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Probertite, $CaNa[B_5O_7(OH)_4].3H_2O$: a Refinement

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Abstract. $CaNa[B_5O_7(OH)_4].3H_2O$, M_r = 351·2, monoclinic, $P2_1/c$, a = 6·588 (1), b = 12·560 (2), c = 13·428 (2) Å, β = 99·97 (1)°, V = 1094·3 (3) Å^3, Z = 4, μ(Mo $K\alpha$) = 0·684 mm^{-1}, F(000) = 712, D_x = 2·132 Mg m^{-3}, D_m = 2·14 Mg m^{-3} {quoted in *Dana's System of Mineralogy* [Palache, Berman & Frondel (1951), Vol. II, pp. 343–344. New York: John Wiley.]} The crystals used are from Ryan, Inyo County, California, USA. The structure, refined to R = 0·036 for 2235 observed reflections, with $F_o > 5\sigma(F_o)$, consists of pentaborate polyanions, polymerized in chains, and clusters of Ca—O and Na—O polyhedra connecting the B—O chains. The cohesion is high in all directions except those perpendicular to {011}, where there are hydrogen bridges and relatively few Na—O and Ca—O bonds.

Introduction. The crystal structure of probertite was determined by Rumanova, Kurbanov & Belov (1966) in the space group $P2_1/a$ to $R \simeq$ 0·12. The proposed model is complete with respect to the borate framework as well as to the calcium and sodium coordination polyhedra. However, the H-atom positions are missing and the proposed hydrogen-bonding system is not without some uncertainties.

Therefore it seemed of some interest to undertake the refinement of this structure, also as part of a systematic investigation on the crystal chemistry of the hydrated borates, especially of sodium.

The present study confirms the known structural model and provides interatomic distances and angles of higher precision, together with the H-atom positions, so the hydrogen-bonding system is now fully elucidated.

Experimental. Colourless, elongated crystals (collection of the Museo di Mineralogia, Università di Firenze, No. 8383), 0·35 × 0·15 × 0·10 mm, Philips PW 1100 four-circle computer-controlled diffractometer, Mo $K\alpha$ (λ = 0·7107 Å), 25 reflections used for measuring lattice parameters, 5789 $\pm h,\pm k,+l$, with θ < 30°, ω–2θ scan technique, 3206 independent, 2235 with $F_o > 5\sigma(F_o)$, three standard reflections tested 13 times with a maximum standard deviation of 0·043; absorption (North, Phillips & Mathews, 1968) and Lp correction; starting atomic parameters from Rumanova *et al.* (1966), after changing the a with the c axis, anisotropic full matrix, H (from ΔF synthesis) isotropic; final R = 0·036, wR = 0·025, $w = 1/\sigma^2(F_o)$; scattering factor curves from *International Tables for X-ray Crystallography* (1974). CII IRIS-80 computer of the Centro di Calcolo dell'Università di Firenze, local version of *ORFLS* (Busing, Martin & Levy, 1962), *BONDLA* (XRAY system, 1972), *PLRTSG*

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

The B values of the non-hydrogen atoms are the equivalent ones, after Hamilton (1959).

