Potassium Fluoride–Malonic Acid, $KF{\cdot}CH_2(CO_2H)_2$: *X*-Ray Crystal Structure Determination and Infrared Spectrum reveals Very Short Hydrogen Bonds

By **John Emsley,* Deborah J. Jones,** and **Reiko Kuroda,** Department of Chemistry, King's College, Strand, London WC2R 2LS

Crystals of the adduct $KF{\cdot}CH_2(CO_2H)_2$, grown from aqueous solution, are unstable with evolution of HF. They show a remarkable cleavage. An *X*-ray crystal structure determination reveals a polymeric crystal arrangement of alternate malonic acid molecules and fluoride ions. Five different malonic acid–fluoride chains can be distinguished within the unit cell and there is a range of hydrogen bond lengths with $R(O \cdots F) = 2.41$—$2.49(4)$ Å. In most of these bonds one proton appears nearer the fluoride so that in effect the chains are composed of alternate HF molecules and hydrogen malonate ions, $[\cdots \overset{-}{O}_2C\text{–}CH_2\text{–}CO_2H \cdots F\text{–}H \cdots \overset{-}{O}_2C\text{–}CH_2\text{–}CO_2H \cdots F\text{–}H \cdots]_n$.

VERY short hydrogen bonds are mostly homonuclear such as those of HF_2^-, the dicarboxylates, $H(RCO_2)_2^-$, and several bis(oxo-anions).[1] The internuclear distances between the heavier atoms in these bonds are sometimes <2.40 Å.[2] Few instances of very short heteronuclear hydrogen bonds are known and even fewer have been investigated by *X*-ray diffraction. In our researches into the very short hydrogen bonding of the fluoride ion we have examined crystals of $KF{\cdot}(CH_2CO_2H)_2$ and $KF{\cdot}(CH_2CO_2D)_2$ and found $R(O \cdots F) = 2.44$ Å in both.[3] An even shorter $O \cdots F$ hydrogen bond of 2.38 Å was recorded in $KH_2PO_3{\cdot}HF$.[4] Other OHF bonds are around 2.60 Å or longer.[1] In this communication we report on the very short hydrogen bonds in crystals of composition $KF{\cdot}CH_2(CO_2H)_2$.

EXPERIMENTAL

Preparation of $KF{\cdot}CH_2(CO_2H)_2$.—Potassium fluoride (2.0 g, 0.034 mol) and malonic acid (3.58 g, 0.034 mol) were dissolved in warm water (10 cm³). The solution was filtered and allowed to cool to yield large transparent crystals of $KF{\cdot}CH_2(CO_2H)_2$, which were dried and stored *in vacuo*; on heating they decomposed at 168 °C (Found: C, 23.2; H, 2.45; F, 10.1. Calc. for $C_3H_4FKO_4$: C, 22.2; H, 2.45; F, 11.7%). Loss of HF on exposure to air is responsible for the discrepancy. Titration of the acid content of the crystals showed two acid protons per formula unit. When a saturated solution of $KF\text{–}CH_2(CO_2H)_2$ is left to crystallise in a shallow dish the crystals display a marked degree of creeping.[5] This results in a layer of crystals deposited on the surface of the bench surrounding the evaporating dish to a radius of a few cm.

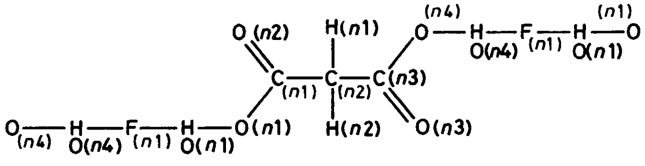
Reaction of KF *and Oxalic Acid*.—Potassium fluoride (0.25 g, 0.0043 mol) and oxalic acid (0.775 g, 0.0086 mol) were dissolved in water on heating. On slow cooling white cubic crystals of $KHC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O$ were deposited (Found: C, 18.9; H, 2.75. Calc. for $C_4H_7KO_{10}$: C, 18.9; H, 2.8%).

Crystal Data.—Crystals of $KF{\cdot}CH_2(CO_2H)_2$ are sensitive to the atmosphere and release HF. Although shiny and transparent when freshly prepared the loss of HF results in a material that gives a complete powder diffraction pattern. The crystals have a pronounced cleavage parallel to the crystal *bc* plane thus it was difficult to cut them to a size suitable for *X*-ray examination. The crystal employed in the *X*-ray diffraction work had dimensions 0.18 × 0.37 × 0.40 mm, and was sealed in a glass capillary tube.

