Crystal Structures of the Acid Salts of Some Monobasic Acids. Part XV.[1] Potassium Hydrogen Diacetate

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The crystal structure of the title compound $KH(AcO)_2$ has been determined by *X*-ray analysis and solved by the heavy-atom method. $Z = 4$ in a monoclinic unit cell of dimensions $a = 4{\cdot}085$, $b = 23{\cdot}84$, $c = 7{\cdot}226$ Å, $\beta = 97{\cdot}4°$, space group is $P2_1/n$. Refinement by anisotropic least-squares analysis has led to a final R of 0·106 for 849 data. This acid salt proves to be of Type *B*, *i.e.* the residues AcOH and AcO^- are crystallographically distinct; these residues are linked through a short unsymmetrical hydrogen bond, with $O \cdots O$ 2·476(8) Å.

THE acid sodium, potassium, and ammonium salts of acetic acid have totally different crystal structures. In the sodium salt,[2] $NaH(AcO)_2$, the $H(AcO)_2^-$anion has crystallographic symmetry, and hence is of Type *A*.[3] The ammonium salt[4] has a more complex structure, better represented by the formula $[NH_4^+H(AcO)_2^-,(NH_4^+\text{-}AcO^-,AcOH)_2]$. The $H(AcO)_2^-$ anion has a symmetrical hydrogen bond (Type *A*), whilst the bond between AcO^- and AcOH is unsymmetrical (Type *B*). The *X*-ray analysis of potassium hydrogen diacetate,

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[1] Part XIV, A. L. Macdonald, J. C. Speakman, and D. Hadži, preceding paper.

[2] J. C. Speakman and H. H. Mills, *J. Chem. Soc.*, 1961, 1164.

[3] For a note on classification see M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923.

[4] I. Nahringbauer, *Acta Chem. Scand.*, 1969, **23**, 1653.

$KH(AcO)_2$, which is now reported, shows the structure of this crystal to be of Type *B*, as had been suggested by its i.r. spectrum.

EXPERIMENTAL

Potassium hydrogen diacetate was prepared by heating an aqueous solution of potassium hydroxide (1 mol) and acetic acid (2 mol). The crystals were difficult to handle, tending to lose acetic acid, and were deliquescent. A crystal of dimensions *ca.* 0·60 × 0·25 × 0·15 (mm) had therefore to be enclosed in a capillary tube in order that *X*-ray measurements could be made.

The cell dimensions were established by means of a least-squares refinement of the positions of a number of reflexions as determined on a Hilger and Watts Y 290, computer-controlled, four-circle diffractometer by use of a Zr-filter to give Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å; 1Å = 100 pm).

Crystal Data.—$KH(C_2H_3O_2)_2$, $M = 158{\cdot}2$, Monoclinic, $a = 4{\cdot}085(5)$, $b = 23{\cdot}84(4)$, $c = 7{\cdot}226(7)$ Å, $\beta = 97{\cdot}4°(0{\cdot}1°)$, $U = 697{\cdot}75$ Å^3, $Z = 4$, $D_c = 1{\cdot}506$. μ(Mo-K_α) = 6·96 cm^{-1}. Space group $P2_1/n(C_{2h}^5)$; no molecular symmetry required.

The intensities of 1226 independent reflexions (0—*h*, 0—*k*, *l*–*l*) out to $\theta = 25°$ were measured on the diffractometer by use of MoK_α radiation. An ω—2θ scan was carried out (80 steps of 0·01°, 1 s^{-1}) and 20 s were spent on each of two background counts.

Corrections for the Lorentz and polarization factors were applied to the intensities, but none was made for absorption, which was assumed to be negligible.

Structure Solution and Refinement.—The structure was solved by the heavy-atom method. Electron-density syntheses, based on K^+ only, enabled the location of all the remaining non-hydrogen atom positions.

