Crystal Structure of Potassium Tetra-acetatoborate

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The crystal structure of the title compound has been solved by direct methods from three-dimensional *X*-ray diffractometer data and refined by least-squares methods to *R* 0·075 for 848 observed reflections. All hydrogen atoms were located. Crystals are monoclinic, space group $P2_1/n$, with a = 17·665(2), b = 12·456(2), c = 6·090(3) Å, β = 100·11°, Z = 4. The structure consists of slightly distorted boron–oxygen tetrahedra held together by potassium ions. Four acetoxy-groups with only one B–O bond form each boron–oxygen tetrahedron of the anionic unit $B(OAc)_4^-$. The potassium ion is co-ordinated to seven oxygen atoms, with K–O distances 2·68—3·02 Å, so that all but one of the oxygen atoms of each anionic unit are linked to K^+ ions. The eighth is far removed.

THERE has been recently considerable interest in the boron acetates and their derivatives with acetates of several cations.[1] We have previously[2] reported the crystal and molecular structure of the tetra-acetyldiborate. To find out more of the co-ordination chemistry and crystallo-chemical behaviour of boron,[3] we have carried out and report here the crystal structure of potassium tetra-acetatoborate.

EXPERIMENTAL

Crystal Data.—$C_8H_{12}BKO_8$, M = 286·08, Monoclinic, a = 17·665(2), b = 12·456(2), c = 6·090(3) Å, β = 100·11 (0·1)°, U = 1319 Å^3, Z = 4, D_c = 1·438 g cm^{-3}, $F(000)$ = 592. Space group $P2_1/n$ from systematic absences: $0k0$ with k odd, and $h0l$ with $(h + l)$ odd. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 4·26 cm^{-1}.

Preparation of the Crystals.—Acetic anhydride (20 ml) was added to orthoboric acid (3·05 g) and heated under nitrogen on a steam-bath, until all solid had dissolved. Anhydrous potassium acetate (4·9 g) was then added and the mixture heated, after addition of further acetic anhydride (15—20 ml), until a clear solution was obtained. From this solution colourless, prismatic crystals, suitable for *X*-ray investigation were obtained after some months. They were air-sensitive and many were twinned; a prismatic crystal, elongated along *c*, with dimensions *ca.* 0·1 × 0·03 × 0·5 mm was mounted in a capillary which was sealed after addition of mother liquor.

Intensity Data.—Intensity data were measured with a Philips PW 1100 computer-controlled automatic diffractometer, by use of Mo-K_α radiation monochromatized with a graphite crystal. Cell dimensions were determined by the least-squares method from 20 high-angle reflections by use of monochromatic Cu-K_α radiation (λ = 1·5418 Å). Intensities were measured by ω-scans, scan rate 0·1° s^{-1}, scan range 1°. The background time was half the scanning time. Rapid data collection was necessary because of crystal instability. (An attempt to use a lower scan-speed failed because the crystal decomposed before a sufficient number of reflections had been collected.)

All reflections in the quadrant of reciprocal space ± h,k,l (with l < 5) were collected to 2θ 40°. Of 1127 independent reflections obtained, 848 having $I > \sigma(I)$ were processed.[4]

Structure Determination and Refinement.—The structure was solved by direct methods, with the MULTAN program.[5] The potassium and all the oxygen atoms were located from the E map.[6] With these co-ordinates, successive three-dimensional Fourier syntheses revealed the positions of all the carbon atoms. These parameters were then refined, first isotropically (3 cycles), then anisotropically (2 cycles) by full-matrix least-squares calculations,[7] yielding R' 0·051. The weighting scheme used throughout refinement was: $\sqrt{w} = 1/\sigma(F_o)$.

A difference-Fourier synthesis gave the positions of all the hydrogen atoms. A structure-factor calculation, taking into account the hydrogen atoms (for which the methyl-carbon isotropic thermal parameter was used), and a further cycle of anisotropic refinement for all the non-hydrogen atoms, yielded a final R' of 0·039 and R 0·075 for all observed reflections.

