Tableau 1. *Paramètres atomiques et coefficients d'agitation thermique* $B_{éq}$

	x	y	z	$B_{éq}(\text{Å}^2)$
U(1)	0,500	0,000	0,000	0,51 (2)
U(2)	0,000	0,500	0,500	0,41 (2)
Bi	0,500	0,500	0,500	0,89 (1)
K(1)	0,2478 (3)	0,2477	0,2477	1,49 (3)
O(1)	0,500	0,000	0,254 (1)	1,4 (3)
O(2)	0,500	0,232 (2)	0,500	1,3 (3)
O(3)	0,282 (2)	0,000	0,000	1,5 (2)
K(2)	0,000	0,000	0,000	2,7 (1)

Tableau 2. *Distances interatomiques* (Å) *et angles* (°)

U(1)	O(3)	1,88 (2) × 2	K(1)	O(3)	3,039 (2) × 4
U(1)	O(1)	2,19 (1) × 4	K(2)	O(3)	2,44 (2) × 6
U(2)	O(2)	2,01 (2) × 2	O(1)	O(1)	3,097 (15)
U(2)	O(1)	2,13 (1) × 4	O(1)	O(1)	3,006 (15)
Bi	O(2)	2,31 (2) × 6	O(1)	O(2)	2,92 (1)
K(1)	O(1)	3,052 (2) × 4	O(1)	O(3)	2,88 (1)
K(1)	O(2)	3,082 (2) × 4			

O(1)	K(1)	O(1)	119,97 (7)	O(1)	K(1)	O(2)	89,53 (8)
O(1)	K(1)	O(1)	61,0 (3)	O(1)	K(1)	O(2)	120,9 (3)
O(1)	K(1)	O(1)	177,8 (4)	O(1)	K(1)	O(3)	56,5 (3)
O(1)	K(1)	O(1)	59,0 (3)	O(1)	K(1)	O(3)	125,6 (3)
O(1)	K(1)	O(2)	56,9 (3)	O(1)	K(1)	O(3)	90,42 (2)

maille. Cette structure est constituée d'un enchaînement d'octaèdres réguliers de potassium et d'octaèdres aplatis d'uranium d'une part, et d'une succession d'octaèdres d'uranium d'autre part; ces deux chaînes sont liées par des octaèdres réguliers de bismuth (Fig. 1). Les distances Bi—O [2,31 (2) Å] et K(1)—O [comprises entre 3,039 (2) et 3,082 (2) Å] sont conformes aux normes habituelles. Dans $K_9U_6O_{22,5}$, *Im3m*, les atomes de potassium des octaèdres sont distribués statistiquement à l'origine et au centre de la maille (Saine, Gasperin, Jové & Cousson, 1987), l'uranium occupe un seul site cristallographique et les lacunes d'oxygène sont réparties dans le plan équatorial de la liaison ura-
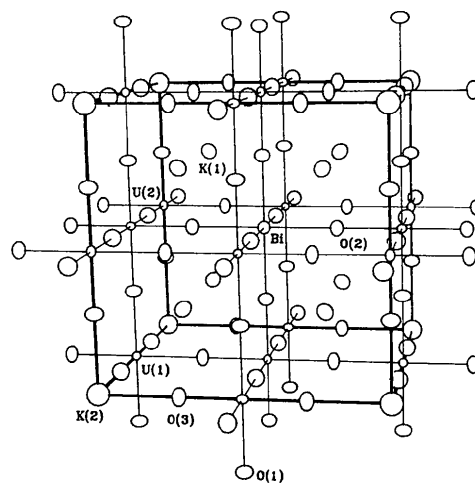
Fig. 1. Représentation d'une maille de $K_9BiU_6O_{24}$.

nyle. L'introduction de bismuth au centre conduit à $K_9BiU_6O_{24}$, *Pm3m*, perovskite non lacunaire. On observe un classement des cations, le potassium en coordinence octaédrique occupe le site à l'origine et le bismuth se place au centre de la maille. Du fait de la différence de charge et de taille entre ces cations il s'ensuit un réarrangement de l'environnement des atomes d'uranium qui conduit à deux liaisons uranyles sensiblement différentes selon que celui-ci est lié au potassium [U(1)—O(3) = 1,88 (2) Å] ou au bismuth [U(2)—O(2) = 2,01 (2) Å].

