complexes. It is interesting to note that $[Cu(\alpha,\omega\text{-}N\text{-}Me_2\text{-}2,2,2\text{-tet})]^{2+}$ is more stable than $[Cu(2,2,2\text{-tet})]^{2+}$; however, $[Cu(\alpha,\omega\text{-}N\text{-}Me_2\text{-}3,2,3\text{-tet})]^{2+}$ is less stable than $[Cu(3,2,3\text{-tet})]^{2+}$. The effects of the two N-methyl groups in $[Cu(\alpha,\omega\text{-}N\text{-}Me_2\text{-}2,2,2\text{-tet})]^{2+}$ and $[Cu(\alpha,\omega\text{-}N\text{-}Me_2\text{-}3,2,3\text{-tet})]^{2+}$ are completely different from each other.

The authors thank the National Science Council for support in the form of both a research grant NSC80-0208-M007-99 and the use of the Nonius CAD-4 diffractometer. They are also indebted to Miss Shu-Fang Tung for collecting the diffraction data.

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Acta Cryst. (1992). C**48**, 623–625

Structure of Potassium Hydrogen Diethylmalonate Monohydrate

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(*Received* 19 *September* 1989; *accepted* 12 *September* 1991)

Abstract. $[K(C_7H_{11}O_4)].H_2O$, $M_r = 216.27$, tetragonal, $P4_3$, $a = 9.251$ (3), $c = 13.123$ (4) Å, $V = 1123$ (1) Å^3, $Z = 4$, $D_x = 1.29$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.45$ mm^{-1}, $F(000) = 456$, $T = 293$ K, $R = 0.041$ for 1121 observed reflections. The asymmetric unit contains one formula unit of potassium hydrogen diethylmalonate linked by a hydrogen bond to the water molecule. Each molecule is intramolecularly hydrogen bonded and the carboxylic and carboxylate groups lying in the same plane of symmetry are equivalent.

Introduction. As part of our studies on malonic acid derivatives (Delarbre, Maury & Bardet, 1985; Dubourg, Rambaud, Delarbre, Maury & Declercq, 1988), we describe herein the crystal structure of potassium hydrogen diethylmalonate. Raman and infrared studies on the KH malonate acid and KH

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Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
K	5367 (1)	3393 (1)	1172	4.4
O(w)	−3901 (5)	5226 (6)	−434 (5)	10.7
O(1)	−1996 (3)	4143 (5)	−2093 (3)	6.7
O(2)	−1473 (4)	3958 (8)	−484 (3)	9.3
O(3)	2715 (3)	4940 (4)	−800 (3)	6.0
O(4)	885 (4)	4454 (6)	170 (2)	8.5
C(1)	475 (4)	4465 (5)	−1645 (3)	5.0
C(2)	−1117 (5)	4185 (6)	−1414 (4)	5.8
C(3)	1439 (4)	4657 (5)	−704 (3)	5.0
C(4)	1043 (6)	3144 (9)	−2244 (5)	8.2
C(5)	983 (12)	1755 (9)	−1653 (11)	13.1
C(6)	591 (8)	5820 (10)	−2323 (5)	9.9
C(7)	−13 (13)	7178 (10)	−1829 (12)	17.5
H(O)	−3844 (109)	5950 (96)	890 (76)	17.4
H(O)′	−2948 (55)	5152 (119)	167 (88)	17.4
H(O2)	−890 (100)	4680 (109)	23 (9)	17.4

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s and potassium coordination distances* (Å) (*average e.s.d.'s* 0.01 Å)

C(2)—O(1)	1.206 (5)	C(3)—C(1)	1.534 (5)
C(2)—O(2)	1.281 (6)	C(4)—C(1)	1.545 (8)
C(3)—O(3)	1.216 (5)	C(6)—C(1)	1.541 (8)
C(3)—O(4)	1.269 (6)	C(5)—C(4)	1.503 (13)
C(2)—C(1)	1.526 (6)	C(7)—C(6)	1.520 (15)

