Journal of Solid State Chemistry **143,** 260–265 (1999)
Article ID jssc.1998.8104, available online at http://www.idealibrary.com on IDEAL®

Crystal Structure and Thermal Behavior of $Cs_2[B_4O_5(OH)_4]3H_2O$

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Received April 21, 1998, in revised form November 9, 1998, accepted November 22, 1998

The crystal structure of synthetic $Cs_2[B_4O_5(OH)_4]3H_2O$ was determined from single-crystal X-ray diffraction data. The compound is monoclinic, space group $P2_1/c$; the unit cell parameters are $a = 8.424(2)$ Å, $b = 11.378(3)$ Å, $c = 13.160(5)$ Å, $\beta = 92.06(3)°$; $Z = 4$. The crystal structure was solved from 6355 reflections until $R = 0.029$; it contains isolated $[B_4O_5(OH)_4]^{2-}$ polyanions separated by free water molecules and Cs^+ ions. Although its formula is the same as that of the tincalconite $Na_2[B_4O_5(OH)_4]3H_2O$, $Cs_2[B_4O_5(OH)_4]3H_2O$ structure is close to that of synthetic $K_2[B_4O_5(OH)_4]2H_2O$ which contains only two isolated water molecules. In the cesium and the potassium borates, the $[B_4O_5(OH)_4]^{2-}$ anions have not a two-fold axis as in the tincalconite; the shorthand notations of these two kinds of anions shall be noted as: 4: $2\Delta+2T$ in the first two borates and 4:$(\Delta+T)_2$ in the tincalconite, Δ and T being triangular and tetrahedral borons, respectively.$Cs_2[B_4O_5(OH)_4]3H_2O$ indexed X-ray powder diffraction pattern is given. The dehydration of this borate occurs in two close steps and leads to an amorphous phase; this process is well explained considering the structure and especially the change in the Cs^+ coordination during the heating. © 1999 Academic Press

INTRODUCTION

There is little information about cesium borates (1–5). Indeed, the best known compound is CsB_3O_5(CBO). Its synthesis and crystal structure were performed by Krogh-Moë in 1958 (6) and 1974 (7), respectively. Large single crystals have recently been obtained by Wu *et al.* (8) who measured some properties which show that CBO is a good nonlinear optical material. Some other papers have been published (9, 10) concerning the effect of boric acid on cesium transport through the primary circuit pipework of a nuclear power plant using a light water reactor (LWR).

It was important to expand our knowledge about hydrated and anhydrous cesium borates to find other interesting compounds and also other routes to synthesize CBO. This paper deals with the hydrated cesium borate $Cs_2B_4O_7 \cdot 5H_2O$. This compound was first pointed out by Rollet and Andrès (1). Kocher (2) published an important paper about cesium borates and especially about $Cs_2B_4O_7 \cdot 5H_2O$ which has a congruent solubility above 19°C; another hydrate, $Cs_2B_4O_7 \cdot 2H_2O$, was found. The nonindexed powder patterns of these two compounds were published (PDF 22-177 and 22-175).

EXPERIMENTAL

To synthesize this borate following Kocher's indication (2), it is necessary to start with an aqueous solution of Cs_2CO_3 and H_3BO_3 with a B/Cs value of 1.9. After CO_2 release, its evaporation under constant stirring and heating led to the wanted compound being a white powder. It is necessary to keep two phases, solution and solid, to prevent the coprecipitation of another borate. Chemical analyses were performed by means of the usual acid-base titration. Large single crystals can easily be obtained by slow evaporation of a diluted solution at room temperature. This compound has been characterized by X-ray powder diffraction (Siemens D5000 diffractometer; $\lambda CuK\alpha_1 = 1.5406$ Å) and by thermal analyses using a Setaram TGDTA 92 apparatus (platinum crucibles; heating rate of 600°C/h, in air; sample amounts around 40 mg) and a Guinier-Lenné camera ($\lambda CuK\alpha = 1.5418$ Å; heating rate of 6°C/h, in air, between 20 and 600°C).