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Refinement of the Structure of Tincalconite

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Abstract. The structure of tincalconite, $Na_2[B_4O_5(OH)_4].2\cdot667H_2O$, $M_r = 285\cdot9$, previously studied by Giacovazzo, Menchetti & Scordari [*Am. Mineral.* (1973), **58**, 523–530], has been refined in the trigonal space group *R*32, $a = 11\cdot097$ (2), $c = 21\cdot114$ (4) Å, $V = 2251\cdot7$ (7) Å^3, $Z = 9$, $D_x = 1\cdot894$ Mg m^{-3}, Cu $K\alpha$

radiation, $\lambda = 1·54184$ Å, $\mu = 2·356$ mm^{-1}, $F(000)$ = 1302, $T = 108$ (2) K, $R = 0·0277$, $wR = 0·0367$ for 636 observed data $[F > 4\sigma(F)]$. One of the two water sites was found to be disordered and only partially occupied as shown by the revised formula.

Introduction. Tincalconite is the mineral name for sodium tetraborate pentahydrate, Na$_2$B$_4$O$_7$.5H$_2$O. The mineral formula is commonly known as borax pentahydrate (Mellor, 1980). The more descriptive crystal-structure formula Na$_2$[B$_4$O$_5$(OH)$_4$].3H$_2$O, is the formula that accurately identifies the borate polyanion and the three molecules of water of crystallization (Giacovazzo, Menchetti & Scordari, 1973, here after referred to as GMS). It has long been recognized that commercially produced crystals of Na$_2$[B$_4$O$_5$(OH)$_4$].3H$_2$O, as well as crystals carefully grown in the laboratory, are not fully hydrated, and that this deficiency is not due to surface dehydration. Incomplete occupancy in the water of crystallization sites is consistent with the larger thermal factors for water reported in the previous room-temperature crystallographic study (GMS). The crystal structure has now been refined in order to identify the incomplete water-occupancy sites within the crystal lattice and to locate the hydrogen atoms.

Experimental. Colorless single crystals of tincalconite were prepared by dissolving 460 g of purified borax (US Borax, 'Special Quality Borax'), Na$_2$[B$_4$O$_5$-(OH)$_4$].8H$_2$O (10 mol), in 540 g of distilled water at 368 K. The solution was filtered using a 0·22 μm cellulose acetate filter into a one litre round-bottom flask fitted with a mechanical stirrer (having a teflon paddle) and a temperature-regulated heating mantle. The solution temperature was lowered to and held at 348 K overnight with stirring. The temperature was then increased to 353 K and held for several hours before being reduced to and held at 348 K for a second night with stirring. The crystals were centrifuged at approximately 7000 r.p.m. in a basket centrifuge, washed with 10 cm^3 of cold distilled water, spread out on paper and allowed to air dry for 10 min before being stored in a sealed vial. The water deficiency as determined by standard titrimetric analysis ranges from 0·25 to 0·30 molecules of water per formula unit (Meites, 1963). A nearly spherical crystal with dimensions 0·25 × 0·30 × 0·30 mm was selected for diffraction analysis. The cell parameters were refined from the setting angles of ten diffraction maxima in the range $45 < 2\theta < 48°$. A Syntex P1̄ single-crystal diffractometer with graphite-monochromated Cu Kα radiation ($\lambda = 1·54184$ Å) was used for all measurements. Intensity data were collected using the Wyckoff-scan method with a scan range of 0·5° ω. A total of 2070 intensities was measured in the range $3·5 < 2\theta < 110°$ ($-11 \leq h \leq 1$,

$-10 \leq k \leq 11$, $-22 \leq l \leq 22$). Three standard peaks (3̄09, 1̄43, 3̄39), which were remeasured after every 50 data, had a maximum intensity variation of 0·06. Cell-parameter data and intensity data were collected at 108 (2) K using a nitrogen-streaming cooling device. Data were corrected for Lorentz and polarization effects; no absorption correction was applied. Symmetry-equivalent data were averaged assuming 3̄ Laue symmetry to give 646 unique data with $R_{int} = 0·034$. Only systematic absences corresponding to the rhombohedral centering were observed.

