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Neutron Diffraction Study of Sodium Hydrogen Maleate Trihydrate, $NaH[C_4H_2O_4].3H_2O$, at 120 K*

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Abstract. $M_r = 192\cdot10$, triclinic, $P\bar{1}$, $a = 5\cdot927$ (2), $b = 6\cdot288$ (2), $c = 11\cdot222$ (4) Å, $\alpha = 104\cdot00$ (2), $\beta = 91\cdot47$ (2), $\gamma = 100\cdot26$ (2)°, $V = 398\cdot3$ (3) Å^3, $Z = 2$, $D_x = 1\cdot60$ (2) g cm^{-3}, $\lambda = 0\cdot8323$ (4) Å, $\mu = 1\cdot62$ (5) cm^{-1}, $F(000) = 118$, $T = 120$ (1·5) K. Final $R = 0\cdot033$ for 2508 independent reflexions. The hydrogen maleate ion forms a close to planar ring structure containing a short but still very asymmetric hydrogen bond: $O\cdots O = 2\cdot445$ (1), $O—H = 1\cdot079$ (2) and $H\cdots O = 1\cdot367$ (2) Å. The three water molecules are crystallographically independent, each with a distorted tetrahedral environment. A comparison is made with intramolecular hydrogen-bond schemes in other hydrogen maleates.

Introduction. In the current hydrogen-bond project an emphasis is presently laid on detailed studies of geometry and electron density of strong hydrogen bonds and of water molecules in different crystal environments. NaH maleate.$3H_2O$ would appear a particularly suitable choice as it contains a strong hydrogen bond, on which no crystallographic symmetry restrictions are imposed, as well as three independent water molecules. Furthermore, for the purposes of electron-density studies, it has the advantage that it is centrosymmetric ($P\bar{1}$) and contains only light elements.

X-ray diffraction studies of the title compound at room temperature by Weissenberg film methods have been reported briefly by Gupta, Prasad & Yadav (1972) and by Gupta & Yadav (1974). The prime purpose of the present neutron diffraction work at 120 K has been to study the detailed geometry of the short intramolecular hydrogen bond and to obtain accurate thermal parameters and hydrogen positions for a subsequent electron density study using the *X–N* technique.

Experimental. *Crystal growth:* NaH maleate.$3H_2O$ prepared from sodium hydroxide and maleic acid; recrystallized several times from aqueous solution. Single crystals grown by slow evaporation of a saturated aqueous solution at room temperature. A crystal of volume 15 mm^3 (polyhedron ~1·6 × 2·9 × 4·5 mm) was mounted on an aluminium pin and covered with polystyrene film by dipping in chloroform solution to prevent water loss.

Crystal data: Cell dimensions determined at 120 K from single-crystal X-ray diffraction data (Olovsson, Kvick & Olovsson, 1984). Linear absorption coefficient determined experimentally by measuring the attenuation of a narrow beam of neutrons through different NaH maleate.$3H_2O$ crystals. From the coefficients for true absorption for Na, H, C and O [corrected to our wavelength, 0·8323 (4) Å] and the incoherent scattering cross-sections for Na, C and O as tabulated in *International Tables for X-ray Crystallography* (1968, 1974), a value of 36 (1) × 10^2 fm^2 was calculated for the mean incoherent scattering cross-section for H.

Data collection and reduction: Intensity data collected at 120 K on a four-circle diffractometer (D9) at the ILL (Institut Laue–Langevin) High-Flux Reactor in Grenoble. Primary beam monochromatized by a Cu crystal [(200) plane in transmission]. Detector: ^{3}He proportional counter. A closed-cycle Displex® system (Model CS-1003, Air Products and Chemicals Inc.) was used for cooling. The crystal was enclosed in a vanadium cylinder which was further surrounded by an evacuated aluminium can. A phase transition in KH_2PO_4 at 122·5 K was used to check the temperature. A difference of 1·0 K between the thermocouple and crystal was noted. Temperature generally constant within ±1·5 K. Flux at sample 3 × 10^6 neutrons cm^{-2}s^{-1} at a wavelength of 0·8323 (4) Å. A 0·25 mm erbium foil was placed in front of the monitor to filter out the second-order ($\lambda/2$) component in the beam. θ–2θ step-scan technique, scan interval for the peak 0·6, 0·6, 1·0, 1·5 and 2·4° for θ values 0, 15, 25,

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* Hydrogen-Bond Studies. 146. Part 145: Hermansson & Lunell (1982).

