

P—OH distances from 1.529 to 1.579 Å and P—O from 1.471 to 1.550 Å were found. These values are in good agreement with the P—OH (mean value 1.564 Å) and P—O (mean value 1.499 Å) distances in $\text{Cd}(\text{H}_2\text{PO}_3)_2 \cdot \text{H}_2\text{O}$ (Loub, Podlahová & Ječný, 1978), and H(42) atoms participate in hydrogen bonding of the anion–anion and water–anion types. The Na—O distances in the Na octahedron are comparable with those found in $\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_{0.5}\text{H}_{2.5}\text{PO}_3$, except for Na—O(11), which is much longer and is, in fact, among the longest found in the literature. The O—Na—O angles vary from 70.84 (9) to 113.50 (10)° and from 156.91 (8) to 163.03 (9)°. The Co octahedron is nearly regular (according to Table 2) without extreme values of the Co—O distances. The O—Co—O angles are in the range 84.75 (10)–95.27 (8)° and 173.77 (7)–175.68 (7)°.

The authors wish to thank Dr Eysseltoová for preparing the single crystals.

References

BRODALLA, D., GOETERS, C., KNIEP, R., MOOTZ, D. & WUNDERLICH, H. (1978). *Z. Anorg. Allg. Chem.* **439**, 265–274.

ČISAŘOVÁ, I., NOVÁK, C., PETŘÍČEK, V., KRATOCHVÍL, B. & LOUB, J. (1982). *Acta Cryst.* **B38**, 1687–1689.
 CORBRIDGE, D. E. C. (1956). *Acta Cryst.* **9**, 991–994.
 EBERT, M. & EYSELTOVÁ, J. (1968). *Z. Chem.* **8**, 69.
 HANDLOVIČ, M. (1969). *Acta Cryst.* **B25**, 227–231.
 HANDLOVIČ, M. (1972). *Chem. Zvesti*, **26**, 494–501.
 HAZELL, R. G., HAZELL, A. C. & KRATOCHVÍL, B. (1982). *Acta Cryst.* **B38**, 1267–1269.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JOHANSSON, G. B. & LINDQVIST, O. (1976). *Acta Cryst.* **B32**, 412–414.
 LOUB, J. & PAULUS, H. (1981a). *Acta Cryst.* **B37**, 1106–1107.
 LOUB, J. & PAULUS, H. (1981b). *Acta Cryst.* **B37**, 2058–2059.
 LOUB, J., PODLAHOVÁ, J. & JEČNÝ, J. (1978). *Acta Cryst.* **B34**, 32–34.
 McDONALD, R. C. & ERIKS, K. (1980). *Inorg. Chem.* **19**(5), 1237–1241.
 PHILIPPOT, E. & LINDQVIST, O. (1970). *Acta Chem. Scand.* **24**, 2803–2810.
 SKLENÁŘ, I. & PETŘÍČEK, V. (1981). TLS system. Institute of Physics, Czechoslovak Academy of Sciences, Prague.

Acta Cryst. (1982). **B38**, 2438–2441

The Calcium Potassium Tetraborate Hydrate $\text{CaK}_2[\text{B}_4\text{O}_5(\text{OH})_4]_2 \cdot 8\text{H}_2\text{O}$

BY X. SOLANS AND M. FONT-ALTABA

Departamento de Cristalografía y Mineralogía, Universidad de Barcelona, Gran Via 585, Barcelona 7, Spain

AND J. SOLANS AND M. V. DOMENECH

Departamento de Cristalografía y Mineralogía, Universidad de Oviedo, Arias de Velasco s/n, Oviedo, Spain

(Received 15 July 1981; accepted 16 March 1982)

Abstract. $\text{CaK}_2[\text{B}_4\text{O}_5(\text{OH})_4]_2 \cdot 8\text{H}_2\text{O}$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 16.597$ (2), $b = 12.469$ (2), $c = 11.569$ (2) Å, $V = 2394.2$ (1) Å³, $\mu(\text{Mo } K\alpha) = 0.698$ mm⁻¹, $D_c = 1.76$ Mg m⁻³. The structure was solved with *MULTAN* and refined by means of full-matrix least-squares methods. The final R value is 0.052 for 3096 observed reflections. The Ca^{2+} ion displays seven coordination, while the two non-equivalent K^+ ions display eight and six coordination. The crystal structure consists of alternate layers of anions and cations parallel to (100). Each tetraborate anion is hydrogen-bonded to two water molecules and the other tetraborate anion within a layer, while the alternate layers consist of three cations and six water molecules.

