Asymmetric hydrogen bonds in centrosymmetric environment: neutron study of very short hydrogen bonds in potassium hydrogen dichloromaleate

I. Olovsson,[a]* H. Ptasiewicz-Bak,[a]† T. Gustafsson[a] and I. Majerz[b]

[a]Materials Chemistry, Ångström Laboratory, University of Uppsala, Box 538, SE-751 21 Uppsala, Sweden, and [b]Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, 50-383 Wroclaw, Poland

† Permanent address: Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.

Correspondence e-mail: ivar.olovsson@mkem.uu.se

The structure of the title compound has been studied by neutron diffraction at 30 and 295 K, with the emphasis on the location of the protons. There are two crystallographically independent H atoms in two very short hydrogen bonds, 2.437 (2) and 2.442 (2) Å at 30 K. The structure could be refined successfully in the centrosymmetric space group $P\bar{1}$, with the H atoms located at the centres of symmetry. However, the form of the thermal ellipsoids of hydrogen indicated either asymmetric hydrogen bonds *or* overlap of two closely spaced, partially occupied positions around the centres of symmetry. Several different types of refinements have then been applied, including unconventional models; with all atoms except hydrogen constrained in $P\bar{1}$, but with hydrogen allowed to refine without any constraints in $P1$, anisotropic refinement of all atoms resulted in clearly off-centred hydrogen positions. Significance tests clearly showed that the results from this constrained refinement give the most satisfactory description of the structure. This structure may be described as 'pseudo-centrosymmetric with non-centred protons'. The results demonstrate that it is very important to also include refinement models with non-centrosymmetric hydrogen in a centrosymmetric environment when studying very short hydrogen bonds. The shifts of the two H atoms from the centres of symmetry are 0.15 (1) and 0.12 (1) Å, respectively, at 30 K, and 0.15 (1) Å for both H atoms at room temperature. At 30 K: $R(F) = 0.036$ for 1485 reflections; at 295 K: $R(F) = 0.035$ for 1349 reflections.

1. Introduction

In very short $O\cdots H\cdots O$ bonds (2.40–2.45 Å) the major alternatives for the distribution of the proton are as follows:

(i) The proton is closer to one of the O atoms (asymmetric hydrogen bond).

(ii) The proton is located precisely at the centre (symmetric or centred hydrogen bond).

(iii) There is a statistical disorder of the proton between two positions on either side of the centre (the proton is closer to one or the other side in different domains of the crystal). A diffraction study will result in two half-occupied positions (or other relative occupancies of the two positions).

(iv) There is a dynamical disorder between two positions as in (iii); the proton jumps between the two positions in the same hydrogen bond.

A fundamental problem in the least-squares refinement of diffraction data is the large correlations between refined parameters of the atoms in the donor and acceptor units when these are close to being related by a centre of symmetry (or by a similar symmetry operation, such as a mirror plane or a twofold axis). Attempts to refine the parameters in a space

Table 1
Experimental details.

	295 K	30 K
Crystal data		
Chemical formula	$K_2Cl_4O_8C_8H_2$	$K_2Cl_4O_8C_8H_2$
Chemical formula weight	446.1	446.1
Cell setting, space group	Triclinic, $P1$	Triclinic, $P1$
a, b, c (Å)	5.083 (3), 7.881 (5), 8.863 (5)	5.022 (2), 7.827 (4), 8.838 (4)
α, β, γ (°)	81.72 (5), 84.78 (5), 89.59 (5)	80.99 (2), 85.13 (2), 88.95 (2)
V (Å^3)	349.9 (2)	341.8 (2)
Z	1	1
D_x (Mg m^{-3})	2.130	2.180
Radiation type	Neutron	Neutron
Wavelength (Å)	1.207	1.207
μ (mm^{-1})	0.086	0.088
Temperature (K)	295	30
Crystal form, colour	Plate with six faces, colourless	Plate with six faces, colourless
Crystal size (mm)	$4.2 \times 3.5 \times 1.0$	$4.2 \times 3.5 \times 1.0$
Data collection		
Diffractometer	Huber–Aracor 400 mm diameter four-circle	Huber–Aracor 400 mm diameter four-circle
Data collection method	θ–2θ scans	θ–2θ scans
Absorption correction	Numerical	Numerical
T_{min}	0.7207	0.7198
T_{max}	0.9253	0.9254
No. of measured, independent and observed parameters	2002, 2002, 1716	2104, 2104, 1871
Criterion for observed reflections	$F_o^2 > 3\sigma(F_o^2)$	$F_o^2 > 3\sigma(F_o^2)$
R_{int}	0.023	0.046
θ_{max} (°)	52	52
Range of h, k, l	$0 \rightarrow h \rightarrow 6$	$0 \rightarrow h \rightarrow 6$
	$-10 \rightarrow k \rightarrow 10$	$-10 \rightarrow k \rightarrow 10$
	$-11 \rightarrow l \rightarrow 11$	$-11 \rightarrow l \rightarrow 11$
No. and frequency of standard reflections	3 every 33 reflections	3 every 33 reflections
Refinement		
Refinement on	F^2	F^2
$R[F^2>3\sigma(F^2)]$, $wR(F^2)$, S	0.0638, 0.0817, 1.0383	0.058, 0.0805, 1.7718
No. of reflections and parameters used in refinement	1349, 119	1485, 119
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
$(\Delta/\sigma)_{max}$	0.05	0.05
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (nucleons Å^{-3})	0.05, −0.05	0.05, −0.05
Extinction method	Lorentzian type I isotropic (Becker & Coppens, 1974, 1975)	Lorentzian type I isotropic (Becker & Coppens, 1974, 1975)
Extinction coefficient	9210.6	7245.1