STRUCTURAL STUDY

A colorless single crystal was chosen; crystal data and intensity collections are given in Table 1. Absorption corrections were made using De Meulenaer and Tompa's analytical method (11). The structure resolution was classical: cesium atom positions were deduced from Patterson functions. Refinement, using the SHELX-76 program (12), led to $R = 0.251$ and $R_w = 0.313$. Ten oxygen atoms were evidenced on the Fourier difference map: the reliability factors got down to 0.151 and 0.169, respectively. Two remaining oxygen and four boron atoms were then localized and led to

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TABLE 1
Crystal Data and Intensity Collections for $Cs_2[B_4O_5(OH)_4]3H_2O$

Formula weight (g/mol)	511.12
Space group	$P2_1/c$ (N°14)
Unit cell parameters	$a = 8.424(2)$ Å; $b = 11.378(3)$ Å; $c = 13.160(5)$ Å; $\beta = 92.06(3)°$
V; Z	1260.5(6) Å^3; 4
Density (g/cm^3)	$Dx = 2.69(1)$
Faces limiting the crystals and distances (mm)$^{(a)}$	(100): 0.08; (-100): 0.08; (011):0.084 (016): 0.12; (0-11): 0.16; (0-2-1): 0.144;(0-1-4):0.06;(01-1):0.172
Diffractometer	CAD4 (Enraf Nonius)
Temperature	298 K
Radiation	Mo$K\alpha$, graphite monochromated $\lambda = 0.71069$ Å
Scattering factors	Neutral atoms (13)
Scan type	θ–2θ
θ range (deg)	2-31
Standard reflections	2-2-4;-1-4-3;-4 1-1
Range in h, k, l	$-12 \leq h \leq 12$; $-17 \leq k \leq 17$; $0 \leq 1 \leq 19$
Maximum scan time	60s
Period of intensity control	7200s
Reflections collected	6872
Reflections with $I > 3\sigma(I)$	6355
R_{int} before absorption correction	0.029
Linear absorption coefficient	59.3 cm^{-1}
Transmission factors	0.462–0.363
Averaged reflections ($I > 3\sigma(I)$)	3026
R_{int} after absorption correction	0.018
Weighing scheme	$1/\sigma^2(F)$
Number of variables	194
R	0.029
R_w	0.029
GOF	3.28

[a] The dimensions given are the distances from the center of the crystal to the eight faces of the platelet.

$R = 0.103$ and $R_w = 0.095$. When the thermal agitation was made anisotropic, the reliability factors fell down to 0.033 and 0.044, respectively. The H atoms were easily found on the Fourier difference map and were refined, being attributed isotropic thermal factors equal to those of the atoms to which they are bound. The final reliability factors were $R = 0.029$ and $R_w = 0.029$. The atomic coordinates and the thermal motion parameters are reported in Tables 2 and 3; significant bond lengths and angles are listed in Table 4.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the crystal structure of $Cs_2[B_4O_5(OH)_4]3H_2O$. It consists of discrete borate anions separated by Cs cations and isolated water molecules. The borate polyanion is constituted of two $BO_2(OH)$ groups (triangular boron Δ) and two $BO_3(OH)$ groups (tetrahedral boron T) (Fig. 2).

TABLE 2
Final Atomic Coordinates and Equivalent Thermal Parameters B_{eq} (Å^2) of $Cs_2[B_4O_5(OH)_4]3H_2O$ with e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq}
Cs(1)	0.26745(3)	0.05555(3)	0.48032(2)	2.715(7)
Cs(2)	0.45359(4)	0.58447(3)	0.35863(3)	3.251(8)
B(1)	− 0.1292(5)	0.8796(4)	0.0777(4)	1.52(9)
B(2)	0.1022(5)	0.6555(4)	0.1972(3)	1.33(9)
B(3)	0.1048(5)	0.8683(4)	0.1985(3)	1.26(9)
B(4)	− 0.1384(5)	0.7691(4)	0.2360(3)	1.38(9)
O(1)	− 0.2058(4)	0.9237(3)	− 0.0085(2)	2.36(8)
O(2)	0.0273(3)	0.9044(2)	0.0975(2)	1.54(6)
O(3)	− 0.2182(3)	0.8138(2)	0.1407(2)	1.60(6)
O(4)	0.1835(3)	0.5509(2)	0.1929(3)	1.92(7)
O(5)	0.1882(3)	0.7556(2)	0.1858(2)	1.46(6)
O(6)	− 0.2617(3)	0.7490(3)	0.3085(2)	1.87(7)
O(7)	− 0.0565(3)	0.6560(2)	0.2148(2)	1.46(6)
O(8)	− 0.0205(3)	0.8545(2)	0.2720(2)	1.24(6)
O(9)	0.2214(3)	0.9553(2)	0.2282(2)	1.63(6)
Ow(1)	0.5211(5)	0.3946(4)	0.1540(3)	4.2(1)
Ow(2)	0.4659(5)	0.7874(5)	0.0714(3)	5.9(2)
Ow(3)	0.9360(6)	0.3256(4)	0.0293(3)	4.1(1)
H(1)	0.178(6)	1.019(5)	0.237(4)	1.6
H(2)	− 0.150(7)	0.950(5)	− 0.040(5)	2.4
H(3)	− 0.219(6)	0.701(5)	0.354(4)	1.9
H(4)	0.134(7)	0.513(5)	0.201(5)	1.8
H(5)	0.601(8)	0.375(6)	0.192(5)	4.2
H(6)	0.442(8)	0.362(6)	0.179(5)	4.2
H(7)	0.553(8)	0.790(6)	0.119(6)	5.9
H(8)	0.388(8)	0.773(7)	0.110(6)	5.9
H(9)	0.847(8)	0.287(6)	0.032(5)	4.1
H(10)	0.933(8)	0.317(6)	0.092(5)	4.1