Introduction. A systematic structural study of borate compounds is being carried out by the Departments of

Crystallography and Mineralogy of the Universities of Oviedo and Barcelona. The title compound is the first tetraborate with two cations to have its crystal structure reported.

Colourless prismatic crystals were prepared by evaporation from aqueous solution. A crystal $0.50 \times 0.06 \times 0.1$ mm was selected for measurement on a Philips PW1100 four-circle diffractometer. The unit cell was measured by centring 25 independent reflections and refining the orientation matrix and unit-cell parameters by least squares. A total of 3175 independent reflections within the range $2\theta \leq 60^\circ$ were measured using graphite-monochromatized Mo $K\alpha$ radiation, with 79 reflections rejected because of the imposed criterion $I < 2.5\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics. Only Lorentz–polarization corrections were made.

The structure was solved with the *MULTAN* system of computer programs (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). An *E* map computed from a set of phases with the highest

Table 1. Atomic coordinates ($\times 10^4$, for H $\times 10^3$) and equivalent isotropic temperature coefficients ($B_{eq} = \frac{8}{3}\pi^2 \text{trace } \bar{U}$) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq} (\AA^2)
Molecule A				
Ca	9719 (1)	292 (1)	9357 (1)	1.25 (3)
K(1)	6264 (1)	2244 (1)	2371 (2)	4.02 (6)
K(2)	4235 (1)	2326 (1)	7564 (1)	3.92 (6)
B(1)	13069 (3)	-339 (4)	8254 (4)	0.9 (1)
O(2)	13508 (2)	-431 (3)	9378 (3)	1.3 (1)
B(3)	13075 (3)	-369 (4)	10384 (4)	1.2 (2)
O(4)	12259 (2)	-200 (3)	10387 (3)	1.3 (1)
B(5)	11818 (3)	-50 (4)	9283 (4)	1.0 (1)
O(6)	11505 (2)	-1104 (3)	8890 (3)	1.4 (1)
B(7)	11989 (3)	-1701 (4)	8190 (4)	1.3 (1)
O(8)	12753 (2)	-1424 (3)	7905 (3)	1.3 (1)
O(9)	12367 (2)	361 (3)	8410 (2)	1.0 (1)
O(10)	13621 (2)	77 (3)	7402 (3)	1.3 (1)
O(11)	13476 (2)	-480 (4)	11413 (3)	1.9 (1)
O(12)	11126 (2)	652 (3)	9473 (3)	1.4 (1)
O(13)	11660 (2)	-2651 (3)	7778 (3)	1.7 (1)
W(1)	2830 (3)	2353 (4)	8887 (5)	3.6 (2)
W(2)	10047 (2)	1656 (3)	4206 (4)	2.4 (1)
W(3)	9952 (3)	377 (8)	11386 (4)	5.8 (1)
W(4)	4670 (3)	2832 (3)	1181 (4)	2.7 (1)
W(5)	4703 (2)	1271 (3)	9533 (4)	2.5 (1)
W(6)	10029 (2)	4 (5)	7336 (3)	3.0 (1)
W(7)	12753 (6)	2507 (5)	6108 (7)	7.6 (3)
W(8)	5079 (2)	1623 (4)	4243 (4)	2.9 (1)
H(O10)	1325 (6)	21 (9)	685 (12)	7 (1)
H(O11)	1314 (6)	-48 (10)	1205 (11)	7 (1)
H(O12)	1107 (7)	119 (9)	1015 (10)	7 (1)
H(O13)	794 (7)	197 (9)	693 (10)	7 (1)
H(W3)	1483 (7)	-14 (9)	671 (11)	7 (1)
H(W3')	1544 (6)	-37 (10)	639 (11)	7 (1)
H(W4)	1010 (7)	-225 (10)	541 (10)	7 (1)
H(W4')	1076 (7)	-278 (10)	639 (10)	7 (1)
H(W6)	1453 (6)	-18 (10)	1188 (11)	7 (1)
H(W6')	1520 (6)	-44 (9)	1181 (11)	7 (1)
H(W8)	1046 (7)	-224 (10)	930 (9)	7 (1)
H(W8')	990 (7)	-239 (10)	992 (10)	7 (1)
Molecule B				
B(1)	7102 (2)	-373 (4)	4274 (4)	0.9 (1)
O(2)	6601 (2)	-523 (3)	5336 (2)	1.1 (1)
B(3)	6987 (3)	-444 (4)	6377 (4)	1.2 (1)
O(4)	7797 (2)	-273 (3)	6430 (3)	1.3 (1)
B(5)	8291 (3)	-26 (4)	5371 (4)	1.1 (1)
O(6)	8674 (2)	-1041 (3)	4984 (3)	1.3 (1)
B(7)	8242 (3)	-1681 (4)	4244 (4)	1.2 (1)
O(8)	7472 (2)	-1426 (3)	3924 (3)	1.3 (1)
O(9)	7756 (2)	380 (2)	4473 (2)	1.0 (1)
O(10)	6518 (2)	-30 (3)	3429 (3)	1.3 (1)
O(11)	6521 (2)	-530 (3)	7353 (3)	1.7 (1)
O(12)	8931 (2)	707 (3)	5681 (3)	1.3 (1)
O(13)	8607 (2)	-2605 (3)	3868 (4)	2.1 (1)
H(O10)	828 (6)	16 (9)	769 (11)	7 (1)
H(O11)	812 (7)	55 (10)	1285 (11)	7 (1)
H(O12)	624 (7)	-111 (10)	1108 (10)	7 (1)
H(O13)	661 (7)	231 (10)	942 (10)	7 (1)

