	D–A	Angle D–H–A
$O_1–H_1 \ldots Cl''$	0.69	2.46	3.130	164°
$O_7–H_2 \ldots O_8''$	0.71	2.04	2.732	169
$O_4–H_3 \ldots Cl$	0.70	2.61	3.231	149
$O_4–H_3 \ldots O_1$	0.70	2.39	2.883	128
$O_3–H_4 \ldots O_8''$	0.77	2.54	3.184	142
$O_3–H_4 \ldots Cl'$	0.77	2.83	3.201	112
$O_3–H_4 \ldots O_2$	0.77	2.84	3.112	103

The refined positional and anisotropic temperature parameters of the Ca, B, O, and Cl atoms were used to construct an electron-density difference synthesis revealing the missing four H atoms. The positions of these were refined as follows: At the first stage the positional parameters were refined for fixed isotropic $B_j = 2.00$ Å^2; at the second stage only B_j were refined. The final coordinates of the basic atoms and the corresponding interatomic distances (Tables I and II) were characterized by a variance factor of $R_{hkl} = 5.1\%$.

The two kinds of Ca cations, both lying in eight-pointed polyhedra,[1)] are distinguished by the fact that two vertices of the Ca_1 polyhedron are occupied by Cl atoms. The B_1 and B_2 atoms with their four nearest neighbors and the B_3 atoms surrounded by three O atoms form a $[B_3O_4(OH)_4]$ ring.

The walls of Ca polyhedra parallel to (010), fundamental in the solongoite structure, are connected to each other by the boron–oxygen radicals $[B_3O_4(OH)_4]$ (Fig. 1).

The location of the H atoms in the solongoite structure confirmed the validity of their earlier identification[2] with OH groups on the basis of the formal balance of valence forces in O_1, O_3, O_4, and O_7, and also confirmed the existence of hydrogen bonds, which helped in uniting the Ca walls (Fig. 1). The distances and angles corresponding to the hydrogen bonds are given in Table III.

The authors wish to thank E. P. Zhelezin for help in obtaining the experimental data, E. L. Belokoneva for executing the calculations, and Yu. K. Egorov-Tismenko for help in formulating the investigation.

[1)]Delta dodecahedra, almost ideal Thomson cubes for Ca_2 and less ideal for Ca_1.

[1]S. V. Malinko, Zap. Vses. Mineral. Obshch., No. 1, 117 (1974).
[2]N. A. Yamnova, Yu. K. Egorov-Tismenko, M. A. Simonov, and N. V. Belov, Dokl. Akad. Nauk SSSR 216, 1281 (1974).

Translated by G. D. Archard