Note. For hydrogen atoms, fixed B_{eq} values correspond to those of the oxygen atom which is linked to them.

This isolated anion $[B_4O_5(OH)_4]^{2-}$ has been found in a lot of hydrated borates; its shorthand notation, following the classification proposed by Heller (14) and Christ and Clark (15) is $4{:}2\Delta + 2T$. Such an isolated anion was described by Morimoto (16) and later by Levy and Lisensky (17) in the mineral borax, $Na_2[B_4O_5(OH)_4]8H_2O$. This polyanion also exists in tincalconite, $Na_2[B_4O_5(OH)_4]3H_2O$ (18), in synthetic $K_2[B_4O_5(OH)_4]2H_2O$ (19), and in several other hydrated borates containing alkaline (or pseudo-alkaline) cations, or alkaline and earth alkaline cations as, for example, $(NH_4)_2[B_4O_5(OH)_4]2H_2O$ (20), $K_{1.67}Na_{0.33}[B_4O_5(OH)_4]3H_2O$ (21), $K_2Ca[B_4O_5(OH)_4]_28H_2O$ (22), $K_2Sr[B_4O_5(OH)_4]_210H_2O$, and $(NH_4)_2Ca[B_4O_5(OH)_4]_2 8H_2O$ (23). However, it is interesting to note that a distinction can be made when considering the structure of the $[B_4O_5(OH)_4]^{2-}$ anion. There are two possibilities: this ion has a two-fold axis or it does not. In the first case, there are only two boron atoms crystallographically independent as, for example, in borax and in tincalconite. In the second case, the structure contains four boron atoms crystallographically independent as in $K_2[B_4O_5(OH)_4]2H_2O$ (19) and in

TABLE 3
Anisotropic Thermal Vibration Parameters (× 10^4) (e.s.d.'s in Parentheses) for All the Atoms of $Cs_2[B_4O_5(OH)_4]3H_2O$ Except Hydrogen Atoms

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs(1)	88.5(4)	61.2(3)	35.4(2)	2.2(2)	– 30.9(2)	65.5(2)
Cs(2)	91.9(4)	74.0(3)	47.6(2)	– 26.0(3)	– 4.8(2)	2.7(2)
B(1)	55 (5)	22 (3)	26 (2)	2 (3)	– 4 (3)	5 (2)
B(2)	59 (5)	18 (3)	20 (2)	2 (3)	1 (3)	0 (2)
B(3)	47 (5)	21 (3)	20 (2)	2 (3)	– 1 (3)	1 (2)
B(4)	44 (5)	22 (3)	25 (2)	– 1 (3)	0 (3)	3 (2)
O(1)	66 (4)	55 (3)	33 (2)	– 20 (3)	– 15 (2)	23 (2)
O(2)	42 (3)	35 (2)	23 (2)	– 4 (2)	– 4 (2)	8 (1)
O(3)	49 (4)	29 (2)	28 (2)	– 7 (2)	– 7 (2)	9 (1)
O(4)	59 (4)	20 (2)	44 (2)	3 (2)	7 (2)	2 (2)
O(5)	42 (3)	16 (2)	34 (2)	0 (2)	6 (2)	0 (1)
O(6)	56 (4)	35 (2)	33 (2)	2 (2)	13 (2)	9 (2)
O(7)	45 (3)	16 (2)	33 (2)	1 (2)	0 (2)	0 (1)
O(8)	50 (3)	16 (2)	22 (1)	– 1 (2)	1 (2)	1 (1)
O(9)	44 (3)	20 (2)	37 (2)	– 4 (2)	– 5 (2)	0 (2)
Ow(1)	104(6)	110(4)	54 (3)	– 48 (4)	– 30 (3)	28 (3)
Ow(2)	207(8)	78 (4)	33 (2)	– 1 (4)	– 12 (4)	1 (2)
Ow(3)	89 (6)	227(8)	50 (3)	– 19 (6)	10 (3)	7 (4)