Four cycles of full-matrix, least-squares refinement, with isotropic vibrational parameters and unit weights, reduced *R* from 0·282 to 0·202. At this stage a difference synthesis was computed, but no significant electron density was found where hydrogen atoms would be expected. After a further three cycles of least-squares refinement, with anisotropic vibrational parameters and unit weights, *R* was reduced to 0·141. For the final five cycles of refinement all data with $I < 3\sigma(I)$ were excluded, and a weighting scheme introduced, such that $w = 1$ for $|F_o| < p$, and $w = \left(\frac{p}{|F_o|}\right)^2$ for $|F_o| > p$; the final value of *p* was 10. Refinement converged with *R* 0·106 and *R′* 0·015 ($R' = \Sigma w\Delta^2/\Sigma w|F_o|^2$) for 849 data. Atom scattering factors for potassium, oxygen, and carbon were taken from ref. 5. Observed structure amplitudes and calculated structure factors are listed in Supplementary Publication No. SUP 20349 (2 pp., 1 microfiche).* Table 1 gives an analysis of the agreement between $|F_o|$ and $|F_c|$. It supports the general validity of the weighting scheme used.

The atomic co-ordinates are listed in Table 2, and vibrational parameters in Table 3 (estimated standard deviations were derived from the inverse of the least-squares matrix).

TABLE 1

Analysis of the agreement of observed and calculated structure factors at the end of the refinement. Structure factors are on the absolute scale

(*a*) As a function of $|F_o|$

Range of $\lvert F_o\rvert$	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	N*	R	$\Sigma\lvert\Delta\rvert/N$
0—5	627	592	114	154	0·182	0·74
5—10	2262	2299	213	310	0·094	0·69
10—20	3242	3282	250	236	0·077	1·06
20—40	3065	3007	308	114	0·101	2·70
Over 40	2089	1956	316	35	0·151	9·04

(*b*) As a function of sin θ/λ

Range of (sin θ) λ						
0·0—0·1	186	161	25	5	0·136	5·06
0·1—0·2	1299	1218	210	39	0·162	5·39
0·2—0·3	2574	2513	365	106	0·142	3·44
0·3—0·4	2462	2508	193	174	0·078	1·11
0·4—0·5	2630	2648	198	248	0·075	0·80
0·5—0·6	2134	2088	210	277	0·098	0·76
All data	11,285	11,135	1202	849	0·106	1·42

* *N* is no. of reflexions.

TABLE 2

Fractional co-ordinates (× 10^5) and absolute orthogonal co-ordinates (in 10^{-3} Å),* with standard deviations in parentheses

	x	*y*	*z*	*X′*	*Y*	*Z′*
K^+	455	21,732	24,710	18(2)	5181(2)	1783(2)
O(1)	52,488	13,625	25,231	2126(6)	3248(6)	1547(6)
O(2)	33,918	8703	47,502	1374(8)	2075(6)	3254(5)
O(11)	1516	21,311	86,476	61(6)	5080(5)	6241(5)
O(12)	18,893	17,636	61,713	765(7)	4204(6)	4360(5)
C(1)	48,106	9178	32,623	1949(9)	2188(8)	2104(8)
C(2)	59,139	3680	25,088	2396(12)	877(10)	1502(9)
C(11)	7052	17,127	77,008	286(8)	4083(8)	5528(7)
C(12)	−1165	11,432	83,588	−47(10)	2725(9)	6046(8)

* Where $X' = ax \sin\beta$ and $Z' = cz + ax \cos\beta$.

