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Crystal Structure and Dehydration Process of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$

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$Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ crystallizes in the trigonal system, space group $P3$, with $a = 6.5534(5)$ Å, $c = 6.1740(7)$ Å ($T = 293$ K), and $Z = 1$. In this compound, there are isolated $Li(H_2O)_4$ and $B(OH)_4$ tetrahedra which are almost regular. Some of the positions of hydrogen atoms were localized with an occupancy factor of 2/3 and 1/3; therefore, all the numerous hydrogen bonds present in the structure were well determined. Knowledge of the structure allows us to propose a dehydration process of three steps; there is a loss of free water molecules ($2H_2O$) from 60°C followed by a loss of lithium-coordinated water molecules ($4H_2O$). This leads to an intermediate borate $LiB(OH)_4$ whose structure is known. The final dehydroxylation occurs at 170°C. Some comparisons are made between the structures of $LiB(OH)_4$ and $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$, especially considering the hydrogen bonds.

INTRODUCTION

The synthesis, structural, and dehydration studies of borates and especially of hydrated lithium borates have attracted a great deal of attention in these past few years. The main reason for the study of these materials is that physical properties, like piezoelectricity in the case of $Li_2B_4O_7$ (1), nonlinear optical behaviour of LiB_3O_5 (2), and fast ionic conduction in $Li_3B_5O_8(OH)_2$ (3), attracted great interest. In a recent paper, Byrappa and Shekar (4) have reported phase crystallization in the Li_2O–B_2O_3–H_2O system under hydrothermal conditions. We have undertaken a systematic study of these compounds by establishing the structure of $LiB_2O_3(OH) \cdot H_2O$ and its dehydration process (5, 6) and publishing the precise X-ray powder diffraction data of $Li_3B_5O_8(OH)_2$ (7) and $LiB(OH)_4$ (8). The starting material for this last compound was crystals of $LiBO_2 \cdot 8H_2O$. We were interested in its structure in order to compare it to those of $LiB(OH)_4$ (9) and monoclinic $LiBO_2$ (10) in which exist isolated $B(OH)_4$ tetrahedra and chains of BO_3 triangles, respectively. $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$, sometimes denoted $LiBO_2 \cdot 8H_2O$, Li_2O-$B_2O_3 \cdot 16H_2O$, or $Li[B(OH)_4] \cdot 6H_2O$, has been known for a long time. It was first described by Le Chatelier in 1897 (11) and by many other workers since. It occurs in the system Li_2O–B_2O_3–H_2O below 56°C (12–15). From optical measurements performed upon large single crystals, Nakamura and Hayashi (16) have given the parameters of an hexagonal cell: $a = 5.70$ Å and $c = 6.20$ Å. The X-ray powder diffraction diagram was indexed with the correct parameters $a = 6.576$ Å and $c = 6.193$ Å (17). In the paper describing the crystal structure of the monoclinic form of lithium metaborate ($LiBO_2$), Zachariasen (10) has given some indications about this hydrated lithium borate; he has found that it was trigonal in the space group $P3$, and with one $LiBO_2 \cdot 8H_2O$ in a cell of dimensions $a = 6.555$ Å, $c = 6.177$ Å. He added that the structure contained complex ions $[B(OH)_4]^-$ and $Li(H_2O)_4^+$ held together by hydrogen bonds and announced a forthcoming paper (10). Surprisingly, Christ and Clark (18) and Heller (19) have not reported this structure in their papers about the structural classifications of hydrated borates. An almost similar structural formula was also used by Dzene and Schwartz (20) when they studied the thermal decomposition of $LiB(OH)_4 \cdot 6H_2O$. Recently, Gode and Skuja (21) have found that there were some discrepancies in the X-ray powder diffraction data of this compound and they have given a table of the powder diagram without indexation.

EXPERIMENTAL PROCEDURE

The hydrated lithium monoborate $LiBO_2 \cdot 8H_2O$ was obtained from an aqueous solution of a stoichiometric

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mixture of $LiOH \cdot H_2O$ and H_3BO_3; its evaporation under constant stirring and heating leads to single crystals. Chemical analyses were performed by means of the usual acid–base titration; however, a glycerol–water mixture (1 : 1 in volume) was added after Li titration to allow the evaluation of B content. The ratio B_2O_3/Li_2O was always equal to 1. Thermogravimetry (TG) was performed with a Mettler TC11 analyzer; all experiments were carried out in air, at a 10°C/min heating rate; sample amounts were about 40 mg. For differential scanning calorimetry (DSC), we have used a DSC 20 Mettler apparatus; samples were put into platinum crucibles and the heating rate was 10°C/min.

