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$Sr_2B_5O_9OH•H_2O$, A SYNTHETIC BORATE RELATED TO HILGARDITE

JACQUES BARBIER[§] AND HYUNSOO PARK

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

ABSTRACT

The crystal structure of a new strontium borate, $Sr_2B_5O_9OH•H_2O$, space group *C*2, *a* 10.2571(6), *b* 8.0487(2), *c* 6.4043(4) Å, β 127.860(2)°, *Z* = 2, has been determined by X-ray diffraction using a single crystal grown under hydrothermal conditions. The structure is closely related to that of the zeolite-like hilgardite minerals, $Ca_2B_5O_9Cl•H_2O$, in particular that of triclinic hilgardite-1*A*. The main structural differences are a more symmetrical conformation of the $[B_5O_{12}]^{9-}$ pentaborate chains and a random distribution of OH^- and H_2O in $Sr_2B_5O_9OH•H_2O$, that result in the monoclinic symmetry. The role of the Sr cations in determining the conformation of the pentaborate chain is discussed by comparison with hilgardite-1*A*.

Keywords: strontium pentaborate hydrate, calcium pentaborate hydrate, hilgardite, crystal chemistry, crystal structure, X-ray diffraction.

SOMMAIRE

La structure cristalline d'un nouveau borate de strontium, $Sr_2B_5O_9OH•H_2O$, groupe d'espace *C*2, *a* 10.2571(6), *b* 8.0487(2), *c* 6.4043(4) Å, β 127.860(2)°, *Z* = 2), a été déterminée par diffraction X sur un monocristal obtenu par croissance hydrothermale. La structure est étroitement reliée à celle des minéraux zéolitiques de type hilgardite, $Ca_2B_5O_9Cl•H_2O$, en particulier celle de l'hilgardite-1*A*, triclinique . Les principales différences structurales proviennent d'une conformation plus symétrique des chaînes pentaborates $[B_5O_{12}]^{9-}$, et d'une distribution désordonnée des ions OH^- et des molécules H_2O dans $Sr_2B_5O_9OH•H_2O$, qui conduisent à la symétrie monoclinique. Le rôle des cations Sr dans la détermination de la conformation des chaines pentaborates est examiné par comparaison avec l'hilgardite-1*A*.

Mots-clés: pentaborate de strontium hydraté, pentaborate de calcium hydraté, hilgardite, cristallochimie, structure cristalline, diffraction X.

INTRODUCTION

The search for new compounds in alkaline-earth gallo-borate systems has recently led to the structural characterization of two new anhydrous borates, $MGa_2B_2O_7$ (M = Sr, Ba) (Park & Barbier 2000a), one new fluoride borate, $BaGaBO_3F_2$ (Park & Barbier 2000b), and one new hydrated borate, $Sr_3Ga_3B_4O_{13}OH$ (Park & Barbier 2000c). The title compound is another new strontium borate that was synthesized during investigation of the system $SrO–Ga_2O_3–B_2O_3$ under hydrothermal conditions.

In the course of its structure determination, it became apparent that $Sr_2B_5O_9OH•H_2O$ is related to the series hilgardite ($Ca_2B_5O_9Cl•H_2O$) – tyretskite ($Ca_2B_5O_9OH•H_2O$). The crystal structures of several of these minerals have been determined, including hilgardite-1*A* (Rumanova *et al*. 1977, Burns & Hawthorne 1994), hilgardite-4*M* (Ghose & Wan 1979), hilgardite-3*A* or "parahilgardite" (Wan & Ghose 1983) and the strontium-dominant analogue of hilgardite (with the name of "kurgantaite" proposed by I.V. Pekov and D. Yu. Pushcharovsky, pers. commun.; Ferro *et al*. 2000a). A number of related synthetic compounds have also been structurally characterized, including $Ca_2B_5O_9Br$ (Lloyd *et al*. 1973), $Eu_2B_5O_9X$ (*X* = Cl, Br) (Machida *et al*. 1981), $Pb_2B_5O_9OH•H_2O$ (Belokoneva *et al*. 1998), $Na_{0.5}Pb_2B_5O_9Cl(OH)_{0.5}$ (Belokoneva *et al*. 2000) and $Ba_2B_5O_9Cl•0.5H_2O$ (Ferro *et al*. 2000b). The close structural relationships among all these compounds have been described in detail previously (Ghose 1982, 1985). On the basis of its unit-cell volume (Table 1), $Sr_2B_5O_9OH•H_2O$ would be the analogue of the hilgardite-2*M* polymorph that has not yet been identified among borate minerals (Grice *et al*. 1999) or synthetic borates (Heller 1986). However, the details of its crystal structure, which is descibed here, show that $Sr_2B_5O_9OH•H_2O$ is distinct from the hilgardite–tyret-