group of lower symmetry will mostly diverge in this situation and the 'symmetric' space group has to be chosen. The proton will then also adopt this higher symmetry and be distributed as in (ii), (iii) or (iv).

The potential energy curve for the proton motion in such a pseudosymmetric situation has quite a broad minimum and very little energy is needed to shift the proton, *e.g.* away from the middle of the O···O bond. One strategy to determine the actual proton position would be to impose an exact symmetry constraint on the donor and acceptor units, but allow the proton to refine without this constraint. This has been the method employed in the present investigation (*cf.* Thomas, 1995).

The hydrogen bonding in the hydrogen maleate anion has long since attracted considerable interest (*cf.* Tomkinson *et al.*,

1982; Bartoszak *et al.*, 1993; Fillaux *et al.*, 1999). Its IR spectrum is typical for very strong hydrogen bonds (Hadzi, 1965; Arbelj *et al.*, 1985), characterized by very intensive continous low-frequency protonic absorption with numerous Evans holes and without ν_s protonic absorption in the high-frequency region (Baran *et al.*, 2000).

2. Experimental

Stoichiometric amounts of potassium carbonate (or KOH) and dichloromaleic anhydride were dissolved in water and single crystals of hydrogen potassium dichloromaleate were grown by slow water evaporation at room temperature.

The neutron diffraction data were measured at the R2 reactor in Studsvik, Sweden, in a beam of wavelength 1.207 Å obtained by reflection from a Cu(220) double monochromator. The four-circle diffractometer was equipped with a two-stage closed-cycle helium refrigerator (Samson *et al.*, 1980). All reflections with $h \geq 0$ up to sin $\theta/\lambda = 0.6527$ Å^{-1} were measured in the θ–2θ mode, step scan with $\Delta\theta = 0.10°$, 40 steps, minimum time 10 s per step. Average instability constants were 0.0073 and 0.0050 at 30 and 295 K, respectively. The unit-cell dimensions were determined from single-crystal X-ray data, 32 reflections in the 2θ interval 50–60° at 30 and 295 K. Cell dimensions determined from single-crystal neutron diffraction data, 16 reflections in the 2θ interval 40– 60°, were not significantly different, but as the precision in the X-ray cell dimensions was significantly better, the X-ray results have been used in the present neutron investigation. Background corrections following Lehmann & Larsen (1974) and Lorentz corrections were applied. Absorption correction was applied by Gaussian integration (Coppens *et al.*, 1965). The data programs used have been described by Lundgren (1982).

3. Refinements

Refinement details are given in Table 1. The scattering lengths for K, Cl, O, C and H were 0.367, 0.9577, 0.5803, 0.6646 and

Table 2
Statistical significance tests: (a) experimental results and (b) comparison between experimental R ratios and statistical estimates (for notation see text).
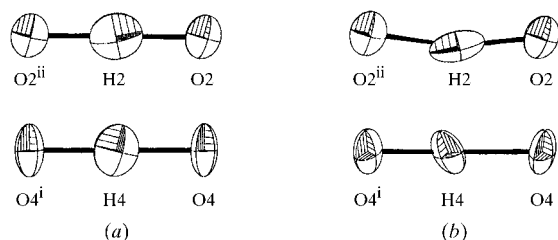
I: Centrosymmetric refinement; II: pseudo-centrosymmetric refinement (heavy atoms in $P\bar{1}$, H atoms in $P1$); III: non-centrosymmetric refinement.