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35 and 50° and higher, respectively; linear interpolation in-between. Step length for the peak chosen to result in 21 steps. Six steps of constant step length 0·12° measured on each side of the peak to sample the background. Reflexions measured within a complete hemisphere of reciprocal space out to $\sin\theta/\lambda = 0{\cdot}663$ Å^{-1}. In the interval $0{\cdot}663 \le \sin\theta/\lambda \le 1{\cdot}041$ Å^{-1} the 730 calculated strongest reflexions ($F_c > 8$) were measured. This structure-factor calculation was based on the refined parameters (with isotropic temperature factors) using the first 2100 reflexions uncorrected for absorption. Range of hkl: $0 \le h \le 11$, $-12 \le k \le 12$, $-22 \le l \le 21$. No significant variations of the two standard reflexions ($01\bar{7}$ and $\bar{4}30$) were observed. Background corrections made using the method of Lehmann & Larsen (1974). After Lorentz correction, intensities corrected for absorption by the Gaussian integration method using a 12 × 8 × 10 grid. Crystal shape described by 17 rational boundary planes. The absorption through the polystyrene film was taken into account by extending the crystal by 0·062 mm in all directions (mean thickness of film 0·075 mm; $\mu_{\rm calc}$ for film 1·34 cm^{-1}). The calculated transmission fell in the range 0·568 to 0·761 for the 2953 collected data. The resulting F_o^2 values for reflexions measured several times and for a few Friedel pairs were averaged; $R_{\rm int} = 0{\cdot}026$. During the experiment, certain orientations were identified at which the cryostat connecting lines could possibly interfere with the primary or diffracted beam. A total of 22 reflexions with abnormally low intensities which might have been affected by this problem were removed, leaving 2508 independent reflexions for the final refinement.

Structure refinement: The starting parameters for the refinements were the final parameters from the X-ray study at 295 K (Olovsson *et al.*, 1984). The function minimized in the full-matrix least-squares program *LINEX*75 (Coppens, 1975) was $\sum w(|F_o|^2 - |F_c|^2)^2$, where $w^{-1} = \sigma^2_{\rm count}(F_o^2) + (0{\cdot}02F_o^2)^2$. The 196 refined parameters included one scale factor, 63 positional, 126 anisotropic thermal parameters and six anisotropic extinction parameters (see below). All negative observed intensities were set equal to zero in the refinement, whereas their standard deviations were kept unchanged. The final agreement factors were: $R = 0{\cdot}033$, $R(F^2) = 0{\cdot}043$, $wR(F^2) = 0{\cdot}059$, $S = 1{\cdot}65$. If the 294 reflexions with $I < 3\sigma(I)$ are excluded from the refinement the corresponding agreement factors are: $R = 0{\cdot}027$, $R(F^2) = 0{\cdot}042$, $wR(F^2) = 0{\cdot}058$, $S = 1{\cdot}73$, but the e.s.d.'s of the positional parameters rise by about 5%. The anisotropic extinction model used was the type I model with a Gaussian distribution (Becker & Coppens, 1975), and the anisotropy of mosaic spread was described according to Thornley & Nelmes (1974). Values of the extinction parameters $G_{ij}(\times 10^{-4})$ were: $G_{11} = 49$ (9), $G_{22} = 26$ (3), $G_{33} = 11$ (3), $G_{12} = -9$ (4), $G_{13} = 14$ (5), $G_{23} = -10$ (3). The lowest extinction factor multiplying F_c^2 was 0·77. Neutron scattering lengths for Na, O, C and H: 3·60, 5·80, 6·65 and −3·74 fm, respectively (Bacon, 1972). A refinement on the scattering lengths for O, Na and H keeping all final parameters fixed gave no significant change. Max. absolute value in residual map corresponded to less than 1% of max. peak in F_o synthesis map. Max. shifts in final refinement $0{\cdot}1\sigma$. Data reduction and refinement was carried out using an ILL modification of the Integrated Crystallographic Computing Library of the State University of New York at Buffalo. The structure analysis was performed at the Institute of Chemistry, University of Uppsala, using programs described by Lundgren (1982).