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[§] *E-mail addresses*: barbier@mcmaster.ca

TABLE 1. UNIT-CELL DATA OF HILGARDITE-RELATED COMPOUNDS

Compound	Formula	Space group	Unit-cell volume (Å^3)	*Z*	Ref.
hilgardite-1*A*	$Ca_2B_5O_9Cl{\bullet}H_2O$	*P*1	204.9	1	1
Sr-substituted hilgardite	$SrCaB_5O_9Cl{\bullet}H_2O$	*P*1	206.9	1	2
tyretskite	$Ca_2B_5O_9OH{\bullet}H_2O$	*P*1	203.2	1	3
synthetic	$Sr_2B_5O_9OH{\bullet}H_2O$	*C*2	417.4	2	4
hilgardite-3*A*	$Ca_2B_5O_9Cl{\bullet}H_2O$	*P*1	614.8	3	5
hilgardite-4*M*	$Ca_2B_5O_9Cl{\bullet}H_2O$	*Aa*	817.8	4	6
synthetic	$Ca_2B_5O_9Br$	*Pnn*2	807.2	4	7
synthetic	$Eu_2B_5O_9Cl$	*Pnn*2	835.2	4	8
synthetic	$Ba_2B_5O_9Cl{\bullet}0.5H_2O$	*Pnn*2	908.5	4	9

Ref.: 1 Burns & Hawthorne (1994); 2 Ferro *et al.* (2000a); 3 Kondrat'eva (1964); 4 this work; 5 Wan & Ghose (1983); 6 Ghose & Wan (1979); 7 Lloyd *et al.* (1973); 8 Machida *et al.* (1981); 9 Ferro *et al.* (2000b).

skite minerals as a result of a unique conformation of the pentaborate anion.

EXPERIMENTAL

$Sr_2B_5O_9OH{\bullet}H_2O$ crystals were recovered in the products of hydrothermal crystallization experiments carried out in 25 mL Teflon-lined Parr reactors heated to 250–275°C for periods of 3 to 10 days. The starting materials consisted of a powder (0.25 g) of either a crystalline phase with a composition of $SrO{\bullet}Ga_2O_3{\bullet}B_2O_3$, or a glass of composition $3SrO{\bullet}3Ga_2O_3{\bullet}14B_2O_3$, together with 10 mL of deionized water. Various initial pH conditions were used by adding small amounts of concentrated nitric acid (for a pH of 1–2) or strontium hydroxide (for a pH of 10–11). In all cases, the final products contained small (0.1 to 0.5 mm) prismatic crystals of $Sr_2B_5O_9OH{\bullet}H_2O$, plus an unidentified microcrystalline phase in a solution of pH in the range 6–8. Owing to the relatively small yield of crystals, no chemical analysis has been carried out. The chemical composition of the crystals has been unambiguously determined during the structure determination.