SINGLE CRYSTAL MEASUREMENTS

Diffracted intensity measurements were performed with a PW1100 Philips diffractometer of the Centre Commun de Mesure of Université de Lille 1, using Mo$K\alpha$ radiation (λ = 0.7107 Å) isolated with a graphite monochromator.

The selected crystal (prismatic form, dimensions of about 0.3 × 0.3 × 0.25 mm) was taken out of its mother solution, immersed in Teflon-based grease, and immediately mounted at the end of a quartz fiber. These precautions were taken to diminish the spontaneous dehydration of the crystal in air. 2102 reflections were measured in half the reciprocal space for $2° \leq \theta \leq 35°$ and $-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $0 \leq l \leq 9$ in $\omega - 2\theta$ scan mode. In spite of the protecting film, the monitoring every 2 hr of three reference reflections showed a steady decrease in the intensities, which attained 11% after 68 hr of data collection. This quasilinear decrease was taken into account in the data reduction of the 2102 intensities reflections; 1638 had an intensity greater than three times their standard deviation and after merging the equivalent reflections, 539 independent reflections were kept for the structure resolution (R_{INT} = 0.0185). Due to the very low absorption coefficient, μ = 0.14 mm^{-1}, no absorption correction was considered necessary.

STRUCTURE RESOLUTION

Cell parameters were refined from the X-ray powder diffraction pattern: a = 6.5534(5) Å, c = 6.1740(7) Å, D_x = 1.402, and Z = 1. Careful examination of the intensities showed the point symmetry to be $\bar{3}$ (nonequivalence of hkl and $\bar{k}\bar{h}l$). The cell containing one formula unit ($LiBO_2 \cdot 8H_2O$), the space group $P3$ (as proposed by Zachariasen (10)) was the most probable. Direct methods (22) gave the positions of six independent oxygen atoms (R = 0.17). A Fourier-difference synthesis provided the positions of B and Li atoms (R = 0.059 with isotropic temperature factors). The introduction of anisotropic temperature motion lowered the reliability factor to 0.042. The difference synthesis showed unambiguously the position of the hydrogen atoms, even if the symmetry implied that some positions had occupancy factor of 2/3 or even 1/3.

The final R values (with isotropic temperature factor for hydrogens fixed at the equivalent B value of the oxygen atom they are bound to) are $R = \Sigma|F_{obs} - F_{calc}|/\Sigma F_{obs} = 0.026$ and $R_w = (\Sigma w(F_{obs} - F_{calc})^2/\Sigma w F_{obs}^2)^{1/2} = 0.028$.

The scattering factors used are those for neutral atoms taken from the "International Tables for Crystallography" (23). No correction for anomalous dispersion was applied. The weighting scheme used is taken from the counting statistics $(\sigma(I) = (I + L + R + 0.04(I - L - R)^2)^{1/2}$ where I, L, and R are the total intensity, left background, and right background respectively). The position and thermal motion parameters are reported in Table 1. Significant bond lengths and angles are listed in Table 2. It is evident that the standard deviations on H positions are very high, essentially for hydrogen sites not fully occupied. This also results in high standard deviations in angles where H atoms are implied.

DESCRIPTION OF THE STRUCTURE

As predicted by Zachariasen (10), the borate synthesized in this work contains isolated $B(OH)_4$ and $Li(H_2O)_4$ tetrahedra as showed in Figs. 1 and 2 (for the sake of clarity, the hydrogen atoms are represented with a small arbitrary radius). It is interesting to note that these tetrahedra are almost regular because they have the 3-point group symmetry. That explains that the averages O–Li–O and O–B–O bond angles are close to the angle of a regular tetrahedron, 109.48° (see Table 2). In the structure, isolated water molecules also exist (often denoted water of crystallization) that lead to the structural formula $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$. These water molecules are localized in wide tunnels parallel to the c axis (Fig. 1). They are formed by one oxygen atom on the threefold axis (O1 and O2) and hydrogen atoms situated also on this axis (H1) or distributed around this axis with an occupancy factor of 2/3 (H3) or 1/3 (H2) (Fig. 2). One water molecule coordinated to the lithium atom is also formed with hydrogen atoms (H6) with an occupancy factor of 2/3. In the classification of molecular water in the borates proposed by Silins *et al.* (24), isolated water molecules belong to class 0, type Z and water molecules in the surrounding of lithium atom belong to class 1′, type I, for O6 and to class 1, type C, for O5. Around the boron atom, there are three classical hydroxyl groups (O4–H5) and another (O3–H4) where the hydrogen atom (H4) has an occupancy of 1/3. Cohesion of the structure results from eight independent hydrogen bonds (Table 2). The oxygen atoms of isolated water molecules are linked together by