Atomic scattering factors used in the structure-factor

[1] G. W. Gerrard and M. Wheelans, *Chem. and Ind.*, 1954, 758; R. G. Hayter, A. W. Laubengayer, and P. G. Thompson, *J. Amer. Chem. Soc.*, 1957, **79**, 4243; A. Perotti, M. Cola, and A. Parmigiani, *Gazzetta*, 1960, **90**, 1020; J. Goubeau and H. Lehmann, *Z. anorg. Chem.*, 1963, **322**, 224; H. A. Lehmann, G. Kessler, P. Denecke, and G. Nickl, *ibid.*, 1965, **340**, 16; U. Kibbel, *ibid.*, 1968, **359**, 272; *Z. Chem.*, 1964, **4**, 104; 1965, **5**, 395; A. Perotti and G. P. Caccini, 1965, Thesis, University of Pavia, Italy; A. Perotti and P. Salvini, 1966, Thesis, University of Pavia, Italy.

[2] A. Dal Negro, L. Ungaretti, and A. Perotti, *J.C.S. Dalton*, 1972, 1639.

[3] A. Dal Negro, C. Sabelli, and L. Ungaretti, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1969, **47**, 353; *Naturwiss.*, 1973, **60**, 350; *Amer. Mineral.*, 1971, **56**, 1553; A. Dal Negro, I. Kumbasar, and L. Ungaretti, *ibid.*, 1973, **58**, 1034; E. Cannillo, A. Dal Negro, and L. Ungaretti, *ibid.*, p. 110.

[4] J. E. Davies and B. M. Gatehouse, *Acta Cryst.*, 1973, **B29**, 1934.

[5] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[6] I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing, *Acta Cryst.*, 1958, **11**, 257.

[7] Program ORFLS, W. R. Busing, K. O. Martin, and H. A. Levy, 1962, U.S. Clearing House Fed. Sci. Technol. Inform. Report ORNL TM 306.

calculations were taken from ref. 8. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21279 (11 pp., 1 microfiche).* Final atomic and thermal parameters for non-hydrogen atoms are listed in Tables 1 and 2, and positional parameters for hydrogen atoms in Table 3.

TABLE 1

Final atomic co-ordinates, with standard deviations in parentheses, and equivalent isotropic temperature factors *

Atom	x/a	y/b	z/c	$B_H/Å^2$
K	0·2072(1)	0·7121(1)	0·9594(2)	3·88
B	0·1583(6)	0·8105(8)	0·4345(17)	3·16
O(1)	0·2360(3)	0·8032(4)	0·5712(7)	3·27
O(2)	0·1105(3)	0·8423(4)	0·5961(7)	3·38
O(3)	0·1557(3)	0·8821(4)	0·2414(7)	3·10
O(4)	0·1349(3)	0·7061(4)	0·3273(7)	3·22
O(5)	0·3089(3)	0·7991(4)	0·2982(9)	4·63
O(6)	0·1151(3)	0·6115(4)	0·6262(10)	5·50
O(7)	0·2184(3)	1·0241(4)	0·4139(9)	4·98
O(8)	−0·0013(3)	0·8481(5)	0·3611(10)	6·83
C(1)	0·3031(5)	0·8100(6)	0·4932(15)	3·29
C(2)	0·0340(6)	0·8517(7)	0·5450(15)	4·54
C(3)	0·1882(4)	0·9794(7)	0·2473(13)	3·06
C(4)	0·1113(4)	0·6196(6)	0·4251(15)	3·35
C(5) †	0·3698(4)	0·8299(7)	0·6708(12)	5·45
C(6) †	−0·0059(5)	0·8645(7)	0·7508(14)	6·37
C(7) †	0·1830(5)	1·0299(5)	0·0169(13)	4·96
C(8) †	0·0784(5)	0·5354(6)	0·2668(12)	4·72

* From W. C. Hamilton, *Acta Cryst.*, 1959, **12**, 609. † Methyl carbon atoms.