$C_3H_4FKO_4$, $M = 162.16$, Monoclinic, space group *Cc*, $a = 19.463(3)$, $b = 18.920(3)$, $c = 8.735(1)$ Å, $\beta = 112.5(1)°$, $U = 2\,971.73$ Å³, $Z = 20$, $D_c = 1.812$ g cm^{-3}, $F(000) = 1\,640$, $\mu(\text{Mo-}K_\alpha) = 7.77$ cm^{-1}.

The symmetry and unit cell parameters were determined from Weissenberg photographs and subsequently refined on a diffractometer. Despite the sealing of the crystal in a capillary tube some deterioration was apparent from the *ca.* 10% loss of standard reflections over the period of data collection.

Intensity data were collected, employing θ—2θ scan mode, to a maximum θ of 30° with Mo-K_α radiation ($\lambda = 0.7107$ Å) using an Enraf-Nonius CAD 4 diffractometer; 4 821 reflections were observed of which 4 708 were unique. The structure was solved and refined using the program SHELX (written by Professor G. Sheldrick). The atomic scattering factors for non-hydrogen and hydrogen atoms were taken from refs. 6 and 7 respectively. The CH protons could not be located and were placed in ideal positions. Hydrogen bonded protons were located however from peaks on the difference map. The structure converged to an *R* factor of 0.116, hence there is still uncertainty as to the exact location of the hydrogen bonded protons. Atomic co-ordinates are given in Table 1. Relevant bond lengths and angles of the five crystallographically different malonic acid–fluoride chains are listed in Tables 2 and 3 respectively. The atoms in the structure unit are numbered as shown below.



The structure of $KF{\cdot}CH_2(CO_2H)_2$ is shown in Figure 1, the environment around potassium [K(1)] is shown in Figure 2, and the bond lengths for the five crystallographically distinguishable types of potassium are listed in Table 4. Figure 3 shows the projection view of one unit cell down *c* illustrating the cleavage and strandlike structure viewed end-on. Observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 23268 (19 pp.).†