the studied compound $Cs_2[B_4O_5(OH)_4]3H_2O$. To distinguish between these possibilities, the shorthand notation of the borate anion should be written as $4{:}(\Delta + T)_2$ when a two-fold axis exists and $4{:}2\Delta + 2T$ when it does not. For

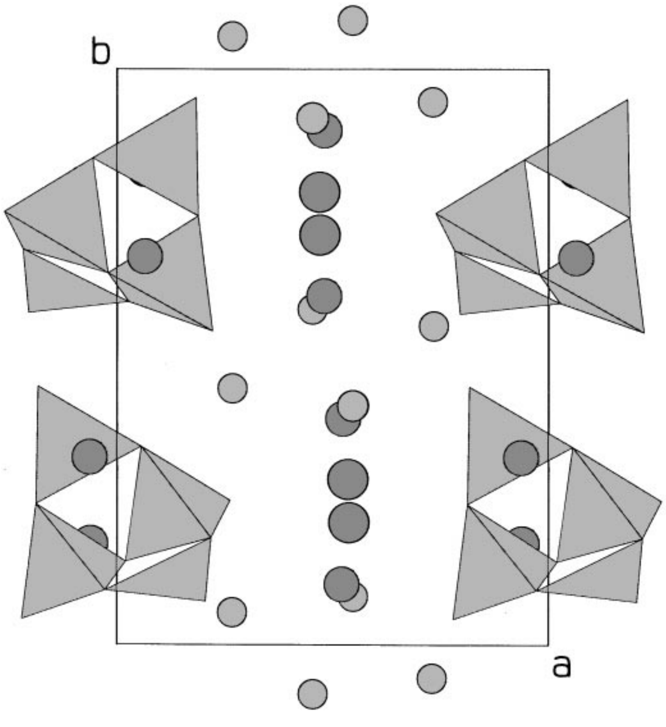

FIG. 1. Projection of the structure of $Cs_2[B_4O_5(OH)_4]3H_2O$ in the (001) plane; dark circles represent Ow atoms and light circles Cs^+ ions. For the sake of clarity, only a part of $[B_4O_5(OH)_4]^{2-}$ ions are reported.

