

Fig. 1. Projection of part of the structure down the b axis of molecules related by the c -glide operation. A similar layer of molecules, generated by the 2_1 axis at $x = 0$, $z = \frac{1}{4}$, completes the structure.

[base N(1),N(3),N(4); apex N(2)]. The coordination sphere is completed with one thiophene S atom of each ligand: $\text{Cu}(1)\cdots\text{S}(1) = 2.960(5) \text{ \AA}$ and $\text{Cu}(1)\cdots\text{S}(3) = 3.155(5) \text{ \AA}$, resulting in a distorted octahedral N_4S_2 coordination. However, the $\text{Cu}\cdots\text{S}$ interaction is probably rather weak in view of the unfavorable coordination geometry and the large distance as compared to that found in other Cu^I complexes: e.g. $2.328(7)$, $2.324(8) \text{ \AA}$ (Drew, Cairns, McFall & Nelson, 1980).

The present structure is very similar to that of the corresponding Ag complex, which crystallizes in $P\bar{1}$ (van Stein, van Koten, Vrieze, Spek, Klop & Brevard, 1984). However, the detailed coordination geometry in the Ag complex is different, probably due to the larger radius of Ag.

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Guanidinium Tetraborate(2–) Dihydrate, $(\text{CH}_6\text{N}_3)_2[\text{B}_4\text{O}_5(\text{OH})_4]\cdot 2\text{H}_2\text{O}$

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Abstract. $M_r = 347.4$, triclinic, $P\bar{1}$, $a = 8.443(10)$, $b = 12.560(15)$, $c = 7.290(10) \text{ \AA}$, $\alpha = 106.76(5)$, $\beta = 103.87(6)$, $\gamma = 90.38(7)^\circ$, $V = 716.25 \text{ \AA}^3$, $Z = 2$,

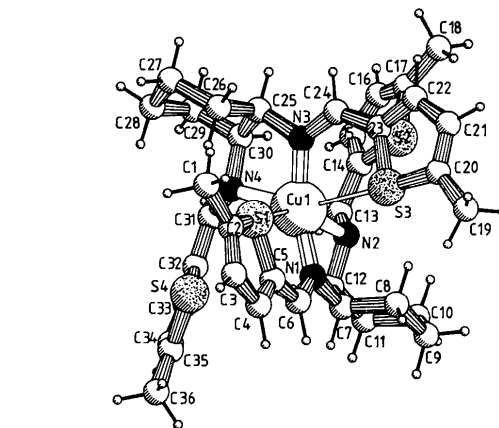


Fig. 2. Drawing of the cation showing the approximate twofold axial symmetry along the bisector of the angle $\text{S}(1)\text{—Cu}(1)\text{—S}(3)$ and the adopted numbering.

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anions each contain two tetrahedral B atoms [B—O(av.) 1.475 Å] and two trigonal B atoms [B—O(av.) 1.369 Å]. All H atoms, other than two atoms of one cation, participate in hydrogen bonds.

Introduction. The structures of borates have recently been reviewed by Farmer (1982). The guanidinium cation can act as a donor in up to six hydrogen bonds and we wished to ascertain whether it could force the occurrence of any unusual borate anion, in particular a deprotonated hydroxy-borate, in a crystalline solid.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) for non-hydrogen atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
O(1)	1740 (3)	886 (2)	1240 (4)	19 (1)
O(2)	4125 (3)	1013 (2)	3921 (3)	14 (1)
O(3)	2983 (3)	2661 (2)	3294 (4)	18 (1)
O(4)	4406 (3)	1491 (2)	1036 (4)	19 (1)
O(5)	6484 (3)	1236 (2)	6674 (3)	16 (1)
O(6)	6763 (3)	1615 (2)	3696 (4)	20 (1)
O(7)	5398 (3)	2849 (2)	5909 (4)	20 (1)
O(8)	3804 (3)	4345 (2)	5969 (4)	28 (1)
O(9)	7134 (3)	1475 (2)	581 (4)	21 (1)
B(1)	3327 (5)	1483 (4)	2376 (6)	14 (1)
B(2)	5679 (5)	1654 (3)	5052 (6)	14 (1)
B(3)	4029 (5)	3261 (4)	5021 (6)	17 (1)
B(4)	6065 (5)	1520 (4)	1770 (6)	16 (1)
N(1)	2500 (4)	1241 (3)	6998 (5)	24 (1)
N(2)	49 (4)	1544 (3)	7863 (5)	23 (1)
N(3)	150 (4)	1255 (3)	4635 (5)	22 (1)
N(4)	1128 (4)	4139 (3)	-1277 (6)	37 (1)
N(5)	3565 (5)	4283 (3)	1008 (5)	33 (1)
N(6)	2642 (4)	5833 (3)	189 (5)	30 (1)
C(1)	892 (4)	1322 (3)	6473 (5)	15 (1)
C(2)	2441 (5)	4755 (3)	-30 (6)	22 (1)
Aq(1)	9709 (3)	3178 (2)	2356 (4)	29 (1)
Aq(2)	1707 (4)	5779 (2)	4524 (5)	33 (1)