	295 K			30 K		
	I	II	III	I	II	III
$R(F^2)$	0.0671	0.0638	0.0614	0.0608	0.0580	0.0569
$wR(F^2)$	0.0844	0.0817	0.0764	0.0862	0.0805	0.0796
$R(F)$	0.0350	0.0334	0.0309	0.0357	0.0329	0.0327
S	1.0700	1.0383	1.0115	1.9003	1.7718	1.7793
n	113	119	215	113	119	215
N	1349	1349	1349	1485	1485	1485

	I/II	II/III	I/III	I/II	II/III	I/III
R_w^c/R_w^u	1.033	1.069	1.105	1.070	1.011	1.082
$\mathcal{R}_{0.005}^{c/u}$	1.007	1.061	1.064	1.007	1.055	1.058
R'	4.7	1.1	1.6	10.0	0.2	1.4

-0.3739×10^{-12} cm, respectively, taken from Sears (1992). The following weighting scheme was used: $w = 1/[\sigma^2(F_o^2) + k^2 F_o^4]$; k was fixed to 0.06 and 0.03 at 295 and 30 K, respectively. The constant k was determined from analyses of the weighted $F_o^2 - F_c^2$ as a function of intensity and $\sin\theta$ for different values of k. The atomic positions for the heavy atoms, determined in a simultaneous X-ray investigation, were used as starting values. There are two H atoms engaged in two crystallographically independent short hydrogen bonds in the structure.

The space group $P\bar{1}$ was first used for all atoms (refinement I). When the two H atoms were placed precisely on the centres of symmetry $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ anisotropic refinements resulted in almost spherical thermal ellipsoids (Fig. 1a). The thermal ellipsoid of hydrogen in an asymmetric hydrogen bond is normally quite elongated perpendicular to the bond axis. The present form of the ellipsoids may then be taken as an indication of overlap of two closely spaced, partially occupied positions around the centres of symmetry. R and S values after refinement I are given in Table 2.

Figure 1
(a) Thermal ellipsoids at 295 K of the atoms involved in the hydrogen bonds after refinement of all atoms in the centrosymmetric space group $P\bar{1}$ (with the protons at the centres of symmetry, refinement I). (b) Thermal ellipsoids after final refinements (II). The ellipsoids correspond to 50% probability. Symmetry codes: (i) $-x-1, -y-1, -z+1$; (ii) $-x, -y, -z$.

In the next series of refinements in space group $P\bar{1}$ the H atoms were refined after slight shifts away from the two centres of symmetry with partially occupied positions on either side of the centres (original shifts from the centres of symmetry: $\Delta x = 0.02$, $\Delta y = 0.01$, $\Delta z = 0.01$; individual occupation factors refined). The refinement proceeded without difficulties and converged at both temperatures, but after several cycles the H atoms moved back to the centres of symmetry. The R and S values were the same as in refinement I. Typically, the refinements would have been stopped at this stage and the hydrogen bonds reported as centred.

However, we considered the possibility that the structure is only pseudocentrosymmetric and that the hydrogen bonds are in fact asymmetric. Two different series of refinements were then performed:

In the first (refinement II) all atoms except hydrogen were constrained in $P\bar{1}$ (corresponding to a pseudocentrosymmetric structure), whereas the H atoms were allowed to refine without any constraints. In practice this was performed in such a way that the space group $P1$ was employed for all atoms, but the parameters of the heavier atoms were constrained to $P\bar{1}$ after each cycle of refinement. Anisotropic refinement of all atoms converged at both temperatures and resulted in clearly off-centred hydrogen positions. R and S values are given in Table 2.

In the second series (refinement III) all atoms were refined without constraints in $P1$. At room temperature simultaneous refinement of positional and displacement parameters proceeded without difficulties and converged, but at low temperature the displacement parameters of pseudocentrosymmetrically related atoms had to be constrained to be equal after each step of the refinements. A possible reason for this difference is that the displacement parameters at low temperature are much smaller at 30 K and the difference between the displacement parameters for atoms which are related by the pseudocentre are correspondingly smaller, resulting in too strong a correlation. This series of refinements resulted in hydrogen positions quite close to those obtained in the previous constrained refinements. R and S values are given in Table 2.

Due to the strong correlation between the parameters for the heavier elements in $P1$ the standard deviations were approximately ten times larger in this case as compared to the constrained refinement (in contrast, the standard deviations for the H atoms were about the same in both cases). The number of independent reflections (1485 at 30 K and 1349 at 295 K) is only about six times the number of parameters in $P1$ (215), which also contributes to the higher standard deviations. The atomic positions were, within the combined standard deviations, the same in both cases and the results from the constrained refinement were accordingly chosen as the most suitable description of the structure.

The statistical significance of the constraints on all atoms to centrosymmetry (I), only on heavy atoms (II) and with all atoms unconstrained (III) was estimated from a comparison with the ratio R_w^c/R_w^u. The usual $\mathcal{R}$-factor definitions are used.