TABLE 4
Interatomic Distances (Å) and Angles (°) in $Cs_2[B_4O_5(OH)_4]3H_2O$

Triangular borons				
B(1)–	O(1)	1.379(6)	O(1) –B(1)– O(2)	120.1(3)
–	O(2)	1.364(5)	O(1) –B(1)– O(3)	116.7(3)
–	O(3)	1.362(5)	O(2) –B(1)– O(3)	123.1(3)
Mean		1.368	Mean	120
distances to the mean plane				
B(1): – 0.007(5);	O(1): 0.002(3);	O(2): 0.002(2);	O(3): 0.002(2)	
B(2)–	O(4)	1.375(5)	O(4) –B(2)– O(5)	116.9(3)
–	O(5)	1.361(5)	O(4) –B(2)– O(7)	120.2(3)
–	O(7)	1.365(5)	O(5) –B(2)– O(7)	122.9(3)
Mean		1.367	Mean	120
distances to the mean plane				
B(2): – 0.009(4);	O(4): 0.003(4);	O(5): 0.003(3);	O(7): 0.003(3)	
Tetrahedral borons				
B(3)–	O(2)	1.516(5)	O(2) –B(3)– O(5)	109.2(3)
–	O(5)	1.475(5)	O(2) –B(3)– O(8)	108.1(2)
–	O(8)	1.466(5)	O(2) –B(3)– O(9)	108.7(3)
–	O(9)	1.439(5)	O(5) –B(3)– O(8)	109.8(2)
			O(5) –B(3)– O(9)	107.8(3)
Mean		1.474	O(8) –B(3)– O(9)	113.3(3)
			Mean	109.5
B(4)–	O(3)	1.491(5)	O(3) –B(4)– O(6)	107.1(3)
–	O(6)	1.454(5)	O(3) –B(4)– O(7)	109.6(3)
–	O(7)	1.491(5)	O(3) –B(4)– O(8)	109.1(3)
–	O(8)	1.456(5)	O(6) –B(4)– O(7)	109.5(3)
	Mean	1.473	O(6) –B(4)– O(8)	112.7(3)
			O(7) –B(4)– O(8)	108.8(2)
			Mean	109.5
B–O–B inside the B_4O_5 unit				
B(1)– O(2)– B(3)		119.6(4)	B(1)– O(3)– B(4)	117.3(4)
B(2)– O(5)– B(3)		117.2(4)	B(2)– O(7)– B(4)	119.9(4)
B(3)– O(8)– B(4)		110.8(3)		
Hydroxyl groups				
O(1)–	H(2)	0.70(6)	B(1)– O(1)– H(2)	110(6)
O(4)–	H(4)	0.61(6)	B(2)– O(4)– H(4)	105(6)
O(6)–	H(3)	0.88(5)	B(4)– O(6)– H(3)	105(4)
O(9)–	H(1)	0.82(6)	B(3)– O(9)– H(1)	110(4)
Water molecules				
Ow(1)–	H(5)	0.85(7)	H(5)– Ow(1)– H(6)	106(8)
Ow(1)–	H(6)	0.84(7)		
Ow(2)–	H(7)	0.95(7)	H(7)– Ow(2)– H(8)	102(8)
Ow(2)–	H(8)	0.86(7)		
Ow(3)–	H(9)	0.87(7)	H(9)– Ow(3)– H(10)	81(8)
Ow(3)–	H(10)	0.83(7)		
Hydrogen bonds (< 2.2 Å) and related O–O bonds				
O(2)–	$H(2^{i})$	2.110(6)	O(2)– $O(1^{i})$	2.754(4)
O(3)–	$H(7^{ii})$	1.96(7)	O(3)– $Ow(2^{ii})$	2.798(5)
O(5)–	H(8)	2.00(7)	O(5)– Ow(2)	2.850(5)
O(6)–	H(6)	2.00(7)	O(6)– Ow(1)	2.800(5)
O(7)–	$H(1^{iii})$	1.98(6)	O(7)– $O(9^{iii})$	2.790(3)
O(8)–	H(4)	2.08(6)	O(8)– O(4)	2.672(3)
O(8)–	$H(10^{iv})$	1.96(7)	O(8)– $Ow(3^{iv})$	2.705(5)
O(9)–	$H(5^{iv})$	2.02(7)	O(9)– $Ow(1^{iv})$	2.710(5)

TABLE 4—*Continued*

Cs–O bonds (< 3.50 Å)			
Cs(1)– Ow(1^{v})	3.124(4)	Cs(2)– O(4)	3.118(3)
– Ow(1^{vi})	3.143(4)	– O(6^{viii})	3.131(3)
– Ow(3^{vi})	3.128(5)	– Ow(2^{ix})	3.155(4)
– Ow(3^{vii})	3.189(5)	– O(9^{vi})	3.345(3)
– O(4^{v})	3.152(4)	– O(1^{x})	3.307(3)
– O(7^{iii})	3.276(3)	– O(1^{iii})	3.448(3)
– O(3^{iii})	3.361(2)		

Note. Symmetry code: (i) $-x,\ 2-y,\ -z$; (ii) $x-1,\ y,\ z$; (iii) $-x,\ y-1/2,\ 1/2-z$; (iv) $1-x,\ 1/2+y,\ 1/2-z$; (v) $x,\ 1/2-y,\ 1/2+z$; (vi) $1-x,\ y-1/2,\ 1/2-z$; (vii) $x-1,\ 1/2-y,\ 1/2+z$; (viii) $1+x,\ y,\ z$; (ix) $x, 1/2-y,\ 1/2+z$; (x) $x+1,\ 1.5-y,\ 1/2+z$.

these reasons, a good comparison can be made between the $[B_4O_5(OH)_4]^{2-}$ anion found in the cesium borate and that described in $K_2[B_4O_5(OH)_4]2H_2O$ (19). In the triangular borons, the B-O bonds go from 1.312 to 1.401 Å in the potassium compound and only from 1.361 to 1.379 Å in the cesium compound; the mean values for B–O bonds are 1.362 and 1.374 Å for the first borate and 1.368 and 1.367 for the second. For the tetrahedral borons, the mean values of the B–O bonds are 1.479 and 1.480 Å in the potassium compound and 1.474 and 1.473 Å in the cesium compound.