	x	y	z	B (Å^2)
Ca	0·34825 (5)	0·58776 (3)	0·09502 (3)	0·67
Na	1·12101 (13)	0·49557 (7)	0·32427 (6)	1·95
OH(1)	0·3323 (2)	0·2970 (1)	−0·1491 (1)	1·26
OH(2)	0·3497 (2)	0·1257 (1)	−0·0627 (1)	1·42
O(3)	0·1431 (2)	0·2618 (1)	−0·0147 (1)	0·98
O(4)	0·5135 (2)	0·2866 (1)	0·0180 (1)	0·99
O(5)	0·2887 (2)	0·3994 (1)	0·0986 (1)	0·93
O(6)	0·6299 (2)	0·4526 (1)	0·0999 (1)	0·74
O(7)	0·5612 (2)	0·2979 (1)	0·1991 (1)	1·11
O(8)	0·9254 (2)	0·3805 (1)	0·0490 (1)	0·93
O(9)	0·9003 (2)	0·3738 (1)	0·2267 (1)	1·04
OH(10)	0·7956 (2)	0·2486 (1)	0·3412 (1)	1·36
OH(11)	0·9633 (2)	0·5398 (1)	0·1521 (1)	1·06
O*w*(12)	0·4330 (2)	0·5700 (1)	0·2789 (1)	1·65
O*w*(13)	0·7867 (2)	0·5057 (2)	0·4092 (1)	2·55
O*w*(14)	1·1737 (3)	0·6419 (1)	0·4357 (1)	2·16
B(1)	0·3383 (3)	0·2414 (2)	−0·0514 (2)	0·93
B(2)	0·5012 (3)	0·3576 (2)	0·1030 (2)	0·84
B(3)	0·1207 (3)	0·3486 (2)	0·0448 (2)	0·86
B(4)	0·8535 (3)	0·4396 (2)	0·1327 (2)	0·83
B(5)	0·7554 (3)	0·3092 (2)	0·2542 (2)	0·93
H(1)	0·346 (4)	0·256 (2)	−0·199 (2)	3·6 (6)
H(2)	0·466 (4)	0·105 (2)	−0·067 (2)	5·0 (7)
H(3)	0·902 (4)	0·255 (2)	0·372 (2)	2·6 (7)
H(4)	0·882 (4)	0·597 (2)	0·161 (2)	3·7 (7)
H(5)	0·461 (4)	0·643 (2)	0·292 (2)	5·7 (8)
H(6)	0·536 (4)	0·543 (2)	0·304 (2)	4·7 (8)
H(7)	0·798 (4)	0·447 (2)	0·450 (2)	4·4 (8)
H(8)	0·755 (4)	0·555 (2)	0·455 (2)	5·4 (8)
H(9)	1·070 (5)	0·675 (3)	0·448 (2)	8·7 (9)
H(10)	1·259 (5)	0·692 (2)	0·446 (2)	6·3 (9)

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(Nardelli, 1965). Positional and thermal parameters are in Table 1.*

Discussion. The Ca atom in probertite is surrounded by nine O atoms (three hydroxyls and a water molecule among them) at the corners of an irregular coordination polyhedron, which shares the OH(11)–O*w*(12) edge with the distorted octahedron around Na (Fig. 1). The Ca polyhedron also shares the O(6)–O(6) edge with another centrosymmetrically related Ca polyhedron. The result is a cluster of four cation polyhedra (Fig. 2).

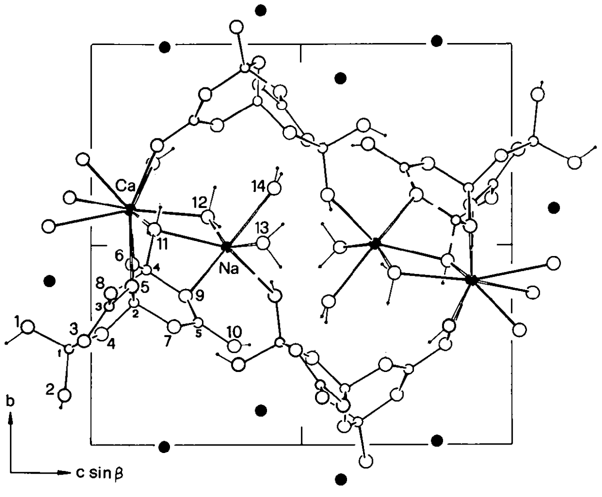

Fig. 1. Projection of the structure down the *a* axis. The numbering is that of Table 1. Filled circles are Na and Ca atoms; open circles are O atoms; smaller open circles are B atoms and dots are H atoms.

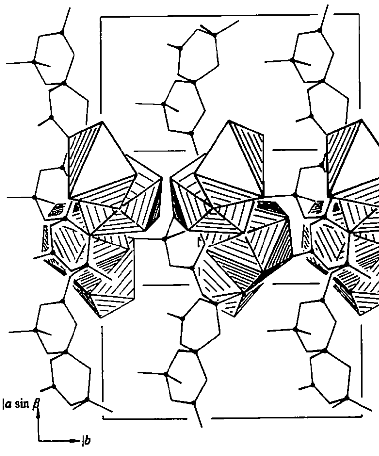

Fig. 2. Projection down the *c* axis of three Na–Ca clusters with three interconnected B–O chains. Three unit cells are outlined. Dots are B atoms. For clarity, some atoms are slightly shifted.