The single-crystal X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo*K*α rotating anode and a SMART–1K CCD area detector. The raw intensity data were processed with the SAINT software, and an empirical absorption correction based on equivalent reflections was applied using the SADABS program (Sheldrick 1996). The structure was then solved and refined anisotropically with the SHELXS (Sheldrick 1990) and SHELXL (Sheldrick 1997) programs. The crystal data and the details of the refinement are listed in Table 2. No significant reflections violating the *C*-centered monoclinic symmetry were observed. The atom coordinates with the isotropic displacement parameters are given in Table 3, and the anisotropic displacement parameters are given in Table 4. Selected bond-distances and bond-angles are listed in Table 5. It should be noted that the *C*2 symmetry of the $Sr_2B_5O_9OH{\bullet}H_2O$ structure implies a complete OH^-–H_2O disorder at the fully occupied O6 site. However, only one hydrogen position could be determined from difference-Fourier maps. The remaining hydrogen atom of the H_2O molecule corresponds to only one half hydrogen atom bonded to O6 and, as such, could not be identified in the residual-electron-density maps. The coordinates of the H atom were refined with a constrained O6–H distance of 0.95 ± 0.01 Å and a fixed isotropic displacement parameter of 0.02 Å^2 (Table 3).

DESCRIPTION OF THE STRUCTURE

The structure of $Sr_2B_5O_9OH{\bullet}H_2O$ is depicted in Figures 1 and 2. Like the hilgardite structure, its fundamental building block (Grice *et al.* 1999) consists of $B_5O_{12}{}^{9-}$ pentaborate anions built of three corner-shared tetrahedra (2 B1 + 1 B2) bridged by two triangles (2 B3). As in hilgardite, the pentaborate anions are linked to one another to form chains along [001], and adjacent chains are further linked into a three-dimensional zeolite-like framework (Ghose & Wan 1979, Wan & Ghose 1983). Both the individual pentaborate anions and the

TABLE 2. REFINEMENT DETAILS FOR $Sr_2B_5O_9OH.H_2O$

formula	$Sr_2B_5O_9OH.H_2O$	2θ max (°)	72.34
space group	*C*2	index ranges	-16 < h < 12
a (Å)	10.2571(6)		-13 < k < 10
b (Å)	8.0487(2)		-10 < l < 10
c (Å)	6.4043(4)	total no. reflections	5193
β (°)	127.860(2)	unique reflections	1490
V (Å^3)	417.43(4)	absorption corr.	SADABS
Z	2	Tmin/Tmax	0.4682
density (g.cm^{-3})	3.241	R_{int}	0.048
crystal size (mm)	0.18×0.10×0.08	refined parameters	86
wavelength	Mo Kα	goodness-of-fit	1.006
absorption (mm^{-1})	12.837	*R* [F>4σ(F)]	0.028
frame exposure (s)	10	$wR(F^2)$	0.060
no. frames	3500	difference map (eÅ^{-3})	-1.73,+0.6
frame width (°)	0.3		

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR $Sr_2B_5O_9OH.H_2O$

	x	*y*	*z*	U_{eq}
Sr	0.20462(3)	0.04088(5)	0.91489(5)	0.00867(7)
B1	0.5739(4)	0.3260(4)	0.2538(7)	0.0061(5)
B2	0.5	0.1593(6)	0.5	0.0063(8)
B3	0.2677(5)	0.0730(3)	0.5085(7)	0.0061(6)
O1	0.6439(3)	0.0518(4)	0.5850(4)	0.0073(4)
O2	0.1464(3)	0.9662(3)	0.4529(5)	0.0085(4)
O3	0.5536(3)	0.2515(3)	0.7371(5)	0.0067(4)
O4	0.5	0.4043(4)	0.0	0.0068(5)
O5	0.2997(3)	0.2020(3)	0.6758(5)	0.0088(4)
O6	0.4329(3)	0.8154(3)	0.1089(5)	0.0150(5)
H	0.526(4)	0.821(7)	0.289(4)	0.020*

* Not refined.