Two Cs^+ ions and three isolated water molecules are disposed between $[B_4O_5(OH)_2]^{2-}$ anions. There are seven and six oxygen atoms around the cesium ions (Table 4); Cs(1) is close to four water molecules (two Ow(1) and two Ow(2)) and three oxygen atoms belonging to two different $[B_4O_5(OH)_4]^{2-}$ anions. Cs(2) is close to one water molecule and five oxygen atoms which belong to five different borate anions. In the potassium borate, the two potassium ions have seven oxygen around them (19).

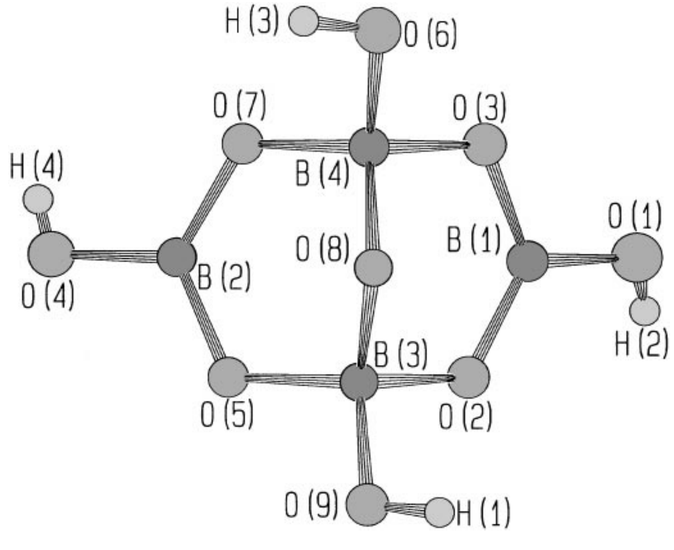

FIG. 2. Configuration of the polyborate ion $[B_4O_5(OH)_4]^{2-}$ in $Cs_2[B_4O_5(OH)_4]3H_2O$. Atoms have arbitrary radii.

In the structure of these two compounds there are eight short oxygen–oxygen distances, which can only be explained in terms of O–H ⋯ O bonds (see Table 4). Although the O ⋯ O distances are almost the same in the two compounds, the values of the O–H and O ⋯ H distances in the potassium compound go from 0.72 to 1.50 Å and 1.43 to 2.27 Å, respectively; the standard of error is high, 0.11 Å (19). In the cesium compound, more normal distances were found (Table 4) between 0.61 and 0.95 Å for O–H distances and 1.96 to 2.11 Å for O ⋯ H distances. The differences may be explained by the more precise location of the hydrogen atoms in the cesium borate (Table 2). Even if the building blocks are identical, these two borates are not similar: the cell volume of $K_2[B_4O_5(OH)_4]2H_2O$ (19) ($a = 12.899$ Å; $b = 11.774$ Å; $c = 6.859$ Å, $V = 1041$ Å^3, $Z = 4$, space group $P2_12_12_1$) is less than that of the cesium borate (see Table 1). The difference is due in part to the difference in radii of the two cations (K^+ and Cs^+) and in part to the supplementary water molecule in the cesium borate. In this compound, all three water oxygens have similar thermal parameters but the hydrogen atoms are less precisely localized.

Other $M_2B_4O_7 \cdot xH_2O$ exist with different borate anions. The structural formula for $Li_2B_4O_7 \cdot 3H_2O$ is $Li[B_2O_3(OH)]H_2O$ with a borate anion in chain; the shorthand notation is $3{:}\,\infty^1(\Delta + 2T)$ (24). In $Tl_2B_4O_7 \cdot 3H_2O$ (25), $Na_2B_4O_7 \cdot 4H_2O$ (26), and $Na_2B_4O_7 \cdot H_2O$ (27), another polyanion was found with the shorthand notation $3{:}\,\infty^1(\Delta + 2T) + \Delta$; its structural formula is $[B_4O_6(OH)_2]^{2-}$. Two other borates can be pointed out, $Ag_2B_4O_7 \cdot 2H_2O$ (28) and $Tl_2B_4O_7 \cdot 1.5H_2O$ (29), where more condensed isopolyanions exist, such as $[B_{12}O_{18}(OH)_6]^{6-}$ and $[B_8O_{12}(OH)_4]^{4-}$, respectively; their shorthand notations are $12{:}(3\Delta + 3T)_2$ and $7{:}\,\infty^1(4\Delta + 3T) + \Delta$, respectively.