TABLE 1
Final Atomic Coordinates, Occupancy Factor (n), Equivalent Isotropic Thermal Vibration Parameters B (Å^2), and Anisotropic Thermal Vibration Parameters (10^4) for All the Atoms Except H Atoms (esd's in Parentheses)

Atom	x	y	z	n	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1	0.000	0.000	0.250(*a*)	1	3.14(4)	219(4)	219(4)	248(6)	109(2)	0	0
O2	0.000	0.000	0.7060(5)	1	2.84(4)	199(3)	222(6)	99(2)	0	0	0
O3	2/3	1/3	0.4750(4)	1	2.15(3)	198(3)	198(3)	89(3)	99(2)	0	0
O4	0.8915(2)	0.5275(2)	0.7949(4)	1	1.95(2)	134(2)	133(3)	137(2)	48(2)	−10(2)	−6(2)
O5	1/3	2/3	0.6068(5)	1	2.22(3)	179(3)	179(3)	135(4)	89(2)	0	0
O6	0.0261(2)	0.4320(2)	0.1883(4)	1	2.52(3)	162(3)	218(3)	148(2)	72(3)	−20(2)	−6(2)
B	2/3	1/3	0.7135(5)	1	1.50(3)	120(3)	120(3)	92(4)	60(2)	0	0
Li	1/3	2/3	0.2895(8)	1	2.06(7)	158(7)	158(7)	138(9)	79(4)	0	0
H1	0.000	0.000	0.576(9)	1	2.80(*b*)						
H2	0.110(17)	0.092(18)	0.747(13)	1/3	2.80						
H3	0.013(7)	0.122(7)	0.211(7)	2/3	3.10						
H4	0.568(14)	0.197(13)	0.440(11)	1/3	2.10						
H5	0.746(6)	0.107(5)	0.779(4)	1	2.00						
H6	0.394(7)	0.589(7)	0.667(6)	2/3	2.20						
H7	0.929(5)	0.419(5)	0.286(5)	1	2.50						
H8	0.458(5)	0.017(5)	0.081(5)	1	2.50						

[a] Used to fix the origin.
[b] B value for the H atoms was fixed at the value of equivalent B of the oxygen atom linked to.

O1 · · · H1–O2. (Fig. 2). Isolated water molecules are also related to a hydroxyl group O2 · · · H5–O4, O4 · · · H2–O2 and to a lithium-coordinated water molecule O6 · · · H3–O1 (Fig. 1). $Li(H_2O)_4$ and $B(OH)_4$ tetrahedra are linked together by the hydrogen bonds: O6 · · · H4–O3, O3 · · · H7–O6, O4 · · · H6–O5, and O4 · · · H8–O6 (Fig. 1).

We have tried to apply to this compound the bond valence model which was developed by Brown (25) or Brese and O'Keeffe (26); the values obtained for hydrogen and oxygen atoms were too high, probably due to the complexity of the hydrogen bonds and the partial occupancy of the hydrogen sites. For these same reasons it was not possible to use the correlation diagrams proposed by Brown and Altermatt (27) or Ferraris and Ivaldi (28) to determine the valence of the hydrogen bonds.

Following the crystal chemical classification of borates proposed by Christ and Clark (18) and Heller (19), the fundamental building block (FBB) existing in this compound is a monoborate; its shorthand notation is 1 : 1T (T = tetrahedron). This FBB has been found in several alkali and alkaline earth borates (18, 19) as in the compound $NaB(OH)_4$ whose structure was recently published (29) and also in $LiB(OH)_4$ (9). It is of interest to compare the structure of this last borate and that of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ which, by spontaneous dehydration, gives $LiB(OH)_4$. In this borate, $B(OH)_4$ and $Li(OH)_4$ tetrahedra are both less symmetrical with four different bonds; the mean values are B–O = 1.480 Å and Li–O = 1.966 Å (9). These values were close to those found in the studied borate 1.472 and 1.934 Å, respectively (Table 2). Therefore, large differences exist in the hydroxyl groups; in $LiB(OH)_4$, there are four values from 0.963 to 1.119 Å with a mean value of 1.05 Å (9) while in $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$, the distances are shorter: 0.83 and 0.73 Å with a mean value of 0.76 Å. And last, there are only four hydrogen bonds in $LiB(OH)_4$; the values of 1.604 to 2.115 Å are very different of those found in our study: 1.91 to 2.17 Å (Table 2). The reason for these differences is probably due to the lack of isolated and coordinated water molecules in $LiB(OH)_4$.