TABLE 3

Anisotropic vibrational parameters (Å^2 × 10^3) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
K^+	66(1)	41(1)	30(1)	0(1)	13(1)	−1(2)
O(1)	87(5)	46(3)	53(4)	9(6)	37(6)	−4(6)
O(2)	127(6)	47(3)	35(3)	4(5)	54(7)	7(7)
O(11)	81(4)	42(3)	37(3)	6(5)	21(5)	−10(6)
O(12)	113(5)	45(3)	26(3)	−4(5)	38(6)	0(6)
C(1)	74(6)	42(4)	34(4)	−8(7)	10(7)	−3(8)
C(2)	111(9)	48(5)	63(6)	−9(9)	69(12)	17(10)
C(11)	60(6)	41(4)	26(3)	6(6)	8(7)	−6(7)
C(12)	96(7)	46(5)	41(5)	−1(8)	29(8)	23(9)

DISCUSSION

The Figure shows the structure in its *a* axial projection. The atoms numbered constitute the crystal-chemical unit (CCU);[6] other symmetry-related units are denoted as follows:

CCU *x*, *y*, *z*
I $-1 + x, y, z$
II $x, y, -1 + z$
III $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
IV $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

In an acid salt of Type *B*, in which there are two non-equivalent residues, one should be recognisable as the neutral molecule AcOH and the other as the anion AcO$^-$; this distinction is apparent in potassium hydrogen

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[5] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[6] J. D. H. Donnay, O. Kennard, and J. C. Speakman, *Acta Cryst.*, 1967, **22**, 445.

diacetate (Table 4). In one residue, comprising C(1), C(2), O(1), and O(2), the C–O distances differ by 0·079 Å, and the C–C–O angles by 7·9°, and it may be concluded that this is the uncharged molecule AcOH. In the other residue, comprising C(11), C(12), O(11), and O(12), the C–O distances differ by only 0·021 Å, and the C–C–O angles by only 0·2°, which leads to the conclusion that this residue is the carboxylate ion AcO^-. A similar situation is found in other acid salts of Type *B*, *e.g.* rubidium hydrogen di(glycollate),[7] and in acid salts of Type B_2, *e.g.* sodium hydrogen oxalate monohydrate.[8]

TABLE 4

Interatomic distances (Å) and bond angles (deg.), with standard deviations in parentheses

(*a*) Distances

C(1)–C(2)	1·510(13)	C(11)–C(12)	1·491(12)
C(1)–O(1)	1·211(10)	C(11)–O(11)	1·247(9)
C(1)–O(2)	1·290(10)	C(11)–O(12)	1·268(9)
O(2) · · · O(12)	2·476(8) Å		

(*b*) Angles

O(1)–C(1)–O(2)	123·5(8)	O(11)–C(11)–O(12)	121·2(7)
C(2)–C(1)–O(2)	114·3(7)	C(12)–C(11)–O(12)	119·5(7)
C(2)–C(1)–O(1)	122·2(8)	C(12)–C(11)–O(11)	119·3(6)
		C(1)–O(2) · · · O(12)	115·6(5)
		C(11)–O(12) · · · O(2)	115·0(5)

The AcOH and AcO^- residues are linked through a non-symmetrical hydrogen bond, O(2) · · · O(12) 2·476(8) Å. This may be compared with O · · · O distances of 2·444(10) Å (Type *A*) in $NaH(AcO)_2$,[2] and of 2·474(6) Å (Type *A*) and 2·517(4) Å (Type *B*) in the ammonium salt.[4]

TABLE 5

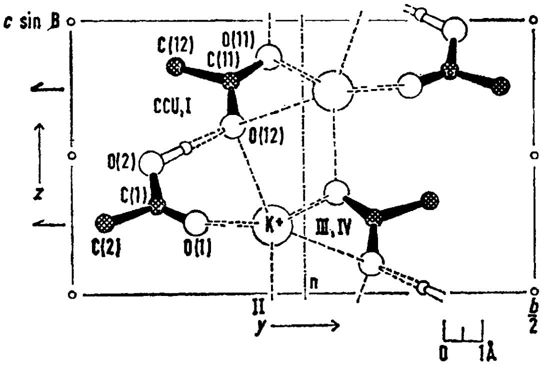
The environment of the potassium ion

K+ · · · O distances (Å)		O · · · K+ · · · O angles (deg.) *						
		O(1)	O(1^{I})	O(11^{II})	O(11^{III})	O(11^{IV})	O(12)	O(12^{IV})
O(1)	2·870(7)		93·1	83·2	82·5	161·4	69·6	151·4
O(1^{I})	2·756(7)			95·2	160·6	82·8	81·4	109·0
O(11^{II})	2·771(6)				103·0	115·2	152·3	77·0
O(11^{III})	2·714(6)					95·3	79·4	82·0
O(11^{IV})	2·812(6)						91·8	44·7
O(12)	2·855(5)							130·2
O(12^{IV})	2·942(5)							

* $\sigma \leqslant 0{\cdot}2°$.