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS FOR $Sr_2B_5O_9OH.H_2O$

	U_1	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.00930(11)	0.00911(10)	0.00679(11)	-0.0014(2)	0.00453(9)	-0.0025(2)
B1	0.0066(14)	0.0069(13)	0.0044(14)	0.0002(10)	0.0031(13)	0.0007(11)
B2	0.007(2)	0.005(2)	0.007(2)	0.000	0.004(2)	0.000
B3	0.0080(14)	0.0035(15)	0.0055(14)	-0.0004(9)	0.0036(13)	-0.0013(9)
O1	0.0085(8)	0.0060(12)	0.0073(8)	0.0010(10)	0.0049(7)	0.0026(10)
O2	0.0085(11)	0.0087(9)	0.0085(10)	-0.0027(8)	0.0053(9)	-0.0030(7)
O3	0.0059(10)	0.0082(9)	0.0046(10)	-0.0007(7)	0.0026(9)	0.0011(7)
O4	0.0087(15)	0.0048(12)	0.0051(14)	0.000	0.0033(13)	0.000
O5	0.0093(11)	0.0096(10)	0.0087(11)	-0.0034(8)	0.0062(10)	-0.0028(8)
O6	0.0111(12)	0.0147(11)	0.0150(13)	0.0000(10)	0.0059(11)	-0.0006(9)

TABLE 5. SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Sr_2B_5O_9OH.H_2O$

Sr - O1	2.564(2)	O4 - B1 - O5	113.3(2)
Sr - O6	2.575(3)	O4 - B1 - O3	110.8(2)
Sr - O6	2.598(3)	O5 - B1 - O3	110.4(3)
Sr - O5	2.610(2)	O4 - B1 - O2	105.6(3)
Sr - O3	2.638(2)	O5 - B1 - O2	111.3(3)
Sr - O3	2.684(2)	O3 - B1 - O2	105.1(2)
Sr - O2	2.703(2)		
Sr - O4	2.705(2)	O3 - B2 - O3	118.9(4)
Sr - O2	2.909(3	O3 - B2 - O1	109.3(2)
		O3 - B2 - O1	104.9(2)
B1 - O4	1.449(4)	O3 - B2 - O1	104.9(2)
B1 - O5	1.470(4)	O3 - B2 - O1	109.3(2)
B1 - O3	1.472(4)	O1 - B2 - O1	109.3(4)
B1 - O2	1.513(4)		
		O2 - B3 - O1	123.2(3)
B2 - O3	1.461(3)	O2 - B3 - O5	114.9(3)
B2 - O3	1.461(3)	O1 - B3 - O5	121.8(3)
B2 - O1	1.496(4)		
B2 - O1	1.496(4)		
B3 - O2	1.367(4)		
B3 - O1	1.370(4)		
B3 - O5	1.379(4)		
O6 - H	0.94(1)		

pentaborate chains in $Sr_2B_5O_9OH{\bullet}H_2O$ possess two-fold symmetry (around the B2 and O4 atoms, Fig. 1), and the *C*-centered symmetry of the structure implies that all pentaborate chains have the same orientation and conformation (Fig. 2). Two-fold symmetry is also present in the pentaborate anion of garrelsite, $NaBa_3Si_2B_7O_{16}(OH)_4$ (Ghose *et al.* 1976), but is absent from all the hilgardite structures.

The Sr cations in $Sr_2B_5O_9OH{\bullet}H_2O$ are located at the intersections of tunnels parallel to the *a* and *b* axes of the unit cell (Fig. 1). The sites are nine-coordinated, with a bond-valence sum equal to 2.12 valence units (*vu*) for the nine Sr–O bonds shorter than 3 Å (Table 5), as calculated with the parameters of Brese & O'Keeffe (1991). Two of the shorter Sr–O bonds correspond to O6 sites located in tunnels parallel to the *c* axis and randomly occupied by OH^- anions and H_2O molecules (Fig. 2). These sites occur in pairs, with alternating short (2.48 Å) and long (4.31 Å) O6…O6 distances along the *c* direction (Fig. 1). The short distance of 2.48 Å indi-