TABLE 2

Final anisotropic thermal parameters (× 10⁴),* with their standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	52(1)	64(2)	98(6)	1(1)	18(2)	3(3)
B	31(5)	45(9)	205(42)	−2(5)	11(12)	19(16)
O(1)	30(2)	74(5)	112(17)	−1(3)	12(6)	5(8)
O(2)	29(2)	70(5)	168(21)	6(3)	19(6)	−16(7)
O(3)	39(3)	46(4)	111(20)	−8(3)	5(5)	3(8)
O(4)	43(2)	43(4)	137(18)	−10(3)	26(5)	−13(9)
O(5)	44(3)	95(5)	203(21)	2(3)	36(6)	−34(10)
O(6)	76(4)	81(6)	161(22)	−27(3)	22(7)	8(10)
O(7)	60(3)	64(5)	221(23)	−12(3)	−16(6)	−20(9)
O(8)	43(2)	180(8)	244(27)	−7(4)	−21(7)	−54(12)
C(1)	31(4)	26(7)	308(42)	1(4)	17(11)	5(14)
C(2)	44(6)	83(9)	239(48)	8(6)	40(12)	−48(15)
C(3)	25(4)	54(8)	207(40)	6(5)	27(9)	18(14)
C(4)	32(4)	41(8)	250(40)	−13(5)	9(9)	−17(16)
C(5)	29(4)	127(10)	311(33)	2(5)	−17(9)	−17(15)
C(6)	38(4)	153(11)	346(39)	4(6)	20(10)	−32(17)
C(7)	80(5)	38(7)	211(35)	−21(5)	40(10)	18(13)
C(8)	52(4)	63(8)	259(33)	−19(5)	8(9)	−24(14)

* In the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

TABLE 3

Hydrogen atom co-ordinates

Atom	x/a	y/b	z/c
H(1)	0·209	0·970	−0·050
H(2)	0·200	1·100	−0·040
H(3)	0·130	0·990	−0·060
H(4)	0·029	0·835	0·885
H(5)	0·0	0·945	0·765
H(6)	−0·062	0·852	0·703
H(7)	0·078	0·550	0·110
H(8)	0·027	0·502	0·285
H(9)	0·110	0·470	0·285
H(10)	0·368	0·895	0·760
H(11)	0·423	0·833	0·600
H(12)	0·389	0·772	0·785

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

DISCUSSION

Figure 1 shows the crystal structure and the tetrahedral environment of the boron atom. Each boron–oxygen tetrahedron, which forms the basic unit of the $[B(OAc)_4]^-$ anion, is built up by a boron atom bonded to four oxygen atoms, one from each acetoxy-group. In the BO_4 tetrahedron the B–O distances (mean 1·472 Å) and the O–B–O angles (Table 4; mean 109·5°) are as expected for such an environment, but O(1)–B–O(2) and O(3)–B–O(4) are significantly less than the mean (103·1 and 102·3°). This is because the two pairs of oxygen atoms [*i.e.* O(1) and O(2), and O(3) and O(4)] are oppositely attracted by two different potassium atoms (Figures 2 and 3); consequently the other O–B–O angles are enlarged and the tetrahedron slightly distorted.