Initial atomic parameters were found by direct methods and refined by full-matrix least squares (on F). Anisotropic thermal parameters were applied to all non-hydrogen atoms. All calculations were performed using the *SHELXTL-Plus* (Sheldrick, 1990) software package on a MicroVAX II computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1). The site occupation factor for water Ow(1) converged to a value close to 1·0 and was kept at this value in the final refinement. Hydrogen atoms were located on a difference map. The positional parameters of the hydrogens were refined except for those of the Ow(2) hydrogens. Thermal parameters for the hydrogens were fixed at values somewhat larger than the isotropic equivalent values for the respective bonded oxygens. The structure model included 102 variables. The structure refinement converged (maximum, mean $\Delta/\sigma = 0·005$, 0·001) to $R = 0·0277$, $wR = 0·0367$ [$w = 1/\sigma^2(F_o)$] and $S = 1·18$ for 636 observed [$F > 4\sigma(F)$] data using weights based upon counting statistics. The final difference map had a maximum peak of 0·24 and a minimum hole of $-0·39$ e Å^{-3}. A secondary-extinction correction (Larsen, 1970) was applied using $F_c^* = F_c[1 + 0·002\chi F_c^2/\sin(2\theta)]^{-0.25}$ with $\chi = 0·0040$ (5).

Discussion. Atomic coordinates are given in Table 1.* Selected bond distances and angles are listed in Table 2. A view of the tetraborate anion of tincalconite is shown in Fig. 1. The anion lies on a twofold rotation axis which passes through the bridgehead oxygen O(1). Two sodiums are coordinated to each of the two borate hydroxyl groups attached to tetrahedral borons, and one sodium is coordinated to each of the two borate hydroxyl groups attached to trigonal borons. There is an independent sodium site, Na(3), in the structure which is bound only by water

Table 1. *Atomic coordinates and equivalent isotropic displacement coefficients* ($\mathring{A}^2 \times 10^4$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Na(1)	1·0	0·3301 (1)	0·5	216 (6)
Na(2)	1·0	1·0	0·5	149 (6)
Na(3)	0·0	0·0	0·0924 (1)	276 (6)
B(1)	0·9084 (3)	0·7331 (13)	0·6181 (1)	159 (12)
B(2)	0·9095 (4)	0·5133 (3)	0·6207 (2)	266 (14)
O(1)	0·8012 (2)	0·66667	0·66667	128 (8)
O(2)	0·9258 (2)	0·6238 (2)	0·5848 (1)	231 (8)
O(3)	0·8808 (2)	0·5036 (2)	0·6837 (1)	193 (8)
OH(4)	0·8720 (2)	0·8052 (2)	0·5719 (1)	159 (7)
OH(5)	0·9281 (3)	0·4142 (2)	0·5911 (1)	518 (14)
Ow(1)	−0·2234 (2)	−0·0901 (2)	0·1344 (1)	313 (9)
Ow(2)*	0·1550 (6)	0·0451 (6)	−0·0038 (4)	384 (38)
H(4)	0·858 (4)	0·857 (4)	0·592 (2)	300
H(5)	0·927 (4)	0·350 (5)	0·614 (2)	800
Hw(1A)	−0·239 (3)	−0·046 (4)	0·182 (2)	500
Hw(1B)	−0·284 (4)	−0·068 (4)	0·117 (2)	500
Hw(2A)*	0·245	0·138	−0·033	700
Hw(2B)*	0·213	0·010	0·017	700

* The site occupancy factor for water Ow(2) was refined to 0·334 (5).

Table 2. *Selected bond distances* ($\mathring{A}$) *and angles* (°)

	This work	GMS
B(1)—O(1)	1·461 (3)	1·460 (12)
B(1)—O(2)	1·495 (4)	1·468 (12)
B(1)—O(3')	1·496 (3)	1·507 (13)
B(1)—OH(4)	1·442 (4)	1·454 (13)
B(2)—O(2)	1·374 (4)	1·358 (14)
B(2)—O(3)	1·361 (3)	1·330 (15)
B(2)—OH(5)	1·367 (5)	1·386 (13)
Na(1)—OH(5)	2·440 (3)	2·442 (8)
Na(1)—OH(4'')	2·493 (2)	2·483 (7)
Na(1)—Ow(1''')	2·436 (2)	2·453 (7)
Na(2)—OH(4)	2·434 (1)	2·419 (6)
Na(3)—Ow(1)	2·335 (2)	2·338 (8)
Na(3)—Ow(2)	2·544 (8)	2·518 (18)
Na(3)—Ow(2)	2·419 (8)	2·518 (18)
O(1)—B(1)—O(2)	108·9 (2)	109·3 (7)
O(1)—B(1)—O(3')	108·8 (2)	108·1 (9)
O(1)—B(1)—OH(4)	111·8 (3)	111·9 (7)
O(2)—B(1)—O(3')	107·4 (3)	107·1 (7)
O(2)—B(1)—OH(4)	108·5 (2)	110·5 (9)
O(3')—B(1)—OH(4)	111·3 (2)	110·7 (7)
O(2)—B(2)—O(3)	122·1 (3)	122·9 (10)
O(2)—B(2)—OH(5)	117·5 (3)	120·1 (10)
O(3)—B(2)—OH(5)	120·4 (3)	116·2 (10)
B(1)—O(1)—B(1')	111·6 (3)	111·4*
B(1)—O(2)—B(2)	116·9 (2)	117·4*
B(1')—O(3)—B(2)	121·2 (3)	121·1*