C(3)—C(1)—C(2)	114.8 (3)	C(1)—C(2)—O(1)	120.6 (4)
C(4)—C(1)—C(2)	107.1 (4)	C(1)—C(2)—O(2)	117.7 (4)
C(4)—C(1)—C(3)	107.7 (4)	O(4)—C(3)—O(3)	121.2 (4)
C(6)—C(1)—C(2)	108.7 (4)	C(1)—C(3)—O(3)	120.4 (4)
C(6)—C(1)—C(3)	109.3 (4)	C(1)—C(3)—O(4)	118.4 (4)
C(6)—C(1)—C(4)	109.0 (5)	C(5)—C(4)—C(1)	113.6 (6)
O(2)—C(2)—O(1)	121.7 (4)	C(7)—C(6)—C(1)	113.6 (8)

K···O(3^{i})	2.88	K···O(w^{iii})	2.82
K···O(1^{ii})	2.81	K···O(1^{iv})	2.69
K···O(w^{ii})	2.79	K···O(3^{v})	2.88
K···O(2^{ii})	3.10	K···O(4^{v})	2.78

Symmetry code: (i) x, y, z; (ii) $x-1, y, z$; (iii) $y-1, 1-x, 0.25+z$; (iv) $-y, x, 0.25+z$; (v) $y, 1-x, 0.25+z$.

diethylmalonate acid salts performed in aqueous solutions revealed that these two anions have the same C_s point-group symmetry, with the carboxyl residues lying in the symmetry plane. However, as expected on the basis of the dissociation-constant ratio $K1/K2$ of the diacids, we concluded that only the KH diethylmalonate acid salt was intramolecularly hydrogen bonded. To confirm this hypothesis, we investigated the crystal structure of the acid salt.

Experimental. Colourless single crystal 0.3 × 0.3 × 0.5 mm grown from water solution at room temperature. Lattice parameters refined using 15 reflections in the range $4 \leq 2\theta \leq 26°$. No absorption correction. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ-scan technique. 1333 independent reflections with $\sin\theta/\lambda \leq 0.649$ Å^{-1}, 1121 with $I \geq 2.5\sigma(I)$. Index range h −7/8, k 0/12, l 0/16. Standard reflection (143) checked every 50 reflections: no significant deviation. Structure was solved in space group $P4_1$ by direct methods using *SHELXS*86 (Sheldrick, 1985). H atoms of the carboxylic group obtained from a difference Fourier synthesis. H atoms of the carbon chain included in the calculation in theoretical positions. Anisotropic least-squares refinement on F with *SHELX*76 (Sheldrick, 1976). All H atoms with common refined isotropic temperature factor (B_{eq} = 16 Å^2). Absolute crystal structure ($P4_1$ or $P4_3$) was studied by refining the two forms (Rogers, 1981) with the z coordinates reversed. The results for $P4_1$ were $R = 0.041$ and $wR = 0.046$ and for $P4_3$ $R = 0.039$ and $wR = 0.044$. Although the difference between the R values is small, it seemed that it was significant enough; consequently, we chose $P4_3$ which gives the smallest R values. $w = 1/[\sigma^2(F) + 0.0011F^2]$. $S = 1.022$ for 1121 observed reflections. Final $(\Delta/\sigma)_{max} = 0.5$; maximum and minimum heights in final difference Fourier synthesis 0.29 and

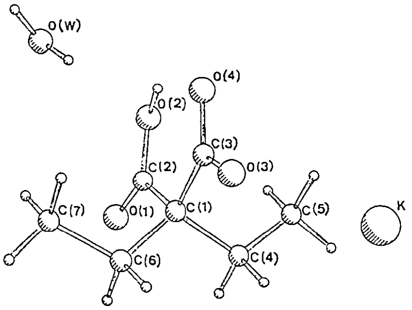

Fig. 1. Perspective view and atomic numbering of potassium hydrogen diethylmalonate.