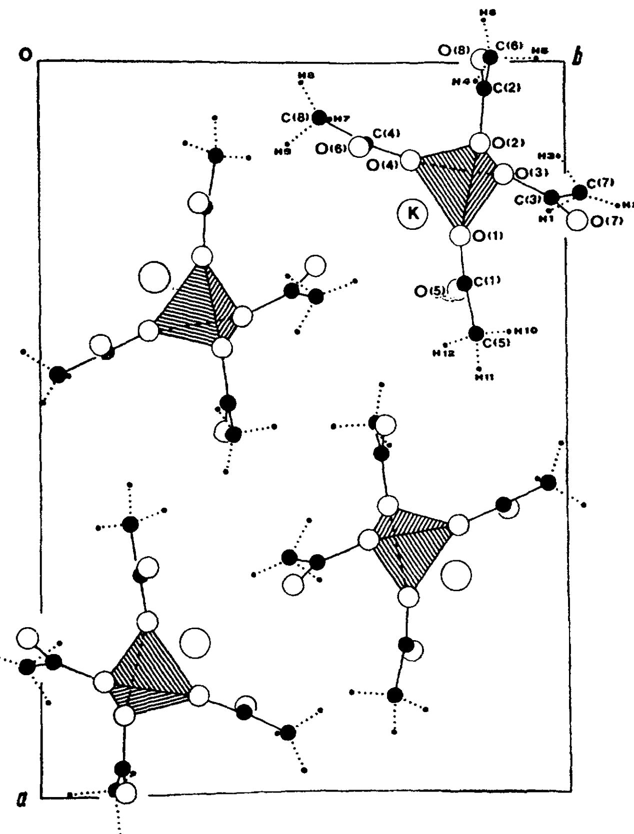

FIGURE 1 Projection down *c* of the unit-cell contents. Boron atoms (not drawn) are in the centre of each tetrahedron

The B–O and C–O bond lengths are interdependent and also sensitive to the K–O distances: C(1)–O(1) is the longest, and K–O(1) is the shortest of the K–O distances involving oxygen atoms of the BO_4 tetrahedron; B–O(1) is one of the longest B–O distances.

[8] H. P. Hanson, F. Herman, I. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1041.

The shortest of the C–O bonds is C(4)–O(4), whereas B–O(4) is the longest B–O bond, and K–O(4) is longer than K–O(1). Finally, C(2)–O(2) and C(3)–O(3) have the same length, intermediate between C(1)–O(1) and C(4)–O(4), since although B–O(2) is shorter than B–O(3), K–O(2) is longer than K–O(3). Whereas all the oxygen atoms of the BO_4 tetrahedron are also co-ordinated to the potassium, only three of every four carbonyl oxygen atoms of the acetoxy-groups are involved in such co-ordination. The C=O bond lengths are therefore mainly related to the K–O distances: O(8), which does not co-ordinate to potassium, forms the shortest (1·183 Å) C=O bond; O(5) and O(6) which form long and nearly equal C=O bonds [C(1)=O(5) and C(4)=O(6)] also have the shortest K–O contacts. The C(3)=O(7) bond (1·198 Å) is intermediate in length, close to the accepted value for organic carboxylic acids.[9] In general we conclude that the shorter K–O, the longer is the corresponding C=O distance, and *vice versa*.

TABLE 4

Bond lengths (Å) involving non-hydrogen atoms, with standard deviations in parentheses

(*a*) Distances

K–O(1)	2·749(5)	B–O(1)	1·478(9)
K–O(2)	3·018(5)	B–O(2)	1·459(9)
K–O(3′)	2·969(5)	B–O(3)	1·470(9)
K–O(4′)	2·768(5)	B–O(4)	1·481(9)
K–O(5′)	2·712(5)	Mean	1·472
K–O(6)	2·679(6)		
K–O(7″)	2·729(5)		
C(1)–O(1)	1·355(8)	C(2)–O(2)	1·339(9)
C(1)–O(5)	1·217(8)	C(2)–O(8)	1·183(8)
C(1)–C(5)	1·473(9)	C(2)–C(6)	1·541(9)
C(3)–O(3)	1·339(8)	C(4)–O(4)	1·333(8)
C(3)–O(7)	1·198(8)	C(4)–O(6)	1·219(8)
C(3)–C(7)	1·526(9)	C(4)–C(8)	1·474(9)

(*b*) Angles O–K–O and O–B–O (°, all ±0·30°)

O(1)–K–O(2)	46·7	O(6)–K–O(7″)	90·6
O(1)–K–O(6)	73·8	O(3′)–K–O(4′)	47·1
O(1)–K–O(3′)	108·9	O(3′)–K–O(5′)	60·3
O(1)–K–O(4′)	152·7	O(3′)–K–O(7″)	129·0
O(1)–K–O(5′)	106·9	O(4′)–K–O(5′)	74·5
O(1)–K–O(7″)	116·4	O)4′)–K–O(7″)	90·9
O(2)–K–O(6)	60·4	O(5′)–K–O(7″)	84·6
O(2)–K–O(3′)	81·3		
O(2)–K–O(4′)	109·0	O(1)–B–O(2)	103·1
O(2)–K–O(5′)	123·8	O(1)–B–O(3)	112·6
O(2)–K–O(7″)	148·2	O(1)–B–O(4)	110·6
O(6)–K–O(3′)	124·4	O(2)–B–O(3)	115·8
O(6)–K–O(4′)	107·2	O(2)–B–O(4)	112·7
O(6)–K–O(5′)	175·0	O(3)–B–O(4)	102·3
		Mean	109·5