---

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

TABLE 1

Fractional atomic co-ordinates of $KF{\cdot}CH_2(CO_2H)_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
K(1)	−0.316 8(5)	0.499 3(5)	−1.155 2(12)
K(2)	0.384 9(6)	0.987 8(5)	0.190 0(13)
K(3)	0.285 8(5)	0.501 5(5)	0.373 0(12)
K(4)	0.485 9(7)	0.488 4(2)	0.360 3(16)
K(5)	0.086 9(6)	0.512 0(4)	0.032 1(12)
F(1)	0.190 2(17)	0.602 3(13)	0.205 4(32)
F(2)	0.381 5(14)	0.398 5(10)	0.356 1(24)
F(3)	−0.218 7(14)	0.601 6(13)	−0.482 2(31)
F(4)	0.483 1(19)	0.896 4(6)	0.360 4(34)
F(5)	0.588 3(17)	0.397 8(14)	0.357 9(37)
C(11)	0.198 0(9)	0.366 2(8)	0.057 3(20)
C(12)	0.191 5(11)	0.324 1(9)	0.204 3(20)
H(11)	0.241 2(11)	0.292 4(9)	0.258 6(20)
H(12)	0.143 7(11)	0.289 9(9)	0.154 1(20)
C(13)	0.182 1(10)	0.367 4(8)	0.344 3(19)
O(11)	0.176 7(7)	0.328 6(6)	−0.070 3(13)
O(12)	0.219 8(7)	0.427 0(6)	0.075 8(15)
O(13)	0.153 3(6)	0.424 6(6)	0.320 4(16)
O(14)	0.202 8(8)	0.329 1(7)	0.478 4(16)
HO(14)	0.191 1(122)	0.351 2(117)	0.562 5(294)
HO(11)	0.181 2(118)	0.406 8(114)	−0.201 0(276)
C(21)	0.394 4(7)	0.388 7(7)	0.013 5(16)
C(22)	0.380 9(13)	0.321 9(10)	−0.141 1(24)
H(21)	0.329 0(13)	0.293 8(10)	−0.172 2(24)
H(22)	0.426 1(13)	0.284 5(10)	−0.109 3(24)
C(23)	0.379 6(11)	0.363 0(8)	−0.290 8(21)
O(21)	0.370 6(9)	0.328 7(7)	0.106 9(17)
HO(21)	0.358 3(120)	0.336 1(116)	0.166 1(284)
O(22)	0.423 1(7)	0.422 3(6)	0.038 4(15)
O(23)	0.357 3(7)	0.429 9(6)	−0.316 4(13)
O(24)	0.396 4(8)	0.328 2(6)	−0.392 4(17)
HO(24)	0.381 2(115)	0.367 0(116)	−0.601 7(275)
C(31)	−0.224 3(9)	0.634 8(9)	0.155 6(19)
C(32)	−0.231 7(11)	0.676 9(9)	0.004 7(23)
H(31)	−0.197 1(11)	0.723 4(9)	0.043 6(23)
H(32)	−0.289 2(11)	0.692 7(9)	−0.055 2(23)
C(33)	−0.210 6(8)	0.639 1(7)	−0.118 1(20)
O(31)	−0.203 4(9)	0.669 5(8)	0.296 3(18)
O(32)	−0.244 6(8)	0.571 3(6)	0.151 4(16)
O(33)	−0.184 0(7)	0.576 6(6)	−0.102 2(15)
O(34)	−0.228 9(8)	0.672 1(7)	−0.256 8(17)
HO(34)	−0.229 8(119)	0.669 4(112)	−0.350 4(275)
HO(31)	−0.208 4(130)	0.644 8(122)	0.371 6(295)
C(41)	0.477 4(12)	0.137 0(10)	0.496 7(23)
C(42)	0.485 2(25)	0.179 2(7)	0.353 4(41)
H(41)	0.534 8(25)	0.211 2(7)	0.403 7(41)
H(42)	0.437 1(28)	0.213 1(7)	0.302 5(41)
C(43)	0.490 9(15)	0.136 5(18)	0.211 4(44)
O(41)	0.502 4(17)	0.169 8(13)	0.633 5(32)
HO(41)	0.451 5(176)	0.138 7(180)	0.731 2(390)
O(42)	0.454 0(12)	0.075 9(10)	0.484 4(27)
O(43)	0.522 5(12)	0.081 1(12)	0.244 3(24)
O(44)	0.469 5(13)	0.172 1(11)	0.082 1(20)
HO(44)	0.439 4(184)	0.168 9(194)	0.050 7(418)
C(51)	0.596 8(8)	0.366 4(9)	0.017 5(21)
C(52)	0.591 4(11)	0.320 6(8)	−0.134 0(21)
H(51)	0.546 7(11)	0.283 1(8)	−0.157 4(21)
H(52)	0.643 5(11)	0.292 7(8)	−0.099 9(21)
C(53)	0.580 2(8)	0.357 2(7)	−0.290 1(23)
O(51)	0.571 2(10)	0.326 9(9)	0.112 1(20)
O(52)	0.619 8(6)	0.425 3(6)	0.039 5(15)
O(53)	0.551 1(7)	0.420 8(7)	−0.318 3(15)
O(54)	0.600 9(8)	0.331 0(7)	−0.398 6(17)
HO(51)	0.567 1(143)	0.335 3(131)	0.203 1(318)
HO(54)	0.567 0(122)	0.380 1(118)	−0.544 2(280)

Following the suggestion of a referee an attempt was made to refine the structure in the space group of *C*2/*c*. In fact the structure has a pseudo inversion centre at *ca*. (0.485 0.5 0.110) in the current unit-cell co-ordinate system. Molecules 1 and 3, including K and F ions, and 2 and 5 are related by inversion centres respectively. Molecule 4 possesses crystallographic symmetry of two-fold rotation, with C(42), K(4), and F(4) atoms at the special position. In the space group *C*2/*c* the structure was refined to a final *R* factor of 0.144, higher than that of space group *Cc* (although the decrease in the number of parameters generally increases the *R* factor). Due to the notable cleavage and partial decomposition of the compound, there must still remain some degree of uncertainty about it. However the general feature of the hydrogen bonding, which is the point of interest, remains intact.