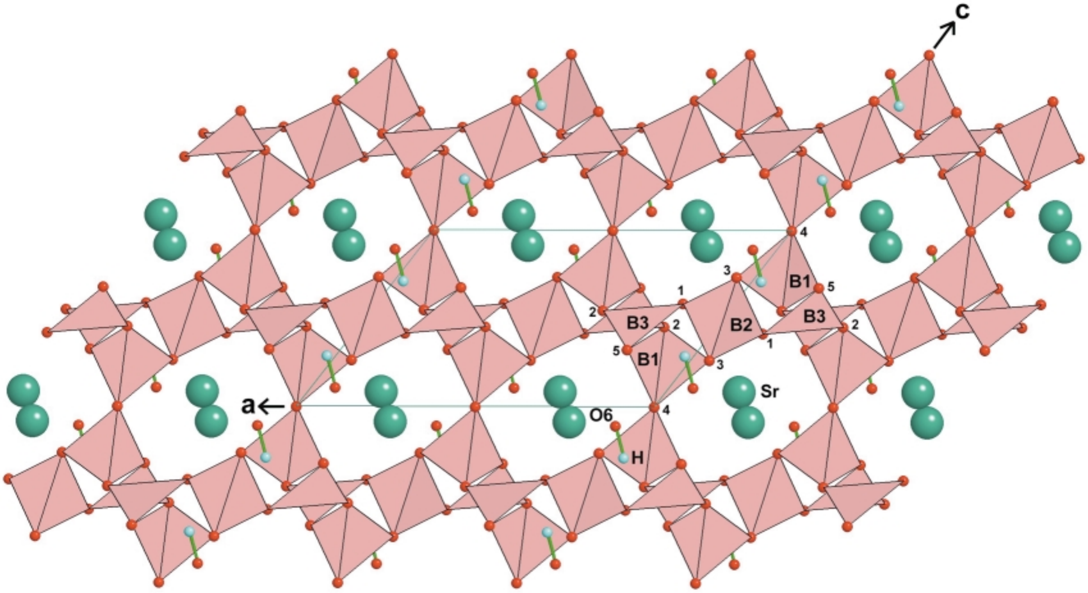

FIG. 1. View of the $Sr_2B_5O_9OH{\bullet}H_2O$ structure projected along the *b* axis. Small numbers refer to the oxygen positions. Only the H atom determined during the structure refinement is shown bonded to the O6 atom. The small numbers at the corners of the polyhedra refer to the oxygen atom positions (*cf.* Table 3).

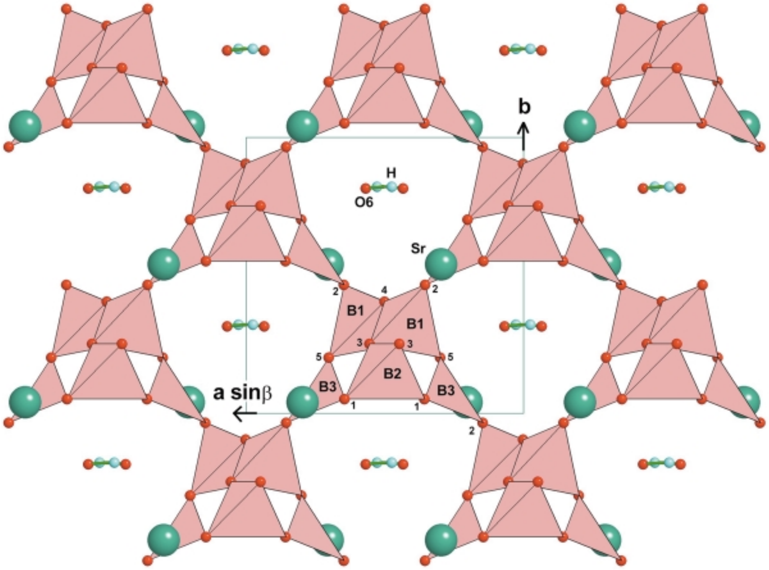

FIG. 2. View of the $Sr_2B_5O_9OH•H_2O$ structure projected along the *c* axis.

cates the formation of hydrogen bonds between adjacent OH^- anions and H_2O molecules, suggesting that the missing second H atom of the H_2O molecule lies directly between adjacent O6 sites. The resulting orientation and geometry of the H_2O molecule would be consistent with the observed H–O6…O6 angle of 101°. A similar scheme of hydrogen bonding also is present between the Cl^- anions and the H_2O molecules in hilgardite, but with more regular O_w …Cl…O_w spacings of 3.15–3.30 Å (Ghose & Wan 1979, Wan & Ghose 1983, Burns & Hawthorne 1994).