Discussion. Final atomic parameters are given in Table 1.* The crystal packing is illustrated stereoscopically in Fig. 1, bond distances and thermal ellipsoids in Fig. 2(*a*) and bond angles in Fig. 2(*b*). The hydrogen maleate ion forms a close to planar ring structure containing a short intramolecular hydrogen bond [O···O = 2·445 (1) Å]; this scheme is normally found also in other acid maleates. The hydrogen maleate ion so formed is interlinked by hydrogen bonds from the water molecules; double layers are thus created parallel to (010). These layers are linked to one another through $\mathrm{Na^+}$···O electrostatic interactions. An easy-cleavage plane has also been observed parallel to (010). The details of the bonding situation are described below. The structures briefly reported by Gupta *et al.* (1972) and Gupta & Yadav (1974) are in qualitative agreement with the present findings; no rigorous comparison is possible here, however, since their results are only preliminary.

The sodium ion. Sodium is surrounded by six oxygen atoms [O(1) belonging to the maleate group and the remainder belonging to water molecules] in a distorted octahedral arrangement (Fig. 1). $\mathrm{Na^+}$···O distances are in the range 2·374–2·446 Å.

The water molecules. The three water molecules are crystallographically independent; each has a distorted tetrahedral environment (Fig. 2). All hydrogen atoms are involved in normal, slightly bent hydrogen bonds (distances O···O = 2·739–2·918 Å; angles O—H···O = 164·5–175·3°); the acceptors are carboxyl oxygen atoms with the exception of the O*W*(3)—H···O*W*(2) bond. Atoms O*W*(1) and O*W*(3) are furthermore coordinated to two $\mathrm{Na^+}$ ions, whereas O*W*(2) is coordinated to one $\mathrm{Na^+}$ ion and receives a hydrogen bond from O*W*(3). This coordination situation on the lone-pair side of the water molecules is typical for a monovalent metal salt hydrate (Chiari & Ferraris,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39427 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic fractional coordinates* (×10⁵) *and equivalent isotropic thermal parameters* (×10³)

U_{eq} is the average r.m.s. component of thermal displacement along the principal axes.

	x	y	z	U_{eq}(Å)
C(1)	56021 (11)	18837 (11)	35256 (6)	105 (1)
C(2)	78591 (11)	21716 (12)	42244 (6)	112 (1)
C(3)	84043 (11)	26564 (12)	54416 (6)	113 (1)
C(4)	69216 (11)	30927 (11)	65078 (6)	106 (1)
O(1)	55266 (14)	13880 (14)	23959 (7)	118 (1)
O(2)	37542 (13)	21431 (14)	41061 (7)	117 (2)
O(3)	47776 (13)	29606 (14)	63158 (7)	114 (1)
O(4)	79049 (14)	35698 (14)	75644 (7)	119 (1)
O*W*(1)	12790 (13)	17171 (14)	13035 (7)	121 (1)
O*W*(2)	22386 (14)	33882 (14)	83890 (7)	118 (1)
O*W*(3)	64530 (13)	24934 (13)	98483 (7)	117 (1)
Na^+	74646 (21)	−3783 (21)	7200 (11)	110 (2)
H(1)	41420 (26)	25202 (28)	50879 (14)	155 (2)
H(2)	92456 (28)	19140 (35)	36183 (15)	173 (3)
H(3)	1988 (27)	27672 (35)	57326 (16)	174 (3)
H(11)	25688 (30)	14080 (31)	17409 (16)	172 (3)
H(12)	14004 (32)	33014 (29)	16044 (17)	177 (3)
H(21)	7334 (27)	34022 (30)	80331 (15)	165 (2)
H(22)	32327 (29)	33353 (30)	77101 (15)	166 (3)
H(31)	68487 (31)	28143 (30)	90743 (14)	169 (3)
H(32)	67993 (30)	39203 (27)	4564 (15)	166 (2)

