Crystal Structures of the Acid Salts of Some Dibasic Acids. Part VII.[1] An *X*-Ray Study of Potassium Hydrogen Acetylenedicarboxylate: the α-Form

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The title compound crystallises with $Z = 4$ in a cell with $a = 7{\cdot}954$, $b = 11{\cdot}926$, $c = 5{\cdot}918$ Å, $\beta = 105{\cdot}4°$, space group $I2/a$. The structure, refined to R 6·0% for 796 reflexions, whose intensities were estimated visually, is of Type A_2: hydrogen-anions, lying across two-fold axes, are linked into infinite chains by very short hydrogen bonds which also lie across two-fold axes [$O \cdots H \cdots O$ 2·445(3) Å].

ACID salts of acetylenedicarboxylic acid ($H_2adc = HO_2C{\cdot}C{:}C{\cdot}CO_2H$) are being studied as part of a project for examining the acid salts of dicarboxylic acids in a search for 'very short' hydrogen bonds. The acid potassium salt KH(adc) is of special interest because it contains only the one hydrogen atom likely to be involved in $O \cdots H \cdots O$ bonding, which should simplify the interpretation of its spectrum. KH(adc) has been known for about a century.[2] Its i.r. spectrum (Figure 1) is of Hadži's Type (ii),[3] which suggested that the crystal structure would probably (though not certainly) be of the symmetrical Type A_2.[4]

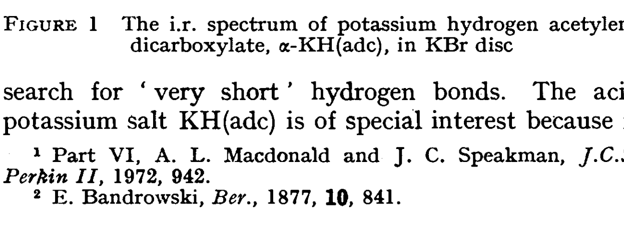

FIGURE 1 The i.r. spectrum of potassium hydrogen acetylene dicarboxylate, α-KH(adc), in KBr disc

EXPERIMENTAL

KH(adc) was prepared by evaporation of an aqueous solution of the commercial material. Good crystals of prismatic habit were obtained from 50% (w) aqueous methyl cyanide. Crystal data were obtained by use of Cu-K_α radiation [$\lambda(\alpha_1) = 1{\cdot}5405$ Å], with a least-squares treatment of high-order reflexions whose sin θ values were compared with those due to powder-lines of Al-wire, for which a was taken as 4·04907 Å.

Crystal Data.—KHC_2O_4, $M = 152{\cdot}2$. Monoclinic, $a = 7{\cdot}954(2)$, $b = 11{\cdot}926(2)$, $c = 5{\cdot}918(2)$ Å, $\beta = 105{\cdot}40(0{\cdot}02)°$,

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[1] Part VI, A. L. Macdonald and J. C. Speakman, *J.C.S. Perkin II*, 1972, 942.

[2] E. Bandrowski, *Ber.*, 1877, **10**, 841.

[3] D. Hadži, *Pure and Appl. Chem.*, 1965, **11**, 435.

[4] M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923.

$U_o = 541{\cdot}3$ Å^3, $D_m = 1{\cdot}84(3)$, $Z = 4$, $D_c = 1{\cdot}867$. μ(Cu-K_α) = 79 cm^{-1}. μ(Mo-K_α) = 8·9 cm^{-1}. Diffraction symbol [5] $I*/a$: the space group $I2/a$ (No. 15), which was implied by the Patterson function, has been borne out by the structure analysis. Our choice of axes corresponds to the equivalent positions $(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \pm (x,y,z;\ x,\ -y,\ \tfrac{1}{2}+z)$.

Samples of RbH(adc) and NH_4H(adc) were also made in Ljubljana. They proved to be isomorphous with the α-form of KH(adc) described here. Their crystal data are more conveniently given in the ensuing paper (Part VIII).

Structure Analysis.—Intensities were estimated visually for *ca.* 2100 reflexions recorded on multiple-exposure sets of precession photographs, by use of Mo-K_α radiation. Reciprocal-lattice nets covered were $hk0$—2, $h0$—3l and 0—3kl, together with diagonal nets hkl up to fifth order. After the usual corrections, cross-scaling and averaging, 796 independent structure amplitudes were obtained, 96% of those that would have been accessible to Cu-radiation.