$Cs_2[B_4O_5(OH)_4]3H_2O$ indexed powder pattern is given in Table 5; calculations, indexing, and refinements were done with the NBS*AIDS83 program (30). The figures of merit are good: $M_{20} = 71$ (31) and $F_{30} = 203$ (0.004,36) (32). It is interesting to note that the intensities calculated from the crystal structure data are often different from the observed intensities; that is probably due to preferred orientations which occur in the analyzed powder obtained by single-crystals grinding.

DEHYDRATION

Figure 3 shows the thermal analyses performed on $Cs_2[B_4O_5(OH)_4]3H_2O$. Two losses appear on the TG curve around 100 and 200°C; the calculations permit us to

TABLE 5
X-ray Powder Diffraction Pattern of $Cs_2[B_4O_5(OH)_4]3H_2O$

hkl	2*θ*° obs	2*θ*° calc	*d* obs (Å)	*I* obs	*I* calc
0 1 1	10.260	10.266	8.610	6	9
1 0 0	10.487	10.483	8.432	9	11
– 1 1 0	13.048	13.053	6.777	10	9
0 0 2	13.446	13.456	6.575	5	2
– 1 1 1	14.524	14.526	6.093	14	11
1 1 1	14.864	14.857	5.958	8	5
0 2 0	15.541	15.546	5.695	28	25
– 1 0 2	16.803	16.798	5.274	15	9
0 2 1	16.948	16.951	5.226	8	8
1 0 2	17.363	17.371	5.101	4	1
– 1 1 2	18.528	18.525	4.7856	72	48
1 2 0	18.785	18.787	4.7196	19	17
1 1 2	19.040	19.048	4.6554	7	4
1 2 1	20.092	20.094	4.4153	55	55
0 2 2	20.612	20.615	4.3049	25	22
0 1 3	21.701	21.706	4.0910	74	62
– 2 1 0	22.464	22.468	3.9540	5	1
– 2 1 1	23.263	23.263	3.8205	76	61
1 2 2	23.380	23.393	3.7997	7	7
2 1 1	23.685	23.686	3.7533	15	22
– 1 1 3	23.849	23.850	3.7278	21	21
0 3 1	24.385	24.381	3.6479	15	6
1 1 3	24.467	24.467	3.6352	12	9
2 0 2	25.460	25.464	3.4951	59	26
0 2 3	25.618	25.624	3.4737	3	2
1 3 0	25.711	25.711	3.4621	4	3
– 2 1 2	25.898	25.897	3.4377	16	8
– 2 2 0	26.274	26.278	3.3886	7	4
– 1 3 1	26.514	26.509	3.3597	3	3
2 1 2	26.657	26.657	3.3413	7	3
– 2 2 1	26.975	26.968	3.3035	3	2
0 0 4	27.100	27.101	3.2876	13	10
2 2 1	27.340	27.337	3.2594	21	16
1 2 3	28.019	28.023	3.1820	16	11
– 1 0 4	28.792	28.783	3.0982	5	2
– 1 3 2	28.957	28.954	3.0810	100	100
1 3 2	29.297	29.299	3.0460	4	4
1 0 4	29.480	29.475	3.0275	42	28
2 2 2	29.968	29.972	2.9793	30	26
1 1 4	30.531	30.523	2.9256	20	14
0 3 3	31.137	31.138	2.8700	6	2
0 4 0	31.387	31.388	2.8478	6	1
2 3 0	31.733	31.688	2.8175	15	2
3 0 0	31.813	31.811	2.8106	13	4
0 4 1	32.129	32.135	2.7836	12	8
– 2 3 1	32.258	32.271	2.7728	4	4
2 3 1	32.595	32.585	2.7449	8	4
3 1 0	32.806	32.792	2.7278	25	11
– 3 1 1	33.285	33.282	2.6896	33	16
– 1 4 1	33.822	33.815	2.6481	5	2
– 2 0 4	33.976	33.971	2.6364	86	24
– 2 3 2	34.262	34.268	2.6151	25	15
2 3 2	34.872	34.862	2.5708	10	8
0 1 5	34.992	34.986	2.5622	24	14
3 0 2	35.132	35.122	2.5523	15	5
3 2 0	35.573	35.590	2.5216	1	1
– 1 4 2	35.818	35.808	2.5050	2	1
– 3 2 1	36.040	36.046	2.4900	11	3
– 1 1 5	36.268	36.266	2.4749	10	9
1 1 5	36.970	36.972	2.4295	9	6
– 1 3 4	37.432	37.427	2.4006	4	4
– 2 2 4	37.563	37.559	2.3925	27	13
0 2 5	37.648	37.641	2.3873	11	2
– 3 2 2	37.785	37.800	2.3790	1	1
1 3 4	37.980	37.977	2.3672	11	13
2 4 0	38.097	38.104	2.3602	11	10
– 3 1 3	38.225	38.234	2.3526	3	2
3 2 2	38.633	38.616	2.3297	16	13
– 1 2 5	38.856	38.846	2.3164	13	6
1 4 3	39.375	39.376	2.2865	11	7
3 3 0	39.871	39.873	2.2591	16	13
0 5 1	40.132	40.139	2.2457	2	1
– 3 2 3	40.711	40.707	2.2147	13	11
2 4 2	40.848	40.842	2.2077	2	3
1 5 0	40.999	41.005	2.1993	2	3
0 0 6	41.148	41.153	2.1917	8	6