Comparison of $Sr_2B_5O_9OH•H_2O$ and hilgardite

The structure of hilgardite-1*A* is depicted in Figure 3 (Burns & Hawthorne 1994). It is one of the three known polymorphic forms of hilgardite (with hilgardite-4*M* and higardite-3*A*, or "parahilgardite") that are based on different combinations of right- or left-handed (or both) pentaborate anions and chains (Ghose 1982). The basic hilgardite-1*A* unit-cell contains only one $Ca_2B_5O_9Cl•H_2O$ formula unit, so that all pentaborate chains in the structure are equivalent and have the same conformation. Consequently, a pseudo *C*-centered symmetry is apparent in the [001] projection (Fig. 3), with unit-cell dimensions very similar to those of the *C*2 monoclinic unit-cell of $Sr_2B_5O_9OH•H_2O$ (Table 6). However, hilgardite-1*A* is triclinic owing to the asymmetric conformation of the pentaborate chains and the Cl^-–H_2O ordering in the [001] tunnels, which preclude the presence of 2-fold axes. The higher symmetries of monoclinic hilgardite-4*M* and of the orthorhombic hilgardite-like synthetic borates (Table 1) are achieved *via* the formation of superstructures containing both right- and left-handed pentaborate chains. In contrast, both the single-chain conformation and the OH^-–H_2O disorder in $Sr_2B_5O_9OH•H_2O$ are compatible with the 2-fold axes required for overall monoclinic symmetry with the smallest possible unit-cell volume. The structure of the new Sr borate therefore represents a holosymmetric form of hilgardite.

The different conformations of the pentaborate chains in $Sr_2B_5O_9OH•H_2O$ and hilgardite-1*A* are illustrated in more detail in Figure 4. The connectivity of the borate tetrahedra and triangles is identical in both structures, but the hilgardite chain lacks 2-fold symme-

TABLE 6. UNIT-CELL RELATIONS BETWEEN HILGARDITE-1*A* AND $Sr_2B_5O_9OH.H_2O$

	hilgardite-1*A*		$Sr_2B_5O_9OH.H_2O$
	triclinic *P*1	pseudo-monoclinic* *C*1	monoclinic *C*2
a (Å)	6.452	10.382	10.257
b	6.559	7.843	8.049
c	6.286	6.286	6.404
α (°)	61.60	89.86	90
β	118.72	126.81	127.86
γ	105.86	90.98	90
V ($Å^3$)	204.9	409.8	417.4