With $Z = 4$, the space group $I2/a$ requires the potassium ion, the hydrogen atom, and the mid-point of the triple bond to lie in special positions. The unsharpened Patterson function was successfully interpreted on the basis that each of these three structural features occupied a set of four-fold positions, $0,y,\tfrac{1}{4}$ [(*e*) of ref. 6]. Positions for all the atoms, except hydrogen, were also easily found from the Patterson function. Refinement was by full-matrix least-squares, using a version of the program ORFLS modified by Shiono.[7] In the later cycles anisotropic vibrational parameters were allocated to all atoms other than hydrogen, and 12 scale-factors were refined. The weighting-scheme, due to Cruickshank,[8] had $w = (A + B|F_o| + C|F_o|^2)^{-1}$; the constants were adjusted during refinement, and had values $A = 0{\cdot}18$, $B = 0{\cdot}02$, and $C = 0{\cdot}01$ in the final cycles. Atomic scattering factors [6] included an anomalous-dispersion correction for K^+. At convergence R was 6%, with R' $(= [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{\frac{1}{2}})$ 9·9%. Structure-amplitudes are listed in Supplementary Publication No. SUP 20654 (2 pp., 1 microfiche).† Table 1 contains an agreement analysis.

TABLE 1

Analysis of agreement between observed and calculated structure amplitudes at the end of the refinement. Structure amplitudes are on the absolute scale $\Sigma|F_c|/\Sigma|F_o| = 1{\cdot}004$

Range of sin θ	N *	R(%)	$\overline{w\Delta^2}$
0·0—0·1	5	7·3	1·13
0·1—0·2	46	7·2	1·19
0·2—0·3	116	5·0	0·61
0·3—0·4	228	5·5	0·79
0·4—0·5	296	6·2	0·48
0·5—0·6	103	7·5	0·43
0·6—0·7	2	12·5	0·78

* N is the no. of reflexions of the group.

DISCUSSION

Description of the Structure.—Figures 2 and 3 show the main features of the structure, and explain the atom-numbering scheme. Final positional and vibrational parameters are listed in Tables 2 and 3.

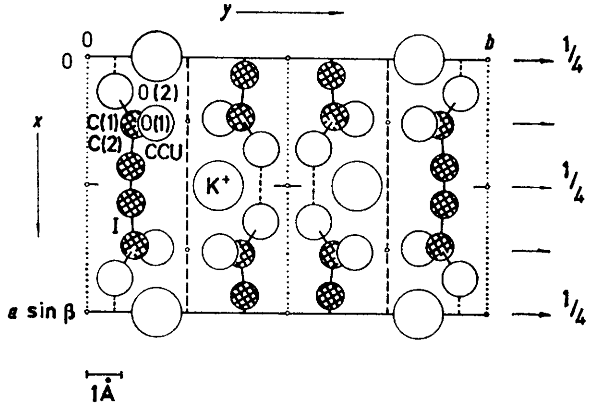

FIGURE 2 The structure of α-KH(adc) in its c-axial projection

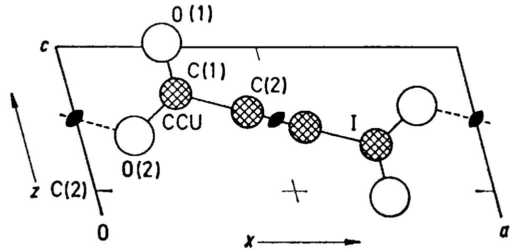

FIGURE 3 The hydrogen-anion in its b-axial projection

KH(adc), in the α-form, is a clear example of a Type A_2 acid salt. It consists of hydrogen-anions, linked at either end by short hydrogen bonds into infinite chains

TABLE 2

Fractional co-ordinates (×10^5) of atoms in the crystal chemical unit (CCU) with standard deviations in parentheses

	x	y	z
K+	50000	32833(8)	25000
O(1)	26076(25)	17080(17)	101319(51)
O(2)	13804(25)	6870(17)	69585(34)
C(1)	26685(25)	11796(17)	83883(34)
C(2)	43227(25)	10853(25)	77509(51)
H	0	9139(520)	75000

TABLE 3

Vibrational parameters (U_{ij} are the tensor components for mean-square amplitude as 10^{-4} Å^2) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K+	295(5)	386(5)	272(10)	0	106(2)	0
O(1)	308(9)	464(11)	378(13)	−73(7)	158(8)	−151(8)
O(2)	211(8)	421(10)	317(12)	−14(6)	96(6)	−68(7)
C(1)	197(10)	289(11)	322(14)	12(7)	116(8)	13(7)
C(2)	210(10)	376(13)	344(15)	−26(9)	117(8)	−39(9)

H [B = 3·0 (isotropic)].

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† For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[5] J. D. H. Donnay and O. Kennard, *Acta Cryst.*, 1964, **17**, 1337.

[6] 'International Tables for *X*-Ray Crystallography,' vols. I and III, Kynoch Press, Birmingham, 1952.

[7] R. Shiono, Oak Ridge Least-Squares Program, modified for the Department of Crystallography of the University of Pittsburgh, 1966.

[8] D. W. J. Cruickshank, in 'Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 45.

in the x direction. The crystal symmetry elements at the centre of the O ··· H ··· O bond and of the C⋮C bond are both digonal axes. Formal differences occur in other Type A_2 structures: in potassium hydrogen malonate,[9] there is a digonal axis at the middle of the anion and a centre of inversion at the middle of the hydrogen bond, whilst in potassium hydrogen succinate,[10] the arrangement is converse.