(*c*) Angles in acetoxy-groups (°, all ±0·35°)

O(1)–C(1)–O(5)	124·3	O(3)–C(3)–O(7)	124·7
O(1)–C(1)–C(5)	112·9	O(3)–C(3)–C(7)	113·1
O(5)–C(1)–C(5)	122·8	O(7)–C(3)–C(7)	122·2
Mean	120·0	Mean	120·0
O(2)–C(2)–O(8)	124·0	O(4)–C(4)–O(6)	123·3
O(2)–C(2)–C(6)	114·0	O(4)–C(4)–C(8)	113·7
O(8)–C(2)–C(6)	121·9	O(6)–C(4)–C(8)	122·9
Mean	120·0	Mean	120·0

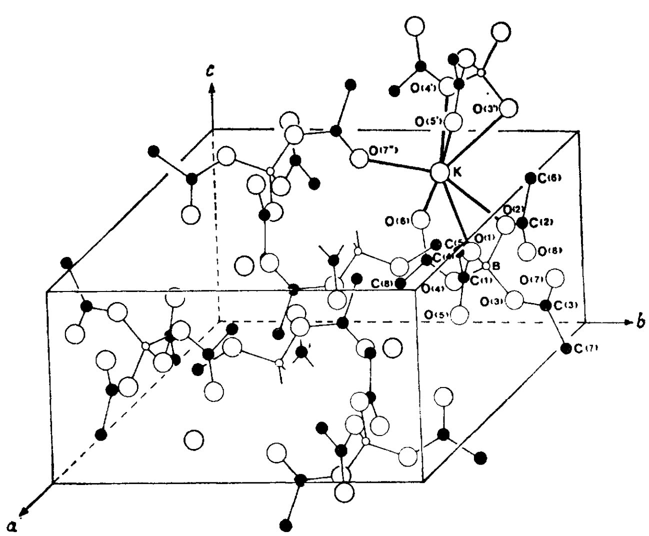

FIGURE 2 Clinographic projection of the unit cell showing the potassium co-ordination. Primed atoms are at *x*, *y*, 1 + *z*, and double primed atoms at ½ − *x*, *y* − ½, $\frac{3}{2}$ − *z*

The C–C are mainly dependent on C=O bond lengths, the longest and shortest of each corresponding: *i.e.* C(2)–C(6) with C(2)=O(8), C(1)–C(5) with C(1)=O(5), and C(4)–C(8) with C(4)=O(6).

Bond angles involving oxygen and carbon atoms for the acetoxy-groups are listed in Table 4; the acetoxy-groups are nearly planar, with a maximum deviation from the plane of 0·009(7) Å (Table 5). Interatomic distances and bond angles involving hydrogen atoms are listed in Table 6.

TABLE 5

(*a*) Equation * of planes through acetoxy-groups, in the form $Ax + By + Cz = D$

	A	*B*	*C*	*D*
Plane (1) O(1), O(5), C(1), C(5)	−1·9270	12·2657	−0·6971	9·0009
Plane (2) O(2), O(8), C(2), C(6)	1·6939	12·3714	−0·4977	10·3139
Plane (3) O(3), O(7), C(3), C(7)	−15·9582	5·2252	1·4996	2·4861
Plane (4) O(4), O(6), C(4), C(8)	−16·0575	5·1200	0·5579	1·6293

(*b*) Deviations (Å) of atoms from planes

Plane (1): O(1) −0·002(4), O(5) −0·002(4), C(1) 0·006(6), C(5) −0·002(7)

Plane (2): O(2) −0·003(4), O(8) −0·004(5), C(2) 0·009(7), C(6) −0·002(7)

Plane (3): O(3) 0·001(4), O(7) 0·001(4), C(3) −0·001(6), C(7) 0·001(7)

Plane (4): O(4) 0·002(4), O(6) 0·003(4), C(4) −0·007(6), C(8) 0·002(7)

* *x*, *y*, *z* are the fractional co-ordinates of the atoms, and *D* is the distance (Å) of the planes from the origin.