Symmetry operations: (i) $\frac{2}{3} + x - y, \frac{4}{3} - y, \frac{4}{3} - z$; (ii) $1 - x + y, 1 - x, z$; (iii) $\frac{1}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$.

* Calculated from coordinates in GMS.

oxygens. The position and occupancy of water Ow(2) are the principle structural differences between this report and the previous report of tincalconite (GMS). GMS report this water sitting on a twofold axis. However, various attempts at anisotropic refinement of Ow(2) on this site led to implausible thermal parameters and to the appearance of two nearby peaks (related by the twofold axis) in the

difference map. When Ow(2) was moved to one of the difference-map peak locations, refinement converged. The Ow(2) reported here must be a disordered site because it lies rather close to the twofold axis. The Ow(2)—Ow(2') distance across the twofold axis is 0·881 (12) Å. Thus the expected occupancy for a fully occupied Ow(2) in its general position is 0·5. The occupancy found by least-squares refinement is 0·334 (5). Fig. 2 shows the bonding environment of Ow(2) and Na(3).

The disorder in water Ow(2) leads to a greatly distorted octahedral coordination sphere for Na(3). The Na(3) cation sits on a threefold axis and is coordinated only to water oxygens Ow(1) and Ow(2). The twofold axis which relates the disordered Ow(2) sites is one of three symmetry-related twofold axes which intersect Na(3)'s threefold axis near the Na(3) position. The octahedral face of Na(3) coordination, formed by three Ow(2) water molecules, is shared with a neighboring Na(3). The lone pairs of oxygen Ow(2) are directed toward this pair of Na(3) sodiums. The two Na(3)—Ow(2) distances are 2·544 (8) and 2·419 (8) Å. The chemically reasonable Ow(2)—Na(3)—Ow(2') angles range from 50·5 (4) to 73·8 (2)°. Three Ow(1) atoms form one nearly regular octahedral face for Na(3) with Na(3)—Ow(1) distances of 2·335 (2) Å and Ow(1)—Na(3)—Ow(1') angles of 106·5 (1)°.

The Na(3) to Na(3') distance through the shared threefold face is 3·902 (4) Å, which is considerably
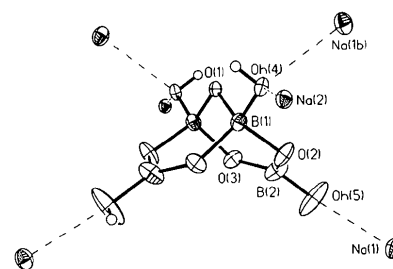

Fig. 1. Thermal ellipsoid plot of the tetraborate anion in tincalconite (50% probability ellipsoids).
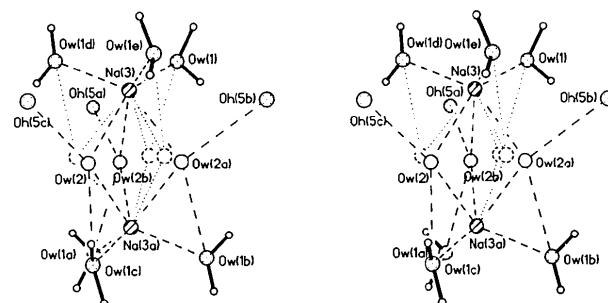

Fig. 2. The bonding environment of Ow(2) and Na(3). The Ow(2) waters (one set solid, labeled and one dashed, unlabeled) are disordered across sets of twofold axes. Ow(2)···Ow(1) and Ow(2)···OH(5) interactions are 2·892 and 2·938 Å, respectively.

longer than the expected 2·236 Å calculated assuming 2·50 Å Na—O distances and ideal geometry. This longer Na—Na distance in tincalconite is believed to be due to the disordered and partially occupied nature of the Ow(2) site. The disorder requires a greater volume of space between the sodiums, and the incomplete occupancy provides less shielding between the repulsive sodium cations.