1982): the water molecules are here normally tetrahedrally surrounded by two cations or hydrogen-bond donors.

In the water molecules, the O—H distance varies from 0·960 to 0·973 Å (e.s.d.'s 0·002 Å), the H—O—H angle from 103·4 to 105·7° (e.s.d.'s 0·2°); values are uncorrected for thermal motion. As expected for such relatively weakly bonded water molecules, deviations from the gas-phase values (0·97 Å and 104·5° in the vibrational ground state) are quite small. A direct comparison is only possible after detailed analysis of the thermal motions, however.

Conformation of the maleate group. Several structure studies of maleic acid/maleate salts and derivatives have been performed over the years. Interest has primarily been focused on the conformation of the maleate group or on the symmetry characteristics of the short intramolecular hydrogen bond occurring in the acid maleate salts.

The seven-membered ring of the hydrogen maleate ion is close to planar; the deviations of the atoms from the least-squares plane defined by C(1–4) are in the range 0·001 (1)–0·033 (1) Å for the heavy atoms and 0·002 (2)–0·007 (2) Å for the hydrogen atoms. The dihedral angle between this least-squares plane and the carboxylate plane of C(1),O(1),O(2) is 1·1°. The corresponding twist of the carboxylate ion C(4),O(3),O(4) is 1·7°. In this context it is interesting to note that some strain must be imposed on the bonds in forming a close to planar ring structure. In a hypothetical cyclic planar maleate ion with normal bond lengths and angles, the oxygen atoms [O(2) and O(3) in Fig. 2] would be only 1·58 Å apart, assuming C(1)—C(2) = C(3)—C(4) = 1·50, C(2)—C(3) = 1·34

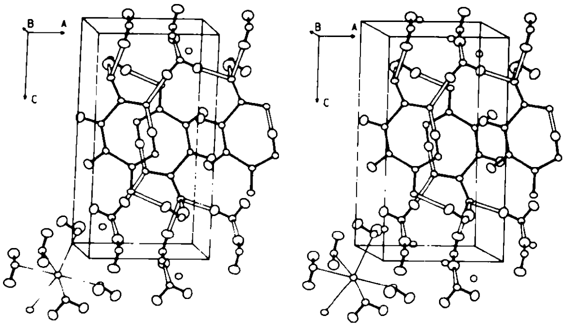

Fig. 1. A stereoscopic view of the molecular packing. Covalent bonds are filled and hydrogen bonds are open. The distorted octahedral arrangement of O atoms around the Na^+ ion is shown in the lower left-hand corner of the figure.