The hydrogen bond has O ··· O 2·446(3) Å, a value virtually identical with that reported for potassium hydrogen glutarate and in good agreement with the weighted average of 2·451(2) Å for six Type A_2 acid salts.[1] The simple and highly symmetrical structure of KH(adc), with this very short O ··· H ··· O bond, matches the simple spectrum sketched in Figure 1.

The dimensions of the carboxylate group are included in Table 4. They are normal for a Type A crystal.

TABLE 4

Principal interatomic distances (Å) and angles (°) with standard deviations in parentheses

C(1)–O(1)	1·221(3)	O(1)–C(1)–O(2)	126·1(2)
C(1)–O(2)	1·285(3)	C(2)–C(1)–O(1)	119·8(2)
	Σ 2·506, Δ 0·064	C(2)–C(1)–O(2)	114·1(2)
C(1)–C(2)	1·466(3)	C(1)–C(2)–C(2^{I})	175·6(3)
C(2)–C(2^{I})	1·191(4)		
O(2) ··· O(^{VII})	2·446(3)	C(1)–O(2) ··· O(2^{VII})	116·2(3)
K^+ ··· O(1^{I}), O(1^{II})	2·774(2)		
K^+ ··· O(1^{III}), O(1^{IV})	2·794(2)		
K^+ ··· O(2^{V}), O(2^{VI})	2·852(2)		

Roman numerals as superscripts refer to the following equivalent positions relative to the CCU at x, y, z:

I	$1 - x, y, 1\frac{1}{2} - z$	V	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$
II	$x, y, -1 + z$	VI	$\frac{1}{2} + x, \frac{1}{2} - y, z$
III	$\frac{1}{2} - x, \frac{1}{2} - y, 1\frac{1}{2} - z$	VII	$-x, y, 1\frac{1}{2} - z$
IV	$\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$		

The mean plane of the four atoms C(1), C(2), O(1), and O(2) is represented by: $0{\cdot}0683\,X' - 0{\cdot}8362\,Y + 0{\cdot}5442\,Z' = 1{\cdot}4776$ Å.* The largest deviation from this plane is 0·005 Å for C(1); none of the deviations is significant.

The dihedral angle between the planes of the carboxy-group of the H(adc)$^-$ anion is 66°. This is in contrast to their coplanarity in the dihydrate of the free acid.[11] However, rotation about a C·C⋮C·C is probably free, so that the dihedral angle is dictated by environmental conditions. That the C(1)–C(2)–C(2^{I}) and the, equivalent, C(2)–C(2^{I})–C(1^{I}) angles differ very significantly from 180° may also be ascribed to packing.

The environment of the potassium ion is shown in Figure 4. It will be discussed in more detail in Part VIII. The three independent K^+ ··· O distances are included in Table 4.

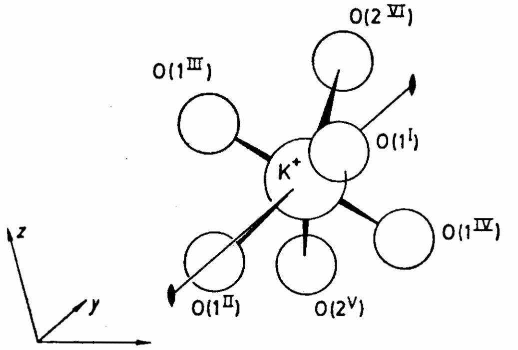

FIGURE 4 The environment of the potassium ion in α-KH(adc)

APPENDIX

Stimulated by a comment made by one of the Referees, we wish to amplify our discussion of the hydrogen bonding. The hydrogen atom was constrained to remain on a two-fold axis, but its y co-ordinate was allowed to vary. At convergence it had moved to a point 0·27 Å above the level of O(2) and O(2^{VII}), so that the ostensible value for the O ··· H ··· O angle is 156°. We regard this result as unacceptable in so short a hydrogen bond, and as yet another example of the pitfalls which beset the X-ray location of hydrogen atoms in special positions.[12] Potassium hydrogen succinate has a short O ··· H ··· O bond of identical symmetry.[10] In our X-ray work on this structure we constrained the y co-ordinate of the hydrogen to follow y for the oxygen atoms. In the neutron-diffraction refinement y was allowed to vary independently, but it converged to a value not significantly different from that of the oxygen atoms.

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* X', Y, and Z' are absolute co-ordinates with respect to orthogonal axes; $X' = ax + cz \cos \beta$, $Y = by$, and $Z' = cz \sin \beta$.

[9] J. G. Sime, J. C. Speakman, and R. Parthasarathy, *J. Chem. Soc.* (*A*), 1970, 1919.

[10] A. McAdam, M. Currie, and J. C. Speakman, *J. Chem. Soc.* (*A*), 1971, 1994.

[11] J. D. Dunitz and J. M. Robertson, *J. Chem. Soc.*, 1947, 148.

[12] A. L. Macdonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 825.