Table 2. Bond lengths (Å) and interbond angles ($^\circ$)

B(1)—O(1)	1.463 (4)	B(3)—O(8)	1.376 (5)
B(1)—O(2)	1.449 (5)	B(4)—O(4)	1.370 (4)
B(1)—O(3)	1.500 (5)	B(4)—O(6)	1.356 (5)
B(1)—O(4)	1.489 (6)	B(4)—O(9)	1.385 (6)
B(2)—O(2)	1.460 (4)	C(1)—N(1)	1.333 (5)
B(2)—O(5)	1.453 (5)	C(1)—N(2)	1.340 (5)
B(2)—O(6)	1.492 (5)	C(1)—N(3)	1.314 (5)
B(2)—O(7)	1.495 (5)	C(2)—N(4)	1.325 (5)
B(3)—O(3)	1.358 (4)	C(2)—N(5)	1.322 (5)
B(3)—O(7)	1.366 (5)	C(2)—N(6)	1.321 (6)
O(1)—B(1)—O(2)	112.1 (3)	O(4)—B(4)—O(6)	122.6 (4)
O(1)—B(1)—O(3)	106.0 (3)	O(4)—B(4)—O(9)	121.5 (4)
O(1)—B(1)—O(4)	110.3 (3)	O(6)—B(4)—O(9)	115.9 (3)
O(2)—B(1)—O(3)	109.3 (3)	B(1)—O(2)—B(2)	110.2 (3)
O(2)—B(1)—O(4)	110.3 (3)	B(1)—O(3)—B(3)	118.0 (3)
O(3)—B(1)—O(4)	108.6 (3)	B(1)—O(4)—B(4)	118.5 (3)
O(2)—B(2)—O(5)	111.8 (3)	B(2)—O(6)—B(4)	118.6 (3)
O(2)—B(2)—O(6)	109.1 (3)	B(2)—O(7)—B(3)	118.8 (3)
O(2)—B(2)—O(7)	110.1 (3)	N(1)—C(1)—N(2)	119.4 (3)
O(5)—B(2)—O(6)	110.2 (3)	N(1)—C(1)—N(3)	120.5 (4)
O(5)—B(2)—O(7)	108.0 (3)	N(2)—C(1)—N(3)	120.0 (3)
O(6)—B(2)—O(7)	107.6 (3)	N(4)—C(2)—N(5)	119.4 (4)
O(3)—B(3)—O(7)	122.8 (3)	N(4)—C(2)—N(6)	121.0 (4)
O(3)—B(3)—O(8)	121.9 (4)	N(5)—C(2)—N(6)	119.7 (3)
O(7)—B(3)—O(8)	115.3 (3)		

Experimental. Title compound crystallized from a solution of 0.1 mol $(\text{CH}_6\text{N}_3)_2\text{CO}_3$ and 0.4 mol H_3BO_3 in 200 ml boiling water; recrystallized from hot water (pH of mother liquor 8.3); found 12.4%, calculated 12.44% B. D_m by flotation. Intensities estimated by microdensitometer (SERC Service, Daresbury Laboratory) from equi-inclination multifilm Weissenberg photographs (layers 0–3kl, h0–2l, and hk0–5); merging R 0.053, no absorption correction; *EEES* direct-methods routine in *SHELX76* (Sheldrick, 1976) gave one cation and most of the anion, other B, C, N, O atoms from difference synthesis; block-matrix refinement on F to $R=0.073$ with anisotropic thermal parameters, difference synthesis then gave all H atoms as 20 strongest peaks at reasonable positions; H atoms fixed in last cycles ($U_H=0.04 \text{ Å}^2$); final convergence at $R=0.052$, $wR=0.061$; unit weights; 208 parameters; max. Δ/σ in last cycle 0.001; $\Delta\rho_{\text{max}} |0.3| e \text{ Å}^{-3}$; no correction for secondary extinction.

Discussion. Final coordinates are in Table 1,* and derived dimensions in Table 2.