* the *P*1 → *C*1 transformation matrix is 1-10 / 110 / 001

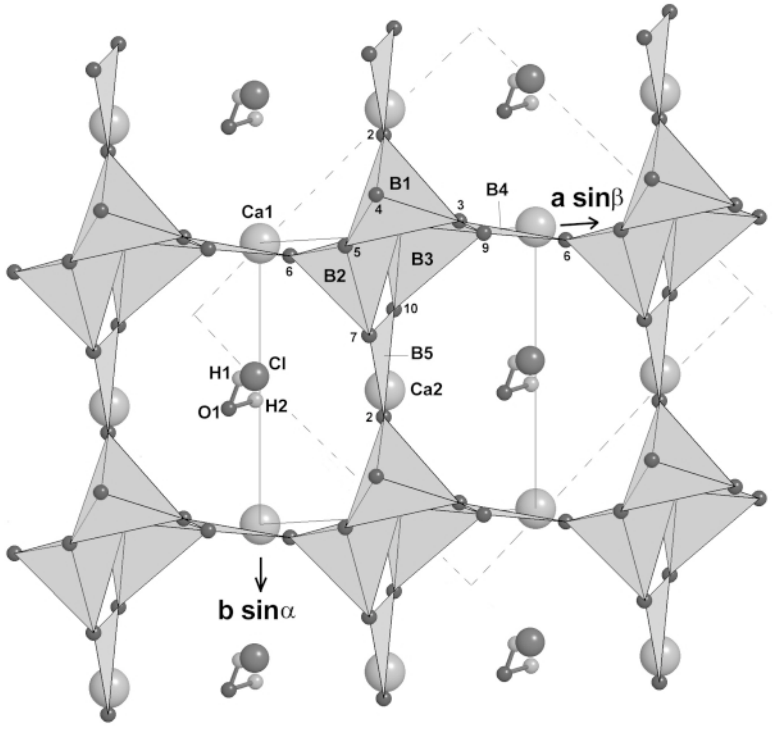

FIG. 3. View of the hilgardite-1*A*, $Ca_2B_5O_9Cl{\bullet}H_2O$, structure in projection along the *c* axis. The dashed line represents the pseudo-monoclinic *C*-centered unit-cell similar to that of $Sr_2B_5O_9OH{\bullet}H_2O$ (*cf*. Table 6). Compare to Figure 2.

try, primarily because of a large rotation of the B1 tetrahedron around its O3…O4 edge (Fig. 4). The more extended chain conformation in $Sr_2B_5O_9OH{\bullet}H_2O$ is associated with larger B–O–B angles around the bridging tetrahedral O atoms: an average of 121.7° around O3 and O4 in $Sr_2B_5O_9OH{\bullet}H_2O$ (Fig. 4, top) *versus* 116.5° around O8, O4 and O5 in hilgardite-1*A* (Fig. 4, bottom). This leads to a slight expansion of the structure along the *c* axis and contributes to the increase in unit-cell volume (Table 6). In that respect, it is noteworthy that the volumes per formula unit for hilgardite, Sr-substituted hilgardite, tyretskite and $Sr_2B_5O_9OH{\bullet}H_2O$ are quite similar, with only minor increases associated with the Sr ↔ Ca and Cl^- ↔ OH^- substitutions (Table 1). It may therefore be argued that the different chain conformation in the $Sr_2B_5O_9OH{\bullet}H_2O$ structure serves to accommodate the larger Sr cations without significantly altering the dimensions of the pentaborate framework. The bonding environments of the alkaline-earth cations are indeed quite distinct in the Ca and Sr structures. In hilgardite-1*A*, the Ca(1) and Ca(2) cations are eight- and seven-coordinated, respectively (by six and five framework O atoms, plus two Cl^- and H_2O ligands), with an average bond-distance of 2.53 Å (Burns & Hawthorne 1994). The Ca(2) site remains slightly underbonded [with a bond-valence sum of 1.85 *versus* 2.00 *vu* for Ca(1)] and, not surprisingly, is the site occupied by Sr in Sr-substituted hilgardite (Ferro *et al.* 2000a). In contrast, as described above, the Sr cations in $Sr_2B_5O_9$ $OH{\bullet}H_2O$ are nine-coordinated [by seven framework O atoms, plus two $O(6)H^-$ and $H_2O(6)$ ligands], with an average bond-distance of 2.66 Å. The volume difference between the SrO_9 and CaO_8 polyhedra (18.82 *versus* 16.19 $Å^3$, or 16.2%, calculated for a spherical coordination environment) is clearly much larger than expected from the difference in unit-cell volumes alone (1.9%, Table 6).