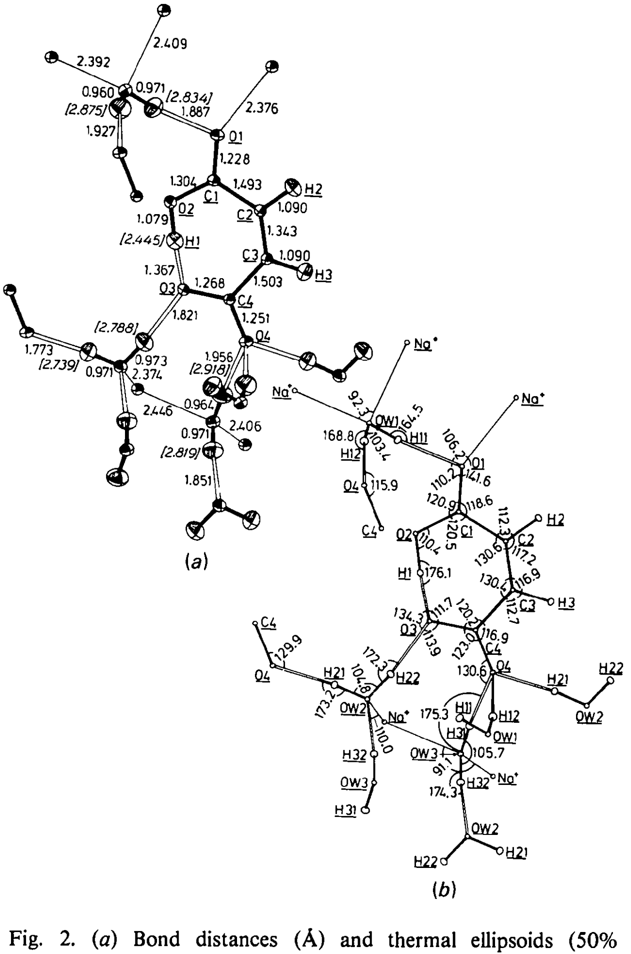

Fig. 2. (*a*) Bond distances (Å) and thermal ellipsoids (50% probability). Covalent bonds are filled, hydrogen bonds open and ionic bonds drawn as single lines. The O···O distances are shown within square brackets. Standard deviations for distances involving only C and O atoms are 0·001 Å, and 0·002 Å for bonds involving other atoms. No distances are corrected for thermal motion. (*b*) Bond angles (°) and atomic notations. Standard deviations for angles involving only O and H atoms are 0·2°, for other angles 0·1°.

and C(1)—O(2) = C(4)—O(3) = 1·26 Å which is a typical C—O distance in a carboxylate ion (Speakman, 1972). The angles around the carbon atoms are set to 120°. In a detailed analysis of the strained configuration of the hydrogen maleate ion in KH maleate, Darlow (1961) estimated the O(2)···O(3) distance in a hypothetical unstrained ion to be 1·47 Å. From Fig. 2 one notices that the larger oxygen separation needed for the hydrogen bond (>2·4 Å) is accommodated largely by opening the C(1)—C(2)—C(3) and C(2)—C(3)—C(4) angles to 130·5° (mean value), whereas all other geometrical features in the ring are practically unaffected. The same situation is also found in other acid maleates: the mean value for the above angles is 130·5 (10)° in the compounds studied previously and listed in Table 2. In contrast, when no intramolecular hydrogen bond is formed, as in Li_2 maleate.$2H_2O$ and Na_2 maleate.H_2O (Town & Small, 1973; James & Williams, 1974) one of the carboxylate ions is considerably twisted out of the plane (by 81·4 and 66·3° respectively) as a result of the repulsion between the oxygen atoms. The O(2)···O(3) distance is thus increased to 3·00 and 3·15 Å respectively: a little more than the normal oxygen–oxygen van der Waals separation of 2·8 Å.

The intramolecular hydrogen bond. The O(2)···O(3) distance, 2·445 (1) Å, is within the range of potentially symmetric hydrogen bonds (2·40–2·50 Å) but the position of this proton is here unusually asymmetrical: O(2)—H = 1·079 (2), H—O(3) = 1·367 (2) Å. The largest axis of the thermal ellipsoid of the proton is perpendicular to the O···O bond and the maleate plane (Fig. 3*a*). An approximate picture of how H(1) vibrates relative to O(2) is given in Fig. 3(*b*) where the thermal motion of O(2) has been subtracted from H(1). The root-mean-square displacements of H(1) along the principal axes and the angles (within square brackets) they make with the O(2)···O(3) bond are: 0·140 (3) [56 (8)], 0·151 (2) [145 (7)] and 0·174 (2) Å [96 (4)°] in Fig. 3(*a*), and 0·091 (4) [56 (8)], 0·099 (4) [88 (19)] and 0·112 (5) Å [34 (9)°] in Fig. 3(*b*). The difference mean-square displacement of H(1) along the O(2)···O(3) bond (Fig. 3*b*) is 0·0112 (9) $Å^2$. Assuming that H(1) acts like a harmonic oscillator along O(2)···O(3) we obtained a calculated stretch frequency of 1500 (100) cm^{-1} using the relationship