DEHYDRATION

Figures 3 and 4 show the thermal analyses performed on $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$. From TG and DTG (derivated thermogravimetry) curves (Fig. 3) one can see only two losses of weight which correspond to the losses of six and two water molecules, respectively. However, on the DSC curve (Fig. 4), we observe three peaks; considering the intensity of the peaks on the DSC curve and the crystal structure of the compound, it is possible to propose a mechanism of three steps for the dehydration process:

$$Li(H_2O)_4B(OH)_4 \cdot 2H_2O \xrightarrow[60°C]{-2H_2O} Li(H_2O)_4B(OH)_4 \xrightarrow[120°C]{-4H_2O} LiB(OH)_4 \xrightarrow[170°C]{-2H_2O} LiBO_2\ (\text{amorphous}) \xrightarrow{470°C} LiBO_2\ (\text{monoclinic}).$$

TABLE 2
Interatomic Distances (Å) and Angles (°)

	B tetrahedron		
B–O3	1.473(4)	O3–B–O4 (3x)	110.0(3)
–O4 (3x)	1.472(2)	O4–B–O4 (3x)	109.0(2)
Mean	1.472	Mean	109.5
O3–O4 (3x)	2.412(3)		
O4–O4 (3x)	2.396(2)		
Mean	2.404		
	Li tetrahedron		
Li–O5	1.960(6)	O5–Li–O6 (3x)	108.9(3)
–O6 (3x)	1.926(2)	O6–Li–O6 (3x)	110.0(2)
Mean	1.934	Mean	109.4
O5–O6 (3x)	3.163(3)		
O6–O6 (3x)	3.156(2)		
Mean	3.159		
	Hydroxyl groups		
O3–H4	0.83(9)	H4–O3–B	105(7)
O4–H5 (3x)	0.73(5)	H5–O4–B	109(5)
Mean	0.76		
	Free water molecules		
O1–H3 (2x)	0.80	H3–O1–H3	111(16)
O2–H1	0.80(6)	H1–O2–H2	111(16)
–H2	0.72(12)		
	Water molecules coordinated to Li		
O5–H6 (2x)	0.87(5)	H6–O5–H6	103(14)
		Li–O5–H6	115(5)
O6–H7	0.85(3)	H7–O6–H8	111(7)
–H8	0.73(3)	Li–O6–H7	106(3)
		Li–O6–H8	121(4)
	Hydrogen bonds (<2.2 Å)		
O1···H1	2.01(6)	O1···H1–O2	180
O1–O2	2.817(3)		
O2···H5	2.15(4)	O2···H5–O4	164(14)
O4···H2	2.16(11)	O4···H2–O2	166(27)
O2–O4	2.861(2)		
O3···H7	1.91(3)	O3···H7–O6	168(14)
O6···H4	2.03(8)	O6···H4–O3	145(13)
O3–O6	2.752(2)		
O4···H6	1.95(6)	O4···H6–O5	169(20)
O4–O5	2.814(2)		
O4···H8	2.04(4)	O4···H8–O6	170(15)
O4–O6	2.762(3)		
O6···H3	2.00(5)	O6···H3–O1	166(18)
O6–O1	2.774(1)		

Note. The esd's are given in parentheses.

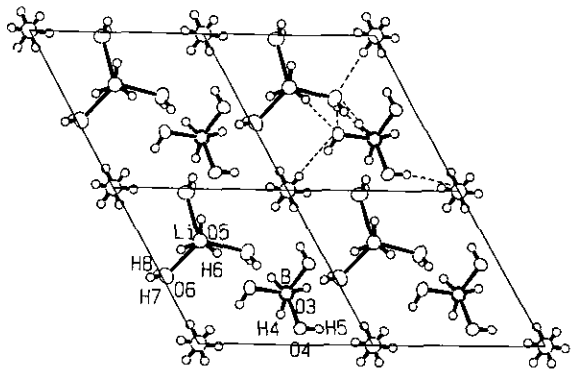

FIG. 1. Projection of the structure of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ in the (001) plane (four cells); dotted lines represent seven different hydrogen bonds.