The Potassium Co-ordination.—Each K^+ ion is linked (Figure 2) to three anionic units as follows: to one *via* a carbonyl oxygen [O(7″)], and to the second and third

[9] See *e.g.*, J. Sime, J. C. Speakman, and R. Parthasaraty, *J. Chem. Soc.* (*A*), 1970, 1919.

via two oxygen atoms of the BO_4 tetrahedron [O(1), O(2) and O(3′), O(4′)] and one carbonyl oxygen [O(6) and O(5′)]. Each potassium atom thus has sevenfold co-ordination; one oxygen atom for every anionic unit [O(8)] does not participate in the potassium co-ordination. The minimum K · · · O(8) contact is 5·00 Å.

TABLE 6

Geometry of C–H bonds

(*a*) Distances (Å)			
C(7)–H(1)	1·00	C(6)–H(4)	1·01
C(7)–H(2)	1·00	C(6)–H(5)	1·01
C(7)–H(3)	1·09	C(6)–H(6)	0·99
C(8)–H(7)	0·97	C(5)–H(10)	0·98
C(8)–H(8)	1·02	C(5)–H(11)	1·10
C(8)–H(9)	0·98	C(5)–H(12)	1·02
(*b*) Angles (°)			
H(1)–C(7)–H(2)	108·9	H(4)–C(6)–H(5)	104·3
H(1)–C(7)–H(3)	84·8	H(4)–C(6)–H(6)	127·5
H(2)–C(7)–H(3)	122·5	H(5)–C(6)–H(6)	105·4
C(3)–C(7)–H(1)	96·5	C(2)–C(6)–H(4)	108·8
C(3)–C(7)–H(2)	134·6	C(2)–C(6)–H(5)	97·2
C(3)–C(7)–H(3)	96·9	C(2)–C(6)–H(6)	109·2
H(7)–C(8)–H(8)	109·2	H(10)–C(5)–H(11)	107·5
H(7)–C(8)–H(9)	99·9	H(10)–C(5)–H(12)	104·3
H(8)–C(8)–H(9)	98·6	H(11)–C(5)–H(12)	95·0
C(4)–C(8)–H(7)	116·3	C(1)–C(5)–H(10)	116·6
C(4)–C(8)–H(8)	118·4	C(1)–C(5)–H(11)	110·2
C(4)–C(8)–H(9)	111·4	C(1)–C(5)–H(12)	120·6

This co-ordination is strictly related to the BO_4 tetrahedra and to the acetoxy-groups' geometry. The O–K–O angles involving oxygen atoms which both belong to acetoxy-groups co-ordinated to the same boron atom are thus the smallest. Furthermore, the smallest among them [O(1)–K–O(2) 46·7 and O(3′)–K–O(4′) 47·1°] result because O(1), O(2) and O(3′), O(4′) belong to two BO_4 tetrahedra (Figure 3) in which the O · · · O distances are necessarily small.

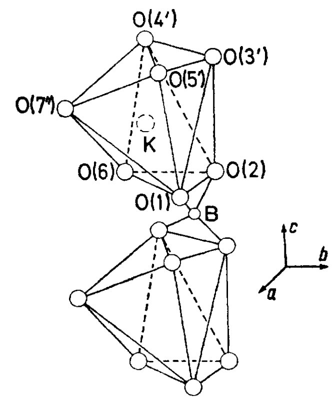

FIGURE 3 Potassium co-ordination pattern (in the same orientation as the clinographic projection of Figure 2)

As a result, the potassium co-ordination pattern consists of a ten-faced polyhedron, which can be considered as being derived from a highly distorted octahedron in which a vertex is split to give two vertices, namely O(2) and O(3′). The base is formed by the vertices O(1), O(6), O(4′), and O(5′), and the apical vertex is O(7″).

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