$$\omega = 16{\cdot}8/m\,\langle r^2\rangle$$

where ω is expressed in cm^{-1}, m in a.m.u. and $\langle r^2\rangle$ in $Å^2$ (Hamilton, 1969). This value is in agreement with typical O—H stretch frequencies (700–1700 cm^{-1}) obtained from IR experiments for hydrogen bonds in the region 2·40–2·50 Å (Novak, 1974). A check was made on the quality of the thermal parameters by calculating the C—H stretch frequencies. Such frequencies are known to be in the region of 3000 cm^{-1}. Our calculated values of 3000 (600) cm^{-1} for C(2)—H(2) and 2000 (200) cm^{-1} for C(3)—H(3) correspond fairly well to the expected value.

In numerous previous investigations it has been clearly established that the location of the proton in short hydrogen bonds is directly related to the degree of asymmetry in the environment on each side of the bond. Even if the immediate environment is chemically identical, small asymmetries in the arrangement of more distant neighbours may cause appreciable shifts of the proton from the centre. In the present case there are appreciable differences in the two carboxyl groups: the C—O distances around C(1) (the 'donor' group) are 1·228 and 1·304 Å respectively, and rather typical for a carboxyl group in crystals (Speakman, 1972), whereas those around C(4) (the 'acceptor' group) are 1·251 and 1·268 Å respectively, corresponding rather closely to a carboxylate ion. In accordance with this difference in ionic character, O(2) has no close contacts, O(1) accepts one hydrogen bond and coordinates with Na^+, whereas O(3) accepts two and O(4) no less than three hydrogen bonds. As is typically the case, the mean value of the two C—O distances in the different carboxyl groups is roughly the same, 1·266 and 1·260 Å respectively. We thus conclude that the asymmetric hydrogen bond in thc present case is

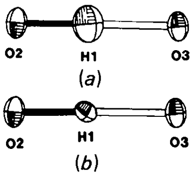

Fig. 3. Thermal ellipsoids (50% probability) for the short intramolecular hydrogen bond. The normal ellipsoids are shown in (*a*). The thermal motion of O(2) has been substracted from H(1) in (*b*). The plane of the hydrogen maleate ion is perpendicular to the plane of the paper.

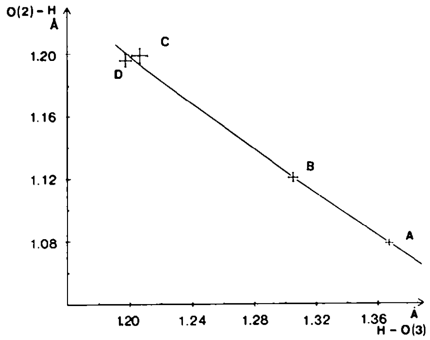

Fig. 4. Correlation between O(2)—H and H—O(3) distances for the hydrogen maleates studied by neutron diffraction in Table 2. The standard deviations of the distances are represented by the size of the crosses. *A* = NaH maleate.$3H_2O$, *B* = Ca(H maleate)$_2$.$5H_2O$, *C* = KH chloromaleate, *D* = imidazolium H maleate.

Table 2. *Bond distances* (Å) *for the intramolecular hydrogen bond and the adjacent carboxyl groups in hydrogen maleates* (*for notation see Fig.* 3)

No distances are corrected for thermal motion.