combined figure-of-merit revealed peaks for 31 non-H atoms. Six O atoms of the water molecules were determined by means of a difference synthesis. Full-matrix least-squares refinements were carried out with the *SHELX 76* (Sheldrick, 1976) program. 16 H atoms, located with a difference Fourier synthesis, were refined with an overall isotropic temperature factor and the rest of the atoms were refined anisotropically. Refinement converged with an *R* index of 0.052 ($R = \sum |F_o| - |F_c| / \sum |F_o|$). * Table 1 shows atomic

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36832 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

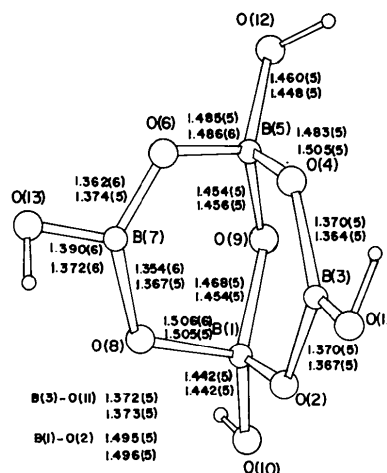


Fig. 1. View of the tetraborate ion, with bond distances in \AA (upper values: molecule A, lower: molecule B).

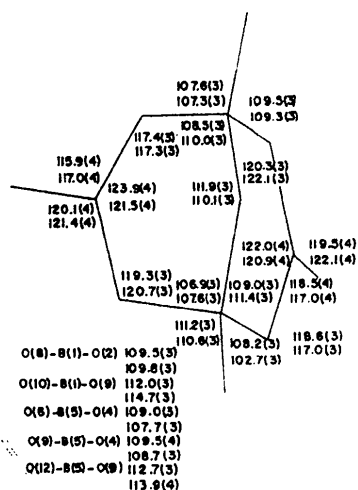


Fig. 2. Bond angles in the tetraborate anion in degrees (upper values: molecule A, lower: molecule B).