TABLE 2

Bond lengths (Å) in $KF{\cdot}CH_2(CO_2H)_2$

	Anion strands [a]				
Bond	M(1) *n* = 1 [b]	M(2) *n* = 2	M(3) *n* = 3	M(4) *n* = 4	M(5) *n* = 5
F(*n*) · · · O(*n*1)	2.45(4)	2.48(3)	2.43(4)	2.49(4)	2.44(5)
F(*n*) · · · O(*n*4)	2.46(4)	2.49(4)	2.45(4)	2.43(4)	2.41(4)
F(*n*) · · · HO(*n*1)	0.92(24)	1.94(24)	1.59(27)	1.25(31)	1.72(26)
F(*n*) · · · HO(*n*4)	1.53(20)	0.70(23)	1.54(25)	2.47(41)	1.13(28)
O(*n*1) · · · HO(*n*1)	1.89(23)	0.66(28)	0.84(27)	1.64(40)	0.84(30)
O(*n*4)–HO(*n*4)	0.95(28)	1.89(24)	0.92(25)	0.55(32)	1.51(22)
O(*n*1)–C(*n*1)	1.25(2)	1.32(2)	1.31(2)	1.27(3)	1.34(3)
O(*n*2)–C(*n*1)	1.22(6)	1.14(2)	1.26(2)	1.23(3)	1.19(2)
O(*n*3)–C(*n*3)	1.20(2)	1.26(2)	1.28(2)	1.19(4)	1.31(2)
O(*n*4)–C(*n*3)	1.30(2)	1.24(3)	1.29(2)	1.24(4)	1.26(3)
C(*n*1)–C(*n*2)	1.56(3)	1.55(3)	1.50(3)	1.54(4)	1.55(3)
C(*n*2)–C(*n*3)	1.54(3)	1.51(3)	1.47(3)	1.52(5)	1.47(3)

[a] $(\cdots \overset{-}{O}_2C–CH_2–CO_2H \cdots F–H \cdots)_n$. [b] See text for numbering of atoms.

DISCUSSION

The adduct of KF and succinic acid, $KF{\cdot}(CH_2CO_2H)_2$, forms readily from an aqueous solution of the two components and is air stable. Its structure and that of the deuteriated analogue[3] show a regular array of infinite chains of succinic acid molecules interlinked through fluoride ions to which they form very short hydrogen bonds with $R(O \cdots F) = 2.44$ Å.

The acidity constants of malonic acid are $pK_1 = 2.86$ and $pK_2 = 5.70$ while those of succinic acid are $pK_1 = 4.21$ and $pK_2 = 5.64$.[8a] In water HF behaves as a weak acid ($pK = 3.18$),[8b] although there are now good grounds for not regarding this as indicating undissociated HF molecules in solution.[9] The species $H_2\overset{+}{O}–H–\overset{-}{F}$ is thought to be the key component in such solutions. In terms of conventional acidity we would not expect a solution of KF and succinic acid in water to generate an appreciable concentration of ' HF.' However we would expect this to happen with malonic acid. Yet such solutions also produced crystals of composition $KF{\cdot}CH_2(CO_2H)_2$, and *X*-ray diffraction studies again reveal a polymeric structure held together by short hydrogen bonds in which one fluoride ion is attached to two malonic acid-carboxylic acid groups.

Crystals of $KF{\cdot}CH_2(CO_2H)_2$ differ from $KF{\cdot}(CH_2CO_2H)_2$ in that there are five crystallographically independent different types of strand [labelled M(1)—M(5)] in the unit cell of the former whereas in the latter there is only one. The $R(O \cdots F)$ distances are all short (Table 2, mean 2.45 Å).

Because of the instability of the crystals the *R* factor

TABLE 3

Bond angles (°) in $KF{\cdot}CH_2(CO_2H)_2$*

Bond	Anion strands M(1) $n = 1$	M(2) $n = 2$	M(3) $n = 3$	M(4) $n = 4$	M(5) $n = 5$
O(*n*1) · · · F(*n*) · · · O(*n*4)	116(1)	116(1)	115(1)	118(1)	115(1)
HO(*n*1) · · · F(*n*) · · · HO(*n*4)	154(16)	84(20)	113(13)	100(19)	110(15)
O(*n*1) · · · HO(*n*1) · · · F(*n*)	117(17)	139(25)	177(27)	118(23)	142(26)
O(*n*1) · · · HO(*n*1) · · · F(*n*)	117(27)	139(25)	177(27)	118(23)	142(26)
O(*n*4) · · · HO(*n*4) · · · F(*n*)	165(23)	144(24)	168(19)	79(42)	131(19)
HO(*n*1)–O(*n*1)–C(*n*1)	91(7)	133(19)	111(16)	103(11)	132(18)
HO(*n*4)–O(*n*4)–O(*n*3)	117(13)	120(7)	121(13)	109(40)	103(10)
O(*n*2)–C(*n*1)–O(*n*1)	130(2)	131(2)	119(2)	123(2)	129(2)
O(*n*4)–C(*n*3)–O(*n*3)	128(2)	123(2)	121(2)	131(4)	117(2)
O(*n*3)–C(*n*3)–C(*n*2)	122(2)	122(2)	126(2)	118(3)	120(2)
O(*n*4)–C(*n*3)–C(*n*2)	109(1)	115(2)	113(1)	111(3)	122(1)
O(*n*1)–C(*n*1)–C(*n*2)	110(1)	103(1)	117(2)	113(2)	107(2)
O(*n*2)–C(*n*1)–C(*n*2)	121(2)	126(2)	124(2)	124(2)	124(2)
C(*n*1)–C(*n*2)–C(*n*3)	117(1)	114(1)	115(1)	117(2)	118(1)

* See footnotes to Table 2.