The presence of the Cl^- anions in the hilgardite structure may also play a role in determining the conformation of the pentaborate chains. Their large size is associated with long Cl…O distances, with the shortest being equal to 3.29 Å in hilgardite-1*A* (Burns & Hawthorne 1994). By comparison, the shortest O6…O distances in the $Sr_2B_5O_9OH{\bullet}H_2O$ structure are 3.08 Å (O6…O1), 3.11 Å (O6…O3) and 3.16 Å (O6…O1), comparable with the OH_2…O distances in hilgardite

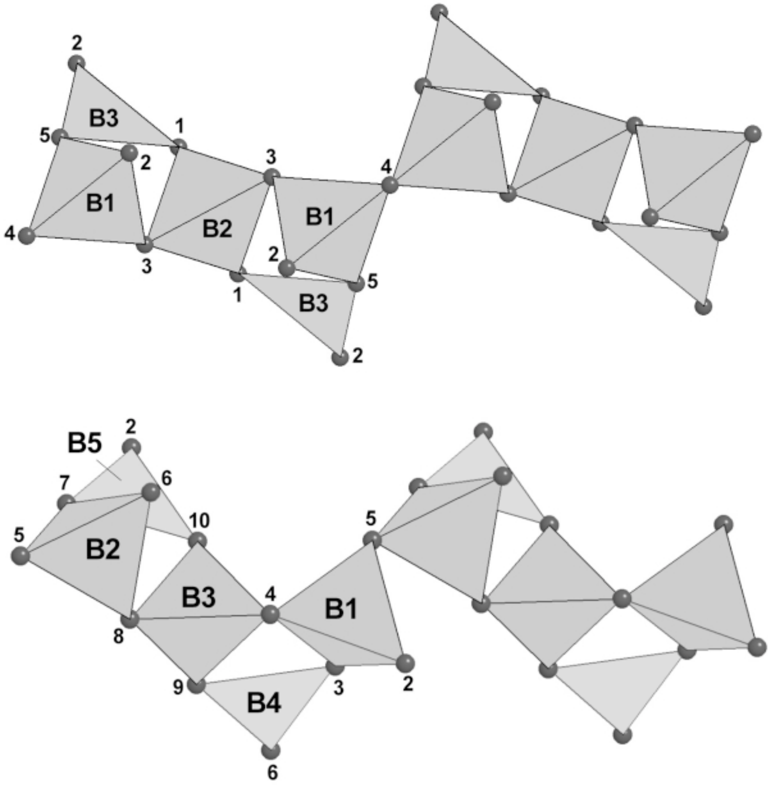

FIG. 4. Conformation of the pentaborate $[B_5O_{12}]^{9-}$ chains in $Sr_2B_5O_9OH{\bullet}H_2O$ (top) and hilgardite-1*A* (bottom). These chains extend in the *c* direction in both structures.

(3.04–3.15 Å). Clearly, the Cl^- anions occupy a larger site than the OH^- anions and H_2O molecules.

It would be of interest to compare the structure of $Sr_2B_5O_9OH{\bullet}H_2O$ with that of tyretskite, $Ca_2B_5O_9OH{\bullet}H_2O$. Unfortunately, no refinement of the tyretskite structure has been carried out to date, and only unit-cell parameters have been determined. These show a similarity to the parameters of hilgardite-1*A* (*a* 6.44 , *b* 6.45, *c* 6.41 Å, α 61.8, β 119.7, γ 106.5°, as quoted in Rumanova *et al*. 1977). However, even these cell parameters are in doubt, as they do not provide a suitable indexing of the published powder X-ray data for tyretskite (ICDD database, file #260002). Furthermore, the published powder-diffraction pattern shows little resemblance with that simulated using the atomic positions of hilgardite-1*A*. True triclinic symmetry would imply an ordered distribution of OH^- and H_2O in tyretskite, but questions remain as to the exact conformation of the pentaborate chains. A predominant role for the size of the alkaline-earth cation would imply a hilgardite-like chain in view of the small size of the Ca ions. However, the presence of the OH^- anions and H_2O molecules in the framework cavities, together with the associated hydrogen bonding, might favor the more symmetrical conformation of chains found in $Sr_2B_5O_9OH{\bullet}H_2O$.

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