coordinates and equivalent isotropic temperature coefficients. The water atoms $W(3)$ and $W(7)$ have very high equivalent isotropic temperature coefficients. The anisotropic temperature coefficients for these atoms are: $U_{11} = 0.015$ (1), $U_{22} = 0.190$ (7), $U_{33} = 0.015$ (2), $U_{23} = 0.003$ (3), $U_{13} = -0.001$ (1) and $U_{12} = 0.007$ (3) \AA^2 for $W(3)$ and $U_{11} = 0.183$ (9), $U_{22} = 0.043$ (3), $U_{33} = 0.061$ (4), $U_{23} = -0.004$ (3), $U_{13} = 0.009$ (5) and $U_{12} = -0.013$ (4) \AA^2 for $W(7)$. As the directions [010] for $W(3)$ and [100] for $W(7)$ correspond to non-bond directions (see Fig. 6), we consider these values solely due to thermal vibration.

Discussion. The two non-equivalent tetraborate ions have similar distances and angles (Figs. 1 and 2), and they are enantiomorphs (torsion angles of anion A are minus the torsion angles of anion B). The slight differences between bond distances and angles in these two anions are within the range of values observed in the literature (Table 2).

The Ca^{2+} , $\text{K}(1)^+$ and $\text{K}(2)^+$ ions display seven, eight and six coordination, respectively. Figs. 3, 4 and 5 and Table 3 show the bond distances and angles of these ions. Other potassium borates show the same coordination for the K^+ ion thus: eight coordination as in potassium tetraborate (Krogh-Moe, 1972), potassium pentaborate (Krogh-Moe, 1965) or potassium pentaborate tetrahydrate (Zachariassen & Plettinger, 1963), or six coordination as in potassium tetraborate (Krogh-Moe, 1972) or potassium tetraborate tetrahydrate (Marezio, Plettinger & Zachariassen, 1963).

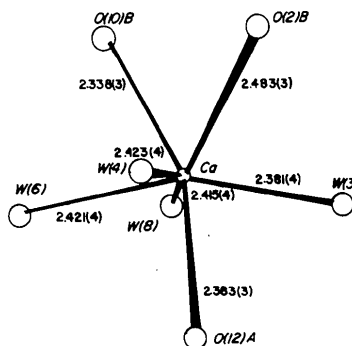


Fig. 3. Bond distances in \AA for Ca coordination.

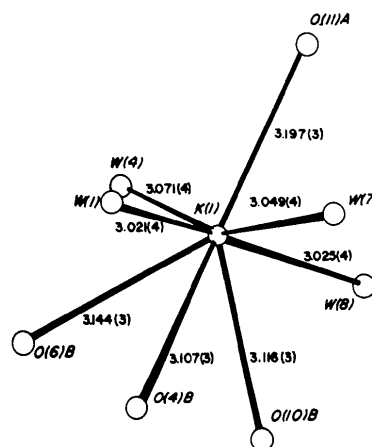


Fig. 4. Bond distances in \AA for $\text{K}(1)$ coordination.

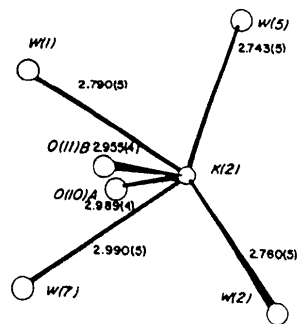


Fig. 5. Bond distances in \AA for $\text{K}(2)$ coordination.

Table 2. *A comparative study of tetraborate anions*

	Title compound		Literature	
	Mean value	Range	Mean value	Range
$\text{B}_{\text{tetra}}-\text{O}$	1.473 \AA	1.422–1.506 \AA	1.472 \AA	1.40–1.51 \AA
$\text{B}_{\text{tri}}-\text{O}$	1.370	1.354–1.390	1.367	1.312–1.412
$\text{O}-\text{B}_{\text{tetra}}-\text{O}$	109.5°	102.7–114.7°	109.5°	102.1–115.2°
$\text{O}-\text{B}_{\text{tri}}-\text{O}$	119.9	115.9–123.9	119.9	114.2–126.0

Literature: Domenech, 1980; Domenech, Solans & Solans, 1981; Jande *et al.*, 1981; Krogh-Moe, 1965, 1972; Marezio, 1969; Marezio *et al.*, 1963; Merlino, 1969; Merlino & Sartori, 1969, 1971; Zachariassen & Plettinger, 1963.