propose a dehydration process in two steps:

$$Cs_2[B_4O_5(OH)_4]3H_2O \xrightarrow{-3H_2O} Cs_2[B_4O_5(OH)_4] \xrightarrow{-2H_2O} Cs_2B_4O_7.$$

This mechanism is in good agreement with the structure of this compound; by heating, the isolated water molecules are first removed and then the hydroxyl groups. However, it was impossible to stabilize the intermediate compound $Cs_2[B_4O_5(OH)_4]$ or $Cs_2B_4O_7 \cdot 2H_2O$. As for previous studies on the dehydration process of other borates (33, 34), this failure can be explained considering the change in the cesium ion coordination during the dehydration. After the first loss, the coordination of Cs(2) changes from six to five but that of Cs(1) changes from seven to three, which is a very unstable situation which leads to the structure collapsing. This explanation is confirmed by the DTA curve (Fig. 3). The first two endothermic peaks concern the dehydration in

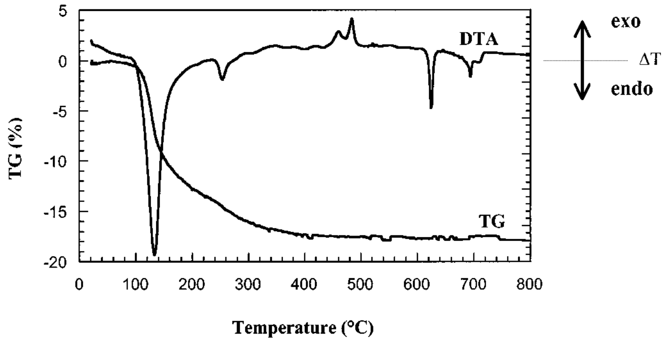

FIG. 3. TG and DTA of $Cs_2[B_4O_5(OH)_4]3H_2O$ with a heating rate of 600° C/h.

two steps, which leads to an amorphous anhydrous borate, $Cs_2B_4O_7$. This one crystallizes around 460°C as proven by the exothermic peaks. The other endothermic phenomena may be correlated with the Cs_2O-B_2O_3 phase diagram (2) where $Cs_2B_4O_7$ melts incongruently around 690°C. All these results are confirmed by examination of the Guinier-Lenné photograph where the powder pattern of the starting material, $Cs_2[B_4O_5(OH)_4]3H_2O$, until 150°C, then an amorphous phase until 450°C, and above this temperature the powder pattern of $Cs_2B_4O_7$ (PDF 21-195) appear successively. The differences between the temperatures observed on the thermal curves (Fig. 3), and those revealed on the Guinier-Lenné photograph are due to the heating rates used, 600 and 6°C/h, respectively.

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