Compound	Method	O(2)···O(3)	O(2)–H	H···O(3)	C(1)–O(1)	C(1)–O(2)		C(4)–O(3)	C(4)–O(4)	Reference
Imidazolium H maleate	ND	2·393 (3)	1·196 (4)	1·197 (4)	1·236 (3)	1·279 (3)		1·271 (3)	1·233 (3)	(1)
	XD	2·397 (2)	[1·20 (2)]	[1·20 (2)]	1·235 (2)	1·280 (2)		1·281 (2)	1·232 (2)	(1)
K_2 *cis*-aconitate	XD	2·425 (2)	[1·13 (7)]	[1·30 (7)]	1·235 (2)	1·291 (2)		1·287 (2)	1·230 (2)	(2)
Bromopheniramine H maleate	XD	2·417 (4)	[1·08 (5)]	[1·34 (5)]	1·209 (6)	1·292 (6)		1·265 (6)	1·230 (6)	(3)
Chloropheniramine H maleate	XD	2·444 (5)	[0·87 (3)]	—	1·209 (5)	1·280 (5)		1·266 (5)	1·236 (5)	(4)
LiH maleate.$2H_2O$	XF*	2·46 (1)	—	—	1·24 (1)	1·30 (1)		1·28 (1)	1·23 (1)	(5)
(NH_4) H maleate	XD	2·432 (2)	1·218 (3)	= (*m*-symmetry)	1·243 (2)	1·277 (2)	=	1·277 (2)	1·243 (2)	(6)
Cu(H maleate)$_2$.$4H_2O$	XD	2·409 (3)	—	= (*m*-symmetry)	1·235 (3)	1·286 (3)	=	1·286 (3)	1·235 (3)	(7)
KH maleate	XF	2·437 (4)	1·22 (4)	= (*m*-symmetry)	1·235 (3)	1·284 (3)	=	1·284 (3)	1·235 (3)	(8)
KH difluoromaleate	XD	2·415 (1)	1·208 (1)	= (*m*-symmetry)	1·227 (1)	1·282 (1)	=	1·282 (1)	1·227 (1)	(9)
KH chloromaleate	ND	2·403 (3)	1·199 (5)	1·206 (5)	1·240 (2)	1·280 (3)		1·277 (3)	1·226 (2)	(10)
Ca(H maleate)$_2$.$5H_2O$	ND	2·424 (2)	1·121 (3)	1·305 (3)	1·239 (3)	1·285 (3)		1·274 (3)	1·238 (3)	(1)
	XD	2·426 (1)	[1·13 (5)]	[1·31 (5)]	1·237 (2)	1·288 (2)		1·281 (2)	1·233 (2)	(11)
NaH maleate.$3H_2O$ (120 K)	ND	2·445 (1)	1·079 (2)	1·367 (2)	1·228 (1)	1·304 (1)		1·268 (1)	1·251 (1)	(12)
	XD	2·445 (1)	[1·04 (2)]	[1·41 (2)]	1·231 (1)	1·302 (1)		1·272 (1)	1·251 (1)	(13)
Weighted ($1/\sigma^2$) mean†		2·429 (5)			1·232 (3)	1·292 (3)		1·276 (2)	1·240 (2)	

References: (1) Hsu & Schlemper (1980). (2) Glusker, Orehowsky, Casciato & Carrell (1972). (3) James & Williams (1971). (4) James & Williams (1974). (5) Gupta, Prasad & Gupta (1975). (6) Golič & Leban (1982). (7) Prout, Carruthers & Rossotti (1971). (8) Darlow & Cochran (1961). (9) Mattes & Göhler (1980). (10) Ellison & Levy (1965). (11) Hsu & Schlemper (1978). (12) This work. (13) Olovsson *et al.* (1984).

* Distances not included in weighted mean.

$$\dagger\ \sigma\,(\text{weighted mean}) = \left[\sum_{i=1}^{n} (x_i - \langle x\rangle)^2/n(n-1)\right]^{1/2}.$$

connected to the rather different bonding situation around O(2) and O(3).