Table 3. Bond angles with Ca or K as the central atom ($^\circ$)

O(12)A—Ca—W(3)	77.1 (1)	O(11)A—K(1)—W(7)	63.0 (1)
O(12)A—Ca—W(6)	82.7 (1)	O(11)A—K(1)—W(4)	90.4 (1)
O(12)A—Ca—W(4)	82.3 (1)	O(11)A—K(1)—W(1)	90.0 (1)
W(6)—Ca—W(4)	84.4 (2)	O(11)A—K(1)—W(8)	89.8 (1)
W(6)—Ca—W(8)	76.7 (2)	O(6)B—K(1)—O(4)B	45.4 (1)
W(6)—Ca—O(10)B	73.9 (1)	O(10)B—K(1)—O(4)B	48.6 (1)
W(8)—Ca—O(10)B	87.7 (1)	O(10)B—K(1)—W(8)	63.8 (1)
O(2)B—Ca—O(10)B	56.7 (1)	W(7)—K(1)—W(1)	64.1 (2)
O(2)B—Ca—W(3)	71.8 (1)	O(4)B—K(1)—W(1)	62.1 (1)
		O(6)B—K(1)—W(1)	88.2 (1)
W(5)—K(2)—W(1)	77.1 (1)	O(6)B—K(1)—W(4)	90.4 (1)
W(5)—K(2)—O(10)A	72.5 (1)	O(10)B—K(1)—W(7)	88.9 (1)
W(5)—K(2)—W(2)	93.6 (2)	W(7)—K(1)—W(8)	89.9 (2)
W(7)—K(2)—O(10)A	75.8 (1)	W(4)—K(1)—W(8)	89.9 (2)
W(7)—K(2)—O(11)B	66.5 (1)	O(4)B—K(1)—W(7)	90.1 (1)
W(7)—K(2)—W(2)	80.5 (2)		
W(7)—K(2)—W(1)	67.7 (2)		
W(1)—K(2)—O(10)A	76.2 (1)		
W(1)—K(2)—O(11)B	67.7 (1)		

 Table 4. Hydrogen-bond distances (Å)

D—H...A	D...A	H...A
W(3)—H(W3)...O(10)A ⁱ	2.705 (6)	2.2 (1)
W(3)—H(W3)'...O(11)B ⁱⁱ	2.695 (6)	2.1 (1)
W(6)—H(W6)...O(11)A ⁱⁱⁱ	2.765 (6)	1.9 (1)
W(6)—H(W6)'...O(12)B ^{iv}	2.784 (6)	2.0 (1)
W(8)—H(W8)...O(6)A ^v	2.738 (6)	2.3 (1)
W(8)—H(W8)'...W(2) ^v	2.798 (6)	1.6 (1)
W(2)—H...O(2)A ⁱⁱⁱ	2.851 (6)	
W(2)—H...O(12)B ^{iv}	2.782 (6)	
W(4)—H(W4)...W(5) ^{vi}	2.725 (6)	2.1 (1)
W(4)—H(W4)'...O(13)A ⁱⁱⁱ	2.887 (6)	1.6 (1)
W(5)—H...O(2)A ^{iv}	2.911 (6)	
W(5)—H...O(6)B ⁱⁱ	2.759 (6)	
W(1)—H...O(9)A ^{iv}	2.657 (6)	
W(1)—H...O(8)B ^{vii}	2.998 (6)	
W(7)—H...O(9)B ^{vii}	2.719 (6)	
W(7)—H...O(4)A ⁱⁱⁱ	2.996 (6)	
O(10)A—H...O(4)A ^{ix}	2.755 (6)	1.9 (1)
O(11)A—H...O(9)A ^x	2.704 (6)	1.8 (1)
O(12)A—H...O(13)B ^{xii}	2.933 (6)	2.0 (1)
O(13)A—H...O(8)B ^{xii}	2.649 (6)	
O(10)B—H...O(4)B ^{xiii}	2.605 (6)	1.7 (1)
O(11)B—H...O(9)B ⁱⁱⁱ	2.738 (6)	2.0 (1)
O(12)B—H...O(13)A ^{vii}	2.887 (6)	2.1 (1)
O(13)B—H...O(8)A ^{viii}	2.772 (6)	