This dehydration often occurs by itself if the *crystals* of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ are left in the ambient air for several days, leading to formation of $LiB(OH)_4$ *powder*. This phenomena is responsible for the diminution of the diffraction intensities during the single crystal X-ray data collection. From a structural point of view, we note that some hydrogen bonds must be broken from ambient temperature, followed by the loss of the two water molecules of crystallization at 60°C and then of the four water molecules which are coordinated to lithium; that confirms the dehydration process proposed. In the intermediate compound, $LiB(OH)_4$, a structural reorganization occurs which can be expressed by bringing together lithium atoms and hydroxyl groups surrounding the B atoms; indeed Li–B distances change from 4.600 Å in $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ to Li–O–B distances of about 3.446 Å that leads to shorter Li–B distances in $LiB(OH)_4$ (9). The movements of the lithium atoms, which are caused by the necessity of these atoms to be surrounded by four oxygen atoms, can explain the lengthening of O–H distances of the hydroxyl groups which increase from 0.76 Å on average in $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ to 1.05 Å on average in

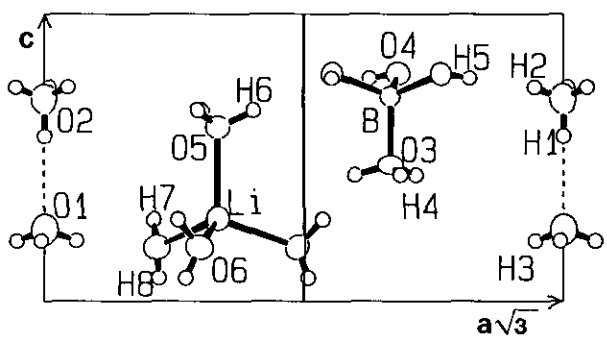

FIG. 2. View of the structure of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ in the (110) plane; dotted lines represent hydrogen bonds.

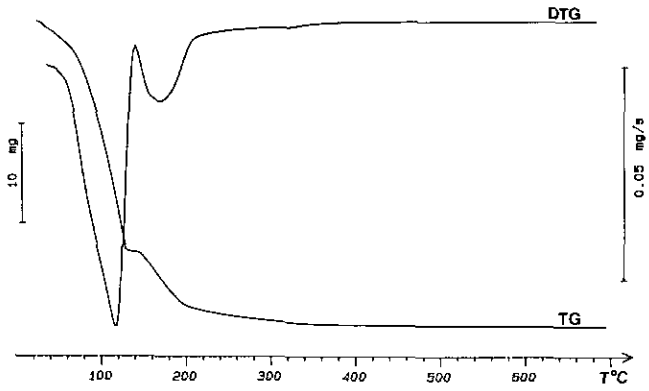

FIG. 3. TG and DTG of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$.

$LiB(OH)_4$ (9). In this last borate, the four oxygen atoms around lithium atoms belong to four different $B(OH)_4$ tetrahedra and each oxygen atom is bonded to one H, one B, and one Li; moreover, four hydrogen bonds link the $B(OH)_4$ tetrahedra between them and maintain the cohesion of the structure.

Even if they contain the same $B(OH)_4$ tetrahedra, the structures of these borates are too different to permit obtaining $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$ by rehydration of $LiB(OH)_4$. It is necessary to dissolve this compound in water and therefore to pass through the solution to get $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$.

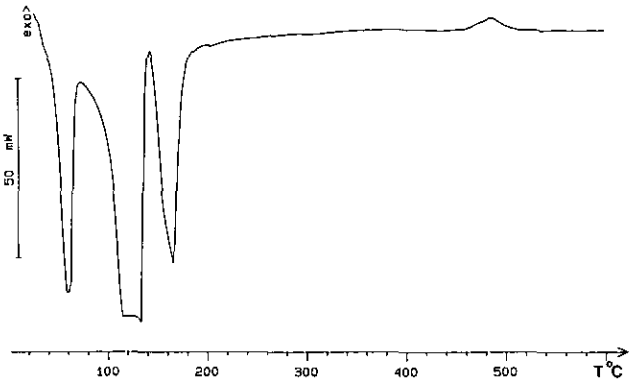

FIG. 4. DSC of $Li(H_2O)_4B(OH)_4 \cdot 2H_2O$.

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