The geometry of the short intramolecular hydrogen bond and the adjacent carboxyl groups in the hydrogen maleates so far studied is summarized in Table 2 (when several structure determinations have been published only the most accurate one is listed). The O···O distance ranges from 2·39–2·44 Å and the hydrogen bond varies from crystallographically symmetric or effectively centred, to very asymmetric. The most asymmetric bond is found in the present compound. There is a clear correlation between the O(2)—H and H—O(3) distance among the structures in Table 2 where the proton position has been accurately determined by neutron diffraction (Fig. 4). The exact form of the correlation curve for the very short asymmetric hydrogen bonds has been much debated in the past. The present results thus fully confirm the form previously derived by Olovsson & Jönsson (1976), according to which the complete correlation curve is quite smooth, without sudden change of the slope in the region of the shortest hydrogen bonds (*cf.* Ichikawa, 1978; Joswig, Fuess & Ferraris, 1982).

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Magnesium Bis(hydrogen maleate) Hexahydrate, $Mg[C_4H_3O_4]_2.6H_2O$

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Abstract. $M_r = 308{\cdot}5$, monoclinic, $P2_1/a$, $a = 6{\cdot}742\,(2)$, $b = 10{\cdot}201\,(1)$, $c = 11{\cdot}816\,(2)$ Å, $\gamma = 104{\cdot}06\,(2)°$, $V = 788{\cdot}3\,(4)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}167$ mm^{-1}, $F(000) = 320$, room temperature. Final $R_w = 0{\cdot}038$ for 1365 observed reflections. The Mg cation, at a centre of inversion, is coordinated by a slightly distorted octahedron of O atoms, all of which belong to water molecules of crystallization. Linkage of the Mg^{2+} ion with the hydrogen maleate ion is brought about by extra-strong hydrogen bonds. The extra strength is due to an enhanced charge on the H atoms of the water molecules caused by a polarization in the $[Mg(H_2O)_6]^{2+}$ unit. The non-H atoms of the hydrogen maleate moiety show nearly C_s symmetry, but this symmetry is broken when the intermolecular hydrogen bond is taken into account, thus rendering the complete hydrogen maleate ion unsymmetrical. Carboxyl groups are rotated over 3 and 4° with respect to the plane through the carbon skeleton. There is strong evidence that this rotation of the opposite carboxyl groups follows a concerted pattern as a compromise between steric hindrance and electronic effects.

Introduction. In an *ab initio* study of the hydrogen maleate moiety (henceforth abbreviated as HM) George, Bock & Trachtman (1983) investigated an unsymmetrical form of the ion (Fig. 1*b*) and a form with C_{2v} symmetry (Fig. 1*a*). Evidently one can discriminate only in the unsymmetrical form between donor and acceptor oxygen in the short intramolecular hydrogen bond. In fact when one shifts the hydrogen from the original donor to the original acceptor one passes the symmetrical form. X-ray and neutron-diffraction determinations of potassium hydrogen maleate and maleic acid show the heavy-atom backbone to be symmetrical (Darlow & Cochran, 1961; James & Williams, 1974), consistent with symmetrical hydrogen bonding. NMR measurements (Gunnarsson, Wennerström, Egan & Forsén, 1976; Altman, Laungani, Gunnarsson, Wennerström & Forsén, 1978) also favour symmetrical bonding. The *ab initio* calculations using the 4-31G basis set and full geometry optimization, however, found the unsymmetrical form $5{\cdot}74$ kJ mol^{-1} more stable than the C_{2v} form.

An obvious explanation for the discrepancy is the difference between an isolated ion and one in a crystalline environment. We will show that the X-ray study of the title compound will provide experimental information related to the *isolated* HM ion. Also we will deal with the following questions:

(i) Is the HM moiety planar as was assumed by George *et al.* (1983)?

(ii) Can donor and acceptor O atoms be discriminated? If the C_{2v} form is present it would indicate that the shift barrier (Fig. 1*c*) is lower than $5{\cdot}74$ kJ mol^{-1} calculated by George *et al.* (1983).

(iii) Is there experimental evidence for a disordered hydrogen bond in HM? If so the double potential-energy well, typical for an isolated HM ion, is detectable in the solid phase. If the equivalence of these two energy minima is broken then crystal-packing forces must have a decisive influence upon the HM moiety.

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