Symmetry code: (i) $0.5 - x, 1 - y, 0.5 + z$; (ii) $1.5 - x, 1 - y, 0.5 + z$; (iii) $0.5 - x, 1 - y, z - 0.5$; (iv) $x, y - 1, z$; (v) $x - 0.5, 0.5 - y, 1 - z$; (vi) $x, y, z - 1$; (vii) $1 - x, y - 0.5, 1.5 - z$; (viii) $0.5 + x, 1.5 - y, 1 - z$; (ix) $0.5 - x, 2 - y, z - 0.5$; (x) $0.5 - x, 2 - y, z + 0.5$; (xi) $1 - x, y + 0.5, 1.5 - z$; (xii) $x - 0.5, 1.5 - y, 1 - z$; (xiii) $1.5 - x, 1 - y, z - 0.5$.

cations and the rest of the water molecules. These layers are parallel to the (100) plane. This packing geometry is also shown in other tetraborate structures (Jande, Heller & Pickardt, 1981; Krogh-Moe, 1965, 1972; Marezio *et al.*, 1963). Within the first layer the tetraborate anions are hydrogen-bonded (Table 4 and

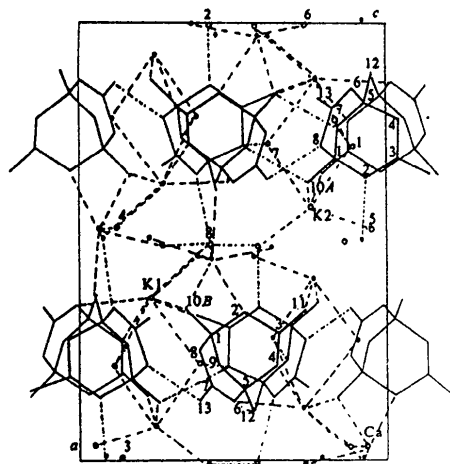

 Fig. 6. Projection down the b axis of the unit-cell contents.

Fig. 6), with strong and weak bonds. Within the second layer the cations are linked by water molecules [$W(4)$ and $W(8)$] coordinated to two anions and hydrogen bonds between water molecules [$W(8) \cdots W(2)$ and $W(4) \cdots W(5)$]. The two layers are linked by electrostatic forces and hydrogen bonds (Table 4).

This work was sponsored by the University of Barcelona.

References

- DOMENECH, V. (1980). *Crystallographic Study on Potassium and Ammonium Borates*. Doctoral Thesis, Univ. of Oviedo, Spain.
- DOMENECH, V., SOLANS, J. & SOLANS, X. (1981). *Acta Cryst.* B37, 643–645.
- JANDE, R., HELLER, G. & PICKARDT, J. (1981). *Z. Kristallogr.* 154, 1–9.
- KROGH-MOE, J. (1965). *Acta Cryst.* 18, 1088–1089.
- KROGH-MOE, J. (1972). *Acta Cryst.* B28, 3089–3093.
- MAIN, P., FISKE, S., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J. P. & WOOLFSON, M. M. (1980). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MAREZIO, M. (1969). *Acta Cryst.* B25, 1787–1795.
- MAREZIO, M., PLETINGER, H. A. & ZACHARIASEN, W. H. (1963). *Acta Cryst.* 16, 975–980.
- MERLINO, S. (1969). *Rend. Accad. Sci. Fis. Mat. Naples*, 47, 85–99.
- MERLINO, S. & SARTORI, F. (1969). *Acta Cryst.* B25, 2264–2270.
- MERLINO, S. & SARTORI, F. (1971). *Science*, 171, 377–379.
- SHELDRIK, G. M. (1976). *SHELX. A program for crystal structure determination*. Univ. of Cambridge, England.
- SUTTON, L. E. (1958). Editor, *Interatomic Distances and Configuration in Molecules and Ions*, Spec. Publ. No. 11. London: The Chemical Society.
- ZACHARIASEN, W. H. & PLETINGER, H. A. (1963). *Acta Cryst.* 16, 376–379.