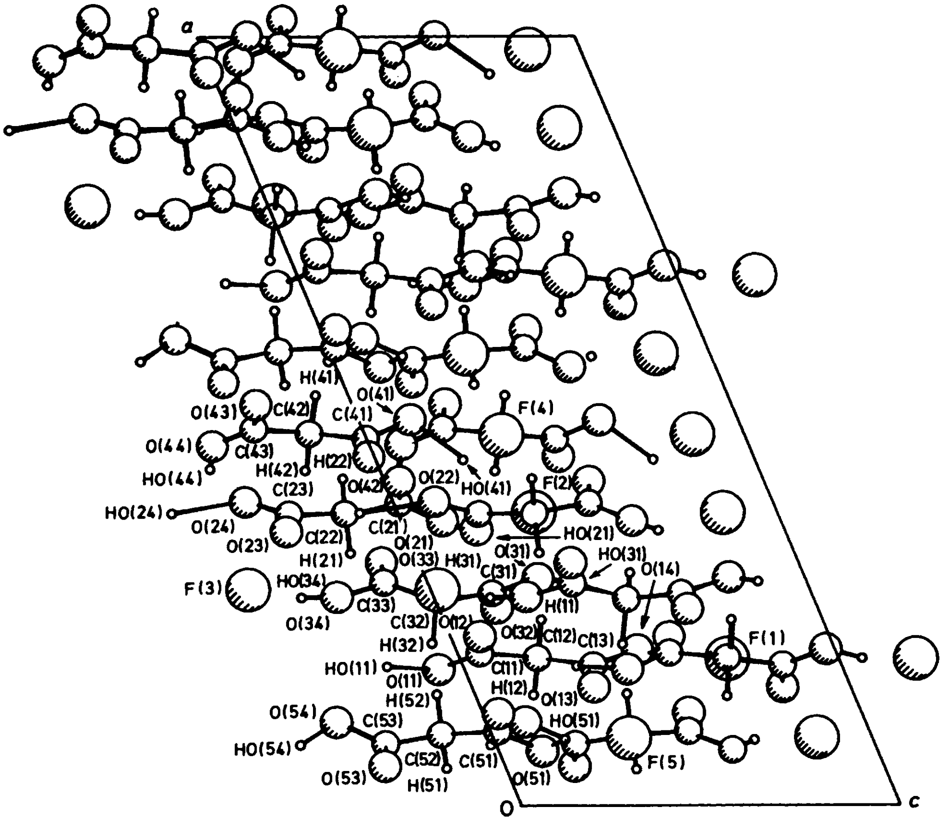


FIGURE 1 Structure of $KF{\cdot}CH_2(CO_2H)_2$

only refined to a value of 0.116 which means that there is a large degree of uncertainty regarding the locations of the protons of the hydrogen bonds (see Table 2). The bond lengths (Å) around the fluoride centres in the five types of stand are shown below.

These internuclear differences may have little significance because of the large estimated standard deviations (e.s.d.s) but they may indicate that the strong hydrogen-bond links along the strands do involve proton transfer, so that the crystals are in effect alternate HF and hydrogen malonate ions. This arrangement of atoms is supported by their physical decomposition into HF and also from their i.r. spectrum which is given in Table 5.

Strand M(1) $\mathrm{O}\overset{0.95}{\text{———}}\mathrm{H}\overset{1.53}{\cdots\cdots}\mathrm{F}\overset{0.92}{\text{———}}\mathrm{H}\overset{1.89}{\cdots\cdots}\mathrm{O}$

Strand M(2) $\mathrm{O}\overset{1.89}{\cdots\cdots}\mathrm{H}\overset{0.70}{\text{———}}\mathrm{F}\overset{1.94}{\cdots\cdots}\mathrm{H}\overset{0.66}{\text{———}}\mathrm{O}$

Strand M(3) $\mathrm{O}\overset{0.92}{\text{———}}\mathrm{H}\overset{1.54}{\cdots\cdots}\mathrm{F}\overset{1.59}{\cdots\cdots}\mathrm{H}\overset{0.89}{\text{———}}\mathrm{O}$