The basic boron–oxygen unit of the structure is the pentaborate polyanion, found also in ulexite (Clark & Appleman, 1964), in heidornite (Burzlaff, 1967) and in synthetic compounds as, for instance, in $Na_3[B_5O_9].H_2O$ (Menchetti, Sabelli & Trosti-Ferroni, 1982). The $[B_5O_7(OH)_4]^{3-}$ polyanion is formed by three tetrahedra and two triangles, all slightly irregular, ordered in two similar six-membered B–O rings. The

Table 2. *Displacements of other atoms from the planes of ring oxygens; dihedral angles in the polyanion*

	Ring 1		Ring 2	
Ring oxygen atoms	O(3), O(4), O(5)		O(6), O(7), O(9)	
Associated atoms	B(1)	−0·283 (3) Å	B(2)	−0·366 (3) Å
	B(2)	0·304 (3)	B(4)	−0·332 (3)
	B(3)	−0·081 (3)	B(5)	0·153 (3)
	OH(1)	−1·730 (1)	O(8)	−1·810 (1)
	OH(2)	0·528 (1)	OH(11)	0·349 (1)
	O(8^{ii})	0·224 (1)	OH(10)	0·470 (1)
Angle between rings		80·4 (1)°		
Oxygen atoms of triangle	O(3), O(5), O(8^{ii})		O(7), O(9), OH(10)	
Boron of triangle	B(3)	−0·007 (3) Å	B(5)	0·003 (3) Å
Triangle–ring angle	6·3 (1)°		13·4 (1)°	

Table 3. *Selected interatomic distances* (Å)

Ca–O(5)	2·400 (1)	B(2)–O(4)	1·462 (3)
Ca–O(6)	2·507 (1)	B(2)–O(5)	1·486 (2)
Ca–O*w*(12)	2·446 (2)	B(2)–O(6)	1·468 (2)
Ca–OH(11^{ii})	2·838 (2)	B(2)–O(7)	1·485 (3)
Ca–OH(1^{iv})	2·554 (2)	Mean	1·475
Ca–O(4^{iv})	2·470 (2)		
Ca–O(6^{iv})	2·694 (1)	B(3)–O(3)	1·374 (3)
Ca–O(8^{iv})	2·438 (2)	B(3)–O(5)	1·370 (2)
Ca–OH(10^{vi})	2·448 (2)	B(3)–O(8^{ii})	1·358 (3)
Mean	2·533	Mean	1·367
Na–O(9)	2·347 (2)	B(4)–O(6)	1·471 (2)
Na–OH(11)	2·429 (2)	B(4)–O(8)	1·491 (3)
Na–O*w*(13)	2·653 (2)	B(4)–O(9)	1·495 (2)
Na–O*w*(14)	2·357 (2)	B(4)–OH(11)	1·452 (2)
Na–O*w*(12^{i})	2·430 (2)	Mean	1·477
Na–OH(2^{vii})	2·470 (2)		
Mean	2·447	B(5)–O(7)	1·369 (2)
		B(5)–O(9)	1·352 (3)
B(1)–OH(1)	1·481 (3)	B(5)–OH(10)	1·381 (3)
B(1)–OH(2)	1·464 (3)	Mean	1·367
B(1)–O(3)	1·477 (3)		
B(1)–O(4)	1·466 (2)		
Mean	1·472		
Ring 1		Ring 2	
B(1)–B(2)	2·609 (3)	B(2)–B(4)	2·506 (3)
B(1)–B(3)	2·485 (3)	B(2)–B(5)	2·473 (3)
B(2)–B(3)	2·495 (3)	B(4)–B(5)	2·475 (3)

Symmetry code

None	x, y, z	(v)	$2-x, \frac{1}{2}+y, \frac{1}{2}-z$
(i)	$1+x, y, z$	(vi)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
(ii)	$-1+x, y, z$	(vii)	$1+x, \frac{1}{2}-y, \frac{1}{2}+z$
(iii)	$2-x, 1-y, 1-z$	(viii)	$x, \frac{1}{2}-y, -\frac{1}{2}+z.$
(iv)	$1-x, 1-y, -z$		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38077 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

acute angle between the planes of the rings, defined by O(3), O(4), O(5) and O(6), O(7), O(9) respectively, is about 80° (see Table 2), on account of the distortion of the central tetrahedron [namely, around B(2)]. The length of *a* is related to the size of the polyanion, which is polymerized triangle-to-tetrahedron, *via* O(8), in a chain parallel to the *a* axis. Each Ca—Na cluster holds two centrosymmetric chains strongly and four other chains weakly. It results, in all, in a high three-dimensional connection of the structure.

Interatomic distances and angles are reported in Tables 3 and 4. The mean values of the bond distances agree with those quoted in the literature from comparable coordinations. On the whole, however, the individual B—O tetrahedral distances are closer to the mean values than those given by Rumanova, Kurbanov & Belov (1966), but a trend to be distributed into two separate ranges is still observed. Indeed, O atoms bridging two tetrahedral B atoms always show the shortest bond distances within each tetrahedron.