The non-hydrogen atoms of each residue are virtually coplanar. The equation of the plane through AcOH is $-0{\cdot}8863\ X' - 0{\cdot}0921\ Y - 0{\cdot}4539\ Z' = -2{\cdot}885$ Å, and the maximum deviation from it is 0·002 Å for C(1). The equation of the plane through AcO^- is $-0{\cdot}9222\ X' + 0{\cdot}0741\ Y - 0{\cdot}3796\ Z' = -2{\cdot}052$ Å, with a maximum deviation from it of 0·007 Å for C(11).

The C–C distances, C(1)–C(2) 1·510(13) and C(11)–C(12) 1·491(12) Å, do not significantly differ from the length 1·505 Å suggested [9] for a single bond between sp^3 and sp^2 carbon atoms, and are similar to those found [2] in $NaH(AcO)_2$ (1·49 Å) and in the ammonium salt [4] (mean 1·50 Å). A comparison with the corresponding bond in potassium hydrogen bis(trifluoroacetate),[1] C–C 1·543 Å (neutron-diffraction analysis), shows that the substitution of the methyl group by a trifluoromethyl group causes a lengthening of the C–C bond; a similar effect is found when ammonium acetate [10] (C–C 1·504 Å) and ammonium trifluoroacetate [11] (C–C 1·535 Å) are compared.



The crystal structure of potassium hydrogen diacetate in its *a* axial projection

The potassium ion makes contact with seven oxygen atoms. The K+ · · · O distances, which are all <3·0 Å, are given in Table 5 along with the O · · · K+ · · · O angles.

There are no unusual non-bonded intermolecular contacts in the structure, the shortest being O(2) · · · C(2^{I}) 3·481 and O(1) · · · C(12^{II}) 3·526 Å.

The very different crystal structures of the acid sodium, potassium, and ammonium salts of acetic acid are not surprising in view of the relatively small size of the acid residues. It is generally found that, when the acid residue is large, it dominates the crystal structure, *e.g.* potassium, ammonium, and rubidium hydrogen bis-(*p*-chlorobenzoate) [12] are all isomorphous. Indeed, even changing the position of the chlorine atom in the phenyl ring has little effect, and the crystal structures of potassium hydrogen bis-(*p*-chlorobenzoate) and potassium

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[7] L. Golič and J. C. Speakman, *J. Chem. Soc.*, 1965, 2521.

[8] R. Tellgren and I. Olovsson, *J. Chem. Phys.*, 1971, **54**, 127.

[9] M. G. Brown, *Trans. Faraday Soc.*, 1959, **55**, 694.

[10] I. Nahringbauer, *Acta Cryst.*, 1967, **23**, 956.

[11] D. W. J. Cruickshank, D. W. Jones, and G. Walker, *J. Chem. Soc.*, 1964, 1303.

[12] H. H. Mills and J. C. Speakman, *J. Chem. Soc.*, 1963, 4355.

hydrogen bis-(*m*-chlorobenzoate) are remarkably similar.[13] In contrast, the crystal structures of the acid lithium,[14] sodium,[8] and potassium [15] salts of oxalic acid, the simplest of the dibasic acids, all differ considerably from one another.

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[13] A. L. Macdonald and J. C. Speakman, to be published.

[14] H. Follner, *Z. anorg. Chem.*, 1970, **373**, 198; J. O. Thomas, unpublished results.

[15] B. F. Pederson, *Acta Chem. Scand.*, 1968, **22**, 2953.