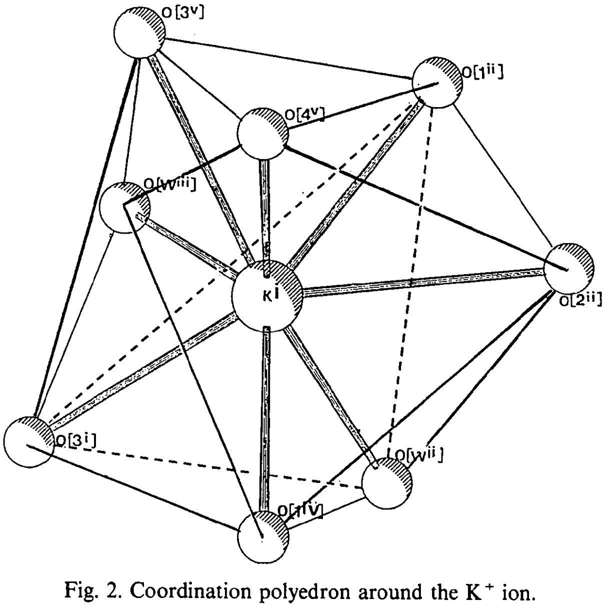

Fig. 2. Coordination polyedron around the K$^+$ ion.

−0.20 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic fractional positional parameters are given in Table 1.* Bond lengths and angles are given in Table 2. The molecular structure and atomic numbering of potassium hydrogen diethylmalonate is illustrated in Fig. 1 (*PLUTO*; Motherwell & Clegg, 1978).

The C—C bond lengths and the C—C—C angles are in good agreement with the values found in our previous study (Dubourg *et al.*, 1988). However, the conformation of the potassium hydrogen diethylmalonatc around the atom C(1) is quite different from that of the acid. Indeed, in the acid salt, the carboxylic and carboxylate groups are in the same plane, nearly perpendicular [82.2 (5)°] to the chain plane (*XANADU*; Roberts & Sheldrick, 1975); moreover, we observed a mirror plane perpendicular to the carboxylic group that passes through the atom C(1). The C—O single and double bonds are exactly the same in the carboxyl and carboxylate groups (Table 2), as was found previously in the potassium hydrogen 1,1-cyclopropane malonate acid (Dubourg, Fabrègue, Maury & Declercq, 1990). Therefore, we concluded that these two acids salts, KH 1,1-cyclopropane dicarboxylate and KH diethylmalonate have a similar chelated ring with a short O—H···O intramolecular hydrogen bond. The crystals are also stabilized by two intermolecular hydrogen bonds (Table 3). K$^+$ is coordinated to eight O atoms at distances less than 3.10 Å as shown in Table 2. Six of the atoms, O(3^{i}), O(1^{iii}), O(w^{iii}), O(1^{iv}), O(3^{v}) and O(4^{v}), form a distorted trigonal prism; the other two O atoms, O(w^{ii}) and O(2^{iii}), face two of the lateral sides (Fig. 2) as in the anion complex [PtL_2H] (LH$_2$ = 5-oxoproline) (Viossat, Rodier, Nguyen-Huy & Guillard, 1986).

Table 3. *Hydrogen-bond parameters: distances* (Å) *and angles* (°)

H(O*w*)—O(*w*)	0.900 (5)	H(O*w*)···O(3')	1.98 (5)
H(O*w*)′—O(*w*)	0.951 (7)	O(2)···O(4)	2.39 (5)
H(O2)—O(2)	1.086 (14)	O(*w*)···O(2)	2.80 (5)
H(O2)···O(4)	1.66 (5)	O(*w*)···O(3')	2.75 (6)
H(O*w*)′···O(2)	1.95 (5)		
C(2)—O(1)—H(O2)	110.8 (8)	O(*w*)—H(O*w*)′···O(2)	149 (7)
H(O2)···O(4)—C(3)	105 (9)	O(*w*)—H(O*w*)···O(3')	142 (7)
O(2)—H(O2)···O(4)	119 (8)		

Symmetry: no code assymetric unit; (i) 1 + y, 1 − x, 0.75 + z.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54595 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1992). C**48**, 625–627

Adduct of Two 1,8-Naphthyridine Molecules (One Protonated) with Tetrachloroferrate(III)

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(*Received* 20 *May* 1991; *accepted* 23 *September* 1991)

Abstract. 1,8-Naphthyridinium tetrachloroferrate(III)–1,8-naphthyridine (1/1), $C_8H_7N_2^+.FeCl_4^-.C_8H_6N_2$, M_r = 458.9, monoclinic, Cc, a = 10.698 (2), b = 25.533 (4), c = 7.315 (2) Å, β = 101.83 (1)°, V = 1955.67 (72) Å^3, Z = 4, D_x = 1.5588 Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, μ = 11.4 mm^{-1}, F(000) = 924,

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