Strand M(4) $\mathrm{O}\overset{0.55}{\text{———}}\mathrm{H}\overset{2.47}{\cdots\cdots}\mathrm{F}\overset{1.25}{\text{———}}\mathrm{H}\overset{1.65}{\cdots\cdots}\mathrm{O}$

Strand M(5) $\mathrm{O}\overset{1.51}{\cdots\cdots}\mathrm{H}\overset{1.13}{\text{———}}\mathrm{F}\overset{1.72}{\cdots\cdots}\mathrm{H}\overset{0.84}{\text{———}}\mathrm{O}$

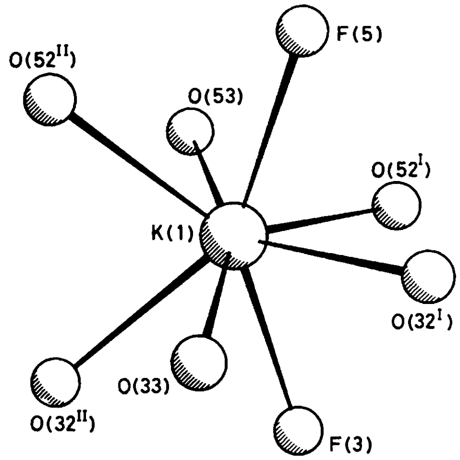


FIGURE 2 Environment of potassium in KF·$CH_2(CO_2H)_2$. For definition of Roman superscripts see footnote *b* Table 4

The i.r. spectrum of KF·$CH_2(CO_2H)_2$ has a typical continuum of the type produced by a substance with very strong hydrogen bonds. The spectrum differs from that of KF·$(CH_2CO_2H)_2$,[10] in that it is most intense over a higher range of frequencies (*i.e.* 2 000—1 700 cm^{-1}). The values reported in Table 5 for peaks in this region are for discernible maxima on the continuum. This spectra can be interpreted in terms of there being two different kinds of strong hydrogen bond in the crystal *viz.* O–H · · · F and F–H · · · O.

The maxima at 1 610 and 1 710 cm^{-1} correspond to ν(C=O) of the CO_2^- and CO_2H groups respectively[11] showing that there are hydrogen malonate groups present. The maxima at 1 820 and 1 900 cm^{-1} are assigned to ν(O–H · · · F) and ν(F–H · · · O) respectively on the assumption that a comparable shift of *ca.* 1 700 and *ca.* 2 000 cm^{-1} has occurred in the stretching vibrations of ν(OH) and ν(HF) of the free, *i.e.* non-hydrogen bonded species, which fall at *ca.* 3 500 and 3 962 cm^{-1} respectively.[12]

In both hydrogen bonds there will be in-plane and out-of-plane bending vibrations (in-plane of higher frequencies). Thus the broad bands at 1 200 and 1 360 cm^{-1} are assigned to the in-plane δ(O–H · · · F) and δ(F–H · · · O) respectively, while the broad bands at 1 050 and 1 090 cm^{-1} are the corresponding out-of-plane modes.

A curious feature of the i.r. spectrum of KF·$CH_2(CO_2H)_2$ is a sharp doublet at 948,930 cm^{-1} which is assigned to the skeletal C–C vibrations; these bands are