Some minor differences in the individual triangular B—O distances, without a clear environmental cause, are noteworthy.

Distances and angles involving H atoms are shown in Table 5. It can be noted that nine hydrogen bridges are reported, while there are ten H atoms; actually suitable distances from the hydroxyl OH(2) were not found. The bonds are rather weak and bent, especially OH(1)—H(1)···O(7). The three water molecules have similar H—*D*—H angles which are a little smaller than the ideal value.

Table 6. *Electrostatic valence balance*

	Ca	Na	B(1)	B(2)	B(3)	B(4)	B(5)	H_d	H_a	Sums
OH(1)	0·20		0·73					0·85	0·18	1·96
OH(2)		0·15	0·77					1·00	0·18	2·10
O(3)			0·74		0·98				0·20 0·16	2·08
O(4)	0·25		0·76	0·78					0·20	1·99
O(5)	0·28			0·73	0·99					2·00
O(6)	0·23 0·15			0·76		0·76				1·90
O(7)				0·73			1·00		0·15 0·17	2·05
O(8)	0·27				1·03	0·72				2·02
O(9)		0·21				0·72	1·04			1·97
OH(10)	0·25						0·96	0·80		2·01
OH(11)	0·11	0·17				0·80		0·82		1·90
O*w*(12)	0·26	0·17						0·83 0·81		2·07
O*w*(13)		0·10						0·82 0·80	0·19	1·91
O*w*(14)		0·20						0·80 0·84	0·20	2·04

Table 4. O—B—O *and* B—O—B *angles* (°)

OH(1)—B(1)—OH(2)	111·7 (2)	O(6)—B(4)—O(8)	105·2 (1)
OH(1)—B(1)—O(3)	108·8 (1)	O(6)—B(4)—O(9)	111·3 (2)
OH(1)—B(1)—O(4)	106·1 (2)	O(6)—B(4)—OH(11)	113·5 (1)
OH(2)—B(1)—O(3)	105·7 (2)	O(8)—B(4)—O(9)	108·4 (1)
OH(2)—B(1)—O(4)	113·7 (2)	O(8)—B(4)—OH(11)	110·7 (2)
O(3)—B(1)—O(4)	110·8 (2)	O(9)—B(4)—OH(11)	107·7 (1)
O(4)—B(2)—O(5)	111·3 (1)	O(7)—B(5)—O(9)	123·5 (2)
O(4)—B(2)—O(6)	111·3 (2)	O(7)—B(5)—OH(10)	115·1 (2)
O(4)—B(2)—O(7)	109·1 (1)	O(9)—B(5)—OH(10)	121·4 (2)
O(5)—B(2)—O(6)	104·8 (1)		
O(5)—B(2)—O(7)	108·6 (2)	Ring 1	
O(6)—B(2)—O(7)	111·5 (1)	B(1)—O(4)—B(2)	126·1 (1)
O(3)—B(3)—O(5)	121·2 (2)	B(1)—O(3)—B(3)	121·3 (1)
O(3)—B(3)—O(8^{ii})	117·1 (2)	B(2)—O(5)—B(3)	121·7 (1)
O(5)—B(3)—O(8^{ii})	121·7 (2)		
		Ring 2	
		B(2)—O(6)—B(4)	117·0 (1)
		B(2)—O(7)—B(5)	120·0 (2)
		B(4)—O(9)—B(5)	120·7 (1)

The general valence balance, calculated according to Brown & Shannon (1973), is reported in Table 6; as can be seen, the contribution of H(2) was wholly assigned to the donor OH(2). Ten O atoms have four neighbours at bonding distances, but it is difficult to speak of a tetrahedral environment, since the angles are very irregular [*e.g.* for OH(1) they range from 97·0 (1) to 146·9 (5)°]. The remaining four O atoms have only three neighbours at bonding distances; their valence balance, however, is very satisfactory.

Thanks are due to Professor L. Ungaretti (Centro di Cristallografia Strutturale del CNR, Università di Pavia) for collecting the data.