The anion (Fig. 1) proves to be the familiar $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ species present in borax, and has virtual symmetry mm (C_{2v}) if H atoms are neglected. Two boron atoms [B(1), B(2)] are tetrahedrally bonded and two [B(3), B(4)] are trigonally bonded. The BO_3 groups are virtually planar [max. deviation 0.010 (7) Å, B(3)]

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and hydrogen-bond lengths have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39855 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

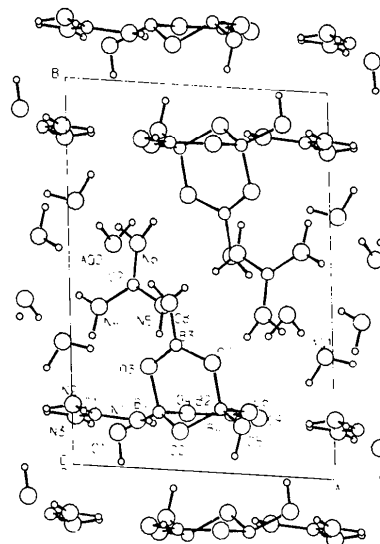


Fig. 1. Unit cell and adjacent atoms in $(\text{CH}_6\text{N}_3)_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 2\text{H}_2\text{O}$; c -axis projection.

and B(1) and B(2) lie close [max. deviation 0.101 (7) Å] to the mean planes, between which the dihedral angle is 68°. The bond angle at O(2), on the local twofold axis and bridging the B_{tet} atoms, is 110.2 (3)°, compared with 118.0 to 118.6 (3)° at the other bridging O atoms. The B—O bond lengths are 1.449 to 1.500 (5) Å (av. 1.475 Å) for B_{tet} and 1.356 to 1.385 (5) Å (av. 1.369 Å) for B_{trig}. These dimensions agree well with those reported in recent years for the same anion in Mg[B₄O₅(OH)₄].7H₂O (Che'ng Wan & Ghose, 1977), K₂Ca[B₄O₅(OH)₄]₂.8H₂O (Sokolova, Yamnova, Simonov & Belov, 1979), and (NH₄)₂[B₄O₅(OH)₄].2H₂O (Janda, Heller & Pickardt, 1981). The H atoms lie at 0.88 to 1.04 Å from O and 0.87 to 1.01 Å from N (bond lengths were not refined). With the exception of N(4)—H(12) and N(5)—H(13), the X—H bonds are closely directed towards a non-bonded near neighbour of the parent atom, the X—H...Y angles

ranging from 152 to 177°. The network of hydrogen bonds includes interanion bonds, O(1)...O(9), O(5)...O(2), and O(9)...O(5). Each terminal (OH) oxygen atom of the anion is the donor in one and the acceptor in one or two hydrogen bonds; each bridging O is the acceptor in one or two bonds; each water molecule is the acceptor in two and the donor in two bonds; and each N atom is the donor in one of two bonds.

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Structure of Decentapicrin A: (–)-(4a*S*)-6-[3'-*O*-(3-Hydroxybenzoyl)-β-D-glucopyranosyloxy]-5-vinyl-4,4*αα*,5β,6*α*-tetrahydro-1*H*,3*H*-pyrano[3,4-*c*]pyran-1-one, C₂₃H₂₆O₁₁

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Abstract. *M_r* = 478.45, orthorhombic, *P*2₁2₁2₁, *a* = 5.8234 (6), *b* = 12.512 (2), *c* = 31.693 (5) Å, *U* = 2309.2 (6) Å³, *Z* = 4, *D_x* = 1.376 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 0.69 cm⁻¹, *F*(000) = 1008, *T* = 294 K. *R* = 0.052 for 1088 observed reflexions. The δ-lactone and pyran rings of the secoiridoid moiety exhibit puckered conformations which can be approximated to an envelope shape with C(6) and C(9) serving as the flaps. The β-glucose moiety occurs in the chair, ⁴C₁, conformation. The molecular packing is dominated by intermolecular hydrogen bonds. A spiral chain is formed along **a** through the bifurcated hydrogen bonds between sugar and secoiridoid moieties [O(2')—

H...O(7), 3.00 (1) and O(2')—H...O(11), 3.16 (1) Å]. Sugar – *m*-hydroxybenzoyl interactions take part in the formation of a double spiral along **b** [O(4'')—H...O(4'), 2.79 (1); O(6')—H...O(1''), 2.75 (1) Å] and also in bridging the spirals running in the perpendicular directions (along **a** and **b**) [O(6')—H...O(1''), 2.75 (1) Å]. Hydrogen bond O(6')—H...O(4''), 3.19 (1) Å, is a part of the connexion along **a**. Sugar – sugar contact O(4')—H...O(6'), 2.65 (1) Å, connects double spiral chains into a layer (*ab* plane).

Introduction. Decentapicrin A (I₃), a natural acyl secoiridoid glucoside isolated from flower tops of *Centaurium littorale* (Gentianaceae) (van der Sluis & Labadie, 1981) and *Centaurium liniariifolium* (Seoane, 1984), and detected in the fruits of *Centaurium chloodes* and *Centaurium scilloides* (van der Sluis &

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