Sodium sites Na(1) and Na(2) have nearly regular octahedral environments. Na(1) sits on a twofold rotation axis and is coordinated to two adjacent OH(5) hydroxyl groups at a distance of 2·440 (3) Å, to two adjacent OH(4) hydroxyl groups at 2·493 (2) Å, and to two opposite Ow(1) waters at 2·436 (2) Å. Na(2) lies on the intersection of a three-fold and three twofold axes and is coordinated to six separate tetraborate anions through OH(4) hydroxyl groups, 2·434 (2) Å. The edge of the Na(1) octahedron formed by OH(4) hydroxyl groups is shared with an Na(2) octahedron, giving an Na(1)···Na(2) distance of 3·663 (1) Å.

The tetraborate anion B$_4$O$_5$(OH)$_4^{2-}$ consists of two BO$_3$(OH) tetrahedra and two BO$_2$(OH) triangles sharing corner oxygens. As with similar tetraborate anions (Levy & Lisensky, 1978; Wan & Ghose, 1977) the trigonal boron of tincalconite has markedly shorter B—O distances [average 1·367 (5) Å] than the tetrahedral boron [average 1·476 (4) Å]. In tincalconite as well as the other tetraborate structures mentioned the hydroxyl oxygens bonded to the trigonal borons have considerable anisotropic motion normal to the BO$_3$ planes. The B(2)—OH(5) bond distance corrected assuming a 2:1 riding model (Johnson, 1970) is 1·373 (5) Å.

Hydroxyl and water hydrogens are coordinated to borate-ring oxygens through hydrogen bonds (Table 3). E.s.d.'s for the distances and angles involving the

hydrogens on Ow(2) are not included because these hydrogens were not refined. No other close contacts in the crystal structure are observed.

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Table 3. *Hydrogen-bond contacts* (Å,°)

O—H···O	O—H	H···O	O···O	O—H···O
OH(4)—H(4)···O(3^i)	0·79 (4)	2·06 (5)	2·831 (4)	169 (4)
OH(5)—H(5)···O(1^{ii})	0·86 (6)	1·83 (6)	2·661 (4)	162 (4)
Ow(1)—Hw(1A)···O(2^{iii})	1·16 (4)	1·62 (5)	2·753 (4)	164 (4)
Ow(1)—Hw(1B)···O(2^{iv})	0·90 (5)	1·99 (5)	2·860 (4)	161 (4)
Ow(2)—Hw(2A)···Ow(1^v)	1·18	2·09	3·063 (8)	137 (9)
Ow(2)—Hw(2B)···OH(5^{vi})	1·01	2·28	2·937 (8)	122 (9)

Symmetry operations: (i) $\frac{5}{3} - x, \frac{4}{3} - x + y, \frac{4}{3} - z$; (ii) $1 - x + y, 1 - x, z$; (iii) $\frac{1}{3} - y, x - y - \frac{1}{3}, z - \frac{1}{3}$; (iv) $x - y - \frac{1}{3}, \frac{2}{3} - y, \frac{2}{3} - z$; (v) $-x, y - x, -z$; (vi) $\frac{4}{3} - x, \frac{2}{3} - x + y, \frac{2}{3} - z$.

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Redetermination of the Structure of Hexaaquaaluminium(III) Nitrate Trihydrate

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Abstract. [Al(H$_2$O)$_6$](NO$_3$)$_3$.3H$_2$O, $M_r = 375·13$, monoclinic, $P2_1/c$, $a = 13·892$ (2), $b = 9·607$ (1), $c = 10·907$ (2) Å, $\beta = 95·51$ (2)°, $V = 1448·9$ Å^3, $Z = 4$, $D_x = 1·719$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2·3$ cm^{-1}, $F(000) = 784$, $T = 293$ K, final $R = 0·041$ for 2137 reflections with $I > 3\sigma(I)$. The structure