Table 5. *Hydrogen-bonding system*

Donor atom (*D*)	Acceptor atom (*A*)	Distances (Å) *D*···*A*	*D*—H	H···*A*	∠*DHA*	Angles (°) ∠H*D*H	∠*ADA*
OH(1)—H(1)	···O(7^{viii})	2·986 (2)	0·86 (2)	2·24 (2)	145 (2)		
OH(2)—H(2)			0·82 (2)				
OH(10)—H(3)	···O(3^{vii})	2·732 (2)	0·76 (2)	2·00 (2)	161 (2)		
OH(11)—H(4)	···OH(1^{iv})	2·822 (2)	0·92 (2)	1·93 (2)	165 (2)		
O*w*(12)—H(5)	···O(7^{vi})	2·877 (2)	0·95 (2)	1·96 (2)	164 (2)	102 (2)	103·3 (1)
O*w*(12)—H(6)	···O*w*(13)	2·780 (3)	0·78 (2)	2·03 (2)	160 (3)		
O*w*(13)—H(7)	···O*w*(14^{iii})	2·766 (3)	0·91 (3)	1·88 (3)	163 (2)	98 (2)	79·0 (1)
O*w*(13)—H(8)	···OH(2^{vi})	2·823 (3)	0·92 (3)	1·92 (3)	165 (2)		
O*w*(14)—H(9)	···O(3^{vi})	2·918 (2)	0·84 (3)	2·10 (3)	166 (2)	98 (2)	97·6 (1)
O*w*(14)—H(10)	···O(4^{v})	2·737 (2)	0·84 (3)	1·91 (2)	169 (2)		

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Structure du *caténa*-Diaqua-μ-(hexaméthylènetétramine-N,N')-dinitratocadmium(II)

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Abstract. $[Cd(C_6H_{12}N_4)(H_2O)_2(NO_3)_2]$, $C_6H_{16}CdN_6O_8$, monoclinic, space group $B2/b$, $a = 8{\cdot}833\ (3)$, $b = 12{\cdot}931\ (5)$, $c = 12{\cdot}097\ (3)$ Å, $\gamma = 109{\cdot}18\ (5)°$, $Z = 4$, $D_x = 2{\cdot}10$, $D_m = 2{\cdot}05\ (5)$ Mg m^{-3}. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares technique. $R = 0{\cdot}020$ and $R_w = 0{\cdot}025$ for 1359 independent reflexions. The structure is made up of $\cdots Cd[(NO_3)_2,(H_2O)_2]-C_6H_{12}N_4-Cd[(NO_3)_2,(H_2O)_2]-\cdots$ chains which zigzag along planes $z = \pm\frac{1}{4}$ and are cross-linked by hydrogen bonds. The Cd atom is surrounded by two O atoms of water molecules, two O atoms of NO_3^- groups and two N atoms of hexamethylenetetramine molecules. Each $C_6H_{12}N_4$ molecule makes use of two N lone pairs and links two Cd atoms. The nitrate ligand is unidentate; it occupies two positions in statistical disorder.

Introduction. La présence, dans la molécule d'hexaméthylènetétramine, de quatre atomes d'azote susceptibles de se coordiner en fait potentiellement un ligand tétradentate et permet de prévoir des structures mono-, bi- et tridimensionnelles. Jusqu'ici, ces composés ont été étudiés essentiellement par spectroscopie infra-rouge. On connaît très peu de structures cristallines dans lesquelles l'hexaméthylènetétramine joue le rôle de ligand. Récemment, Pickardt (1981) a décrit très brièvement deux composés du cuivre(II) et un du mercure(II). On peut y ajouter les structures de $2C_6H_{12}N_4.3CdI_2.4H_2O$ (Mak, 1981) et de $AgNO_3.C_6H_{12}N_4$ (Michelet, Viossat, Khodadad & Rodier, 1981).

L'étude, par diffraction X, de $Cd(NO_3)_2.C_6H_{12}N_4.2H_2O$ a été entreprise dans le cadre de l'étude des composés de coordination de l'hexaméthylènetétramine poursuivie par l'un d'entre nous. Elle a eu pour objectif de préciser l'environnement de l'atome de cadmium et pour perspective la mise en évidence d'une organisation différente de celle rencontrée dans $AgNO_3.C_6H_{12}N_4$.

Les spectres de Weissenberg, réalisés avec le rayonnement Cu $K\alpha$, montrent un réseau de symétrie monoclinique. Les extinctions systématiques sont celles des groupes spatiaux Bb et $B2/b$. Le test mis au point par Jerphagnon (1972), dans lequel on compare l'action du rayonnement émis par un laser à néodyme sur la poudre du produit étudié et sur la poudre de quartz, n'a pas permis de choisir entre les deux groupes. L'expérience, réalisée au Centre National d'Etudes des Télécommunications à Bagneux, montre que la poudre de $Cd(NO_3)_2.C_6H_{12}N_4.2H_2O$ donne un signal dont l'intensité est de l'ordre de deux millièmes de l'intensité