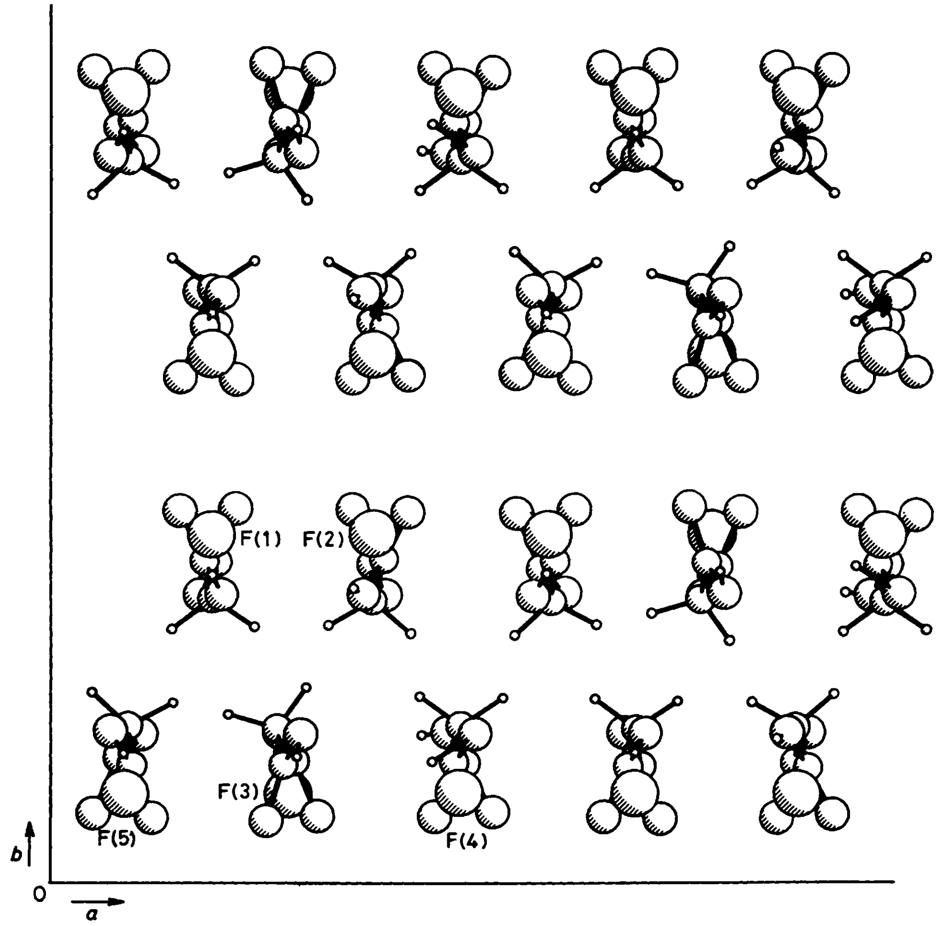


FIGURE 3 Projection view of unit cell down *c* showing strands end-on

TABLE 4

Potassium co-ordination in $KF{\cdot}CH_2(CO_2H)_2$.[a] Internuclear distances (Å)

K(1)	F(3)	2.715	K(2)	F(4)	2.584	K(3)	F(1)	2.675
	F(5)	2.715		F(3)	2.620		F(2)	2.738
	$O(32^{I})$ [b]	2.850		$O(42^{I})$	2.925		$O(12^{I})$	2.797
	$O(32^{II})$	2.904		$O(42^{II})$	2.887		$O(12^{II})$	2.892
	$O(52^{I})$	2.824		O(43)	3.089		O(13)	2.843
	$O(52^{II})$	2.854		O(32)	2.884		O(22)	2.889
	O(33)	2.850		$O(33^{I})$	2.918		$O(23^{I})$	2.885
	O(53)	2.836		$O(33^{II})$	2.905		$O(23^{II})$	2.908
K(4)	F(2)	2.641	K(5)	F(1)	2.631			
	F(5)	2.635		F(4)	2.649			
	$O(22^{I})$	2.887		O(12)	2.944			
	$O(22^{II})$	2.868		$O(13^{I})$	2.873			
	O(23)	2.885		$O(13^{II})$	2.892			
	$O(53^{I})$	2.899		$O(43^{I})$	2.914			
	$O(53^{II})$	2.917		$O(43^{II})$	2.929			
	O(52)	2.963		O(42)	2.966			

[a] For each of the five independent K atoms there are eight atoms (two fluorine and six carbonyl oxygens) at a distance of <3.1 Å. [b] Roman numeral superscripts refer to atoms in the positions: I x, y, z; II $x, -y, \frac{1}{2} + z$.

obscured in the spectrum of malonic acid itself by a broad hydrogen bond bending mode.

In the i.r. spectrum of malonic acid there is a pair of intensive broad bands at 450 and 425 cm^{-1}. These are absent from $KF{\cdot}CH_2(CO_2H)_2$; instead two broad bands appear at 382 and 310 cm^{-1}. These are allotted to the bending modes of the two CO_2 fragments of the acid vibrating in and out of phase with each other.

TABLE 5

Infrared spectrum (cm^{-1}) of $KF{\cdot}CH_2(CO_2H)_2$ *

310s, br 382s, br	$\delta(CO_2)$
485mw	
535mw	
615w	
653m;	MA
710w;	MA
750m;	MA
805vw;	MA
910 (sh);	MA
930, 948	s (doublet); MA ν(C–C)
1 050s, br;	δ(O–H · · · F) out-of-plane
1 090s, br;	δ(F–H · · · O) out-of-plane
1 155 (sh);	MA
1 200s, br;	δ(O–H · · · F) in-plane and $\delta(CH_2)$
1 360s, br;	δ(F–H · · · O) in-plane
1 395w	
1 445s, br;	ν(C–O)
ca. 1 610s, vbr;	ν(C=O)
ca. 1 710s, vbr;	ν(C=O)
ca. 1 820s, vbr;	ν(O–H · · · F)
ca. 1 900ms, vbr;	ν(F–H · · · O)
ca. 2 250m, br;	δ(O–H · · · F) in- and out-of-plane combination
ca. 2 420m, br;	δ(F–H · · · O) in- and out-of-plane combination
2 940w 2 980w	$\nu(CH_2)$

* MA = Malonic acid mode.

When KF is dissolved in glacial acetic acid the solution establishes equilibrium [equation (1)].[13] With KF and malonic acid in water it would therefore seem likely that equations (2) and (3) would be established.

$$2\,CH_3CO_2HF^- \rightleftharpoons HF_2^- + H(CH_3CO_2)_2^- \quad (1)$$

$$CH_2(CO_2H)_2 + F^- \rightleftharpoons HF + CH_2(CO_2H)CO_2^- \quad (2)$$

$$HF + F^- \rightleftharpoons HF_2^- \quad (3)$$

The solid phase which crystallises from $KF–CH_3CO_2H$ is a mixture of KHF_2 and $KH(CH_3CO_2)_2$, but from an aqueous solution of these only KHF_2 crystals can be obtained.[14] Hence it is surprising that $KF{\cdot}CH_2(CO_2H)_2$ crystallises from KF and malonic acid in water, being in effect a strong hydrogen bonded complex between the right hand side components of equation (2).

When a saturated solution of KF and oxalic acid crystallises it yields $KHC_2O_4{\cdot}H_2C_2O_4{\cdot}2H_2O$, whose crystal structure[15] reveals a network of oxalic acid molecules, hydrogen oxalate ions, and water molecules held together by short hydrogen bonds including some of the shortest hydrogen bonds involving water ever reported. In view of the acid strengths of oxalic acid, $pK_1 = 1.27$ and $pK_2 = 4.27$, it is perhaps not surprising that the equivalent equilibrium to equation (2) should lie to the right. Yet the crystals of potassium hydrogen oxalate which grow from such a solution neither incorporate F^- nor HF but $H_2C_2O_4$ and H_2O. When potassium hydrogen malonate crystallises by itself it produces crystals that consist of chains of $\bar{O}_2C{\cdot}CH_2CO_2H$ joined head to tail *via* short (2.46 Å) hydrogen bonds.[16] These crystals were first reported exactly a century ago.[17]

We thank the S.R.C. for grants (to D. J. J. and R. K.).

[1/1390 *Received, 3rd September,* 1981]

REFERENCES

[1] J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91.
[2] Table 2 in, W. G. Kehr, D. K. Breitinger, and G. Bauer, *Acta Crystallogr., Sect. B*, 1980, **36**, 2540.
[3] H-form, J. Emsley, D. J. Jones, and R. S. Osborn, *J. Chem. Soc., Chem. Commun.*, 1980, 703; D-form, J. Emsley, D. J. Jones, and R. Kuroda, *J. Chem. Soc., Dalton Trans.*, 1981, 2141.
[4] H. Altenburg and D. Mootz, *Acta Crystallogr., Sect. B*, 1971, **27**, 1982.
[5] E. R. Washburn, *J. Phys. Chem.*, 1927, **31**, 1246.
[6] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.
[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
[8] 'Lange's Handbook of Chemistry,' ed. J. A. Dean, 12th edn., McGraw-Hill, New York, (*a*) Table 5.8; (*b*) Table 5.7.
[9] P. A. Giguère and S. Turrell, *J. Am. Chem. Soc.*, 1980, **102**, 5473.

[10] J. Emsley, D. J. Jones, R. S. Osborn, and R. E. Overill, unpublished results.

[11] G. Socrates, ' Infrared Characteristic Group Frequencies,' Wiley, Chichester, 1980, p. 64.

[12] K. Nakamoto, ' Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963, p. 72.

[13] J. Emsley, J. Lucas, and R. E. Overill, unpublished results.

[14] J. H. Clark, J. Emsley, D. J. Jones, and R. E. Overill, *J. Chem. Soc., Dalton Trans.*, 1981, 1219.

[15] J. Emsley, D. J. Jones, and R. Kuroda, *J. Inorg. Nucl. Chem.* 1981, **43**, 2243.

[16] J. G. Sime, J. C. Speakman, and R. Pathasarathy, *J. Chem. Soc. A*, 1970, 1919; M. Currie and J. C. Speakman, *ibid.*, p. 1923.

[17] Reported in J. C. Speakman, *Struct. Bonding* (*Berlin*), 1972, **12**, 169.