Table 3
Fractional atomic coordinates and equivalent isotropic displacement parameters.

The heavy-atom structure is centrosymmetric ($P\bar{1}$) and only atoms in the asymmetric part (molecule M) are listed; the H atoms are non-centred ($P1$). The symmetry-related heavy atoms in molecule M^i are denoted O4^i, O3^i etc. in Fig. 3.

	x	y	z	U_{eq}
295 K				
K	0.3020 (4)	−0.1562 (2)	0.6231 (2)	0.0300 (8)
Cl1	0.4644 (1)	−0.2475 (1)	0.0566 (1)	0.0293 (4)
Cl2	0.1282 (2)	−0.5706 (1)	0.2002 (1)	0.0345 (4)
O1	0.2368 (2)	−0.0052 (1)	0.3322 (1)	0.0300 (6)
O2	0.0284 (2)	0.0470 (1)	0.1236 (1)	0.0265 (5)
O3	−0.2492 (2)	−0.2221 (1)	0.4025 (1)	0.0296 (5)
O4	−0.2996 (2)	−0.5053 (1)	0.4134 (1)	0.0292 (5)
C1	0.1503 (2)	−0.0523 (1)	0.2206 (1)	0.0185 (4)
C2	0.1979 (2)	−0.2340 (1)	0.1873 (1)	0.0176 (4)
C3	0.0526 (2)	−0.3719 (1)	0.2503 (1)	0.0188 (4)
C4	−0.1834 (2)	−0.3612 (1)	0.3646 (1)	0.0190 (4)
H2	0.0296 (18)	−0.0042 (18)	0.0008 (17)	0.0349 (24)
H4	−0.5098 (26)	−0.5122 (15)	0.5146 (14)	0.0331 (27)
30 K				
K	0.3016 (3)	−0.1559 (2)	0.6242 (2)	0.0062 (7)
Cl1	0.4754 (1)	−0.2442 (1)	0.0603 (1)	0.0065 (3)
Cl2	0.1381 (1)	−0.5711 (1)	0.2032 (1)	0.0072 (3)
O1	0.2346 (2)	−0.0015 (1)	0.3347 (1)	0.0071 (4)
O2	0.0246 (2)	0.0508 (1)	0.1215 (1)	0.0072 (4)
O3	−0.2508 (2)	−0.2200 (1)	0.4018 (1)	0.0076 (5)
O4	−0.2962 (2)	−0.5066 (1)	0.4153 (1)	0.0072 (5)
C1	0.1507 (2)	−0.0491 (1)	0.2216 (1)	0.0052 (4)
C2	0.2044 (2)	−0.2316 (1)	0.1902 (1)	0.0056 (4)
C3	0.0592 (2)	−0.3710 (1)	0.2526 (1)	0.0059 (4)
C4	−0.1812 (2)	−0.3605 (1)	0.3656 (1)	0.0055 (4)
H2	0.0231 (20)	0.0065 (17)	−0.0104 (11)	0.0147 (18)
H4	−0.4914 (26)	−0.4957 (18)	0.5116 (15)	0.0160 (18)

At a chosen level of the F distribution $F_{(b,\ N-n,\ \alpha)}$, the quantity $\mathcal{R}_{\alpha}^{c/u}$ is

$$\mathcal{R}_{\alpha}^{c/u} = \{1 + [b/(N-n)]F_{(b,N-n,\alpha)}\}^{1/2},$$

N is the number of reflections used in the refinement, n is the number of parameters in the unconstrained (u) refinement, b is the difference between the numbers of parameters in the unconstrained (u) and constrained refinement (c). The various values are given in Table 2.

Pawley (1972) has empirically suggested the use of $R' = (R_w^c/R_w^u - 1)/(\mathcal{R}_{\alpha}^{c/u} - 1)$ when comparing the results of similar constrained refinements: if $R' \leq 3.0$ the constraints are physically insignificant. The results in Table 2 clearly show that constraint to centrosymmetry (I) does not give a correct description of the structure. In contrast, refinement III is not significant in comparison with refinement II. We conclude that the centrosymmetric structure (I) as well as the non-centrosymmetric structure (III) should be rejected.

The positional and displacement parameters for the final 'pseudo-centrosymmetric' structure with non-centred protons are given in Table 3[1] (the heavy atoms are described in $P\bar{1}$).

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0070). Services for accessing these data are described at the back of the journal.

The symmetry-related atoms are denoted O4^i, O3^{i}etc. in Figs. 1 and 3).

4. Results and discussion

A stereoscopic picture of the structure finally chosen is shown in Fig. 2, the numbering and bonding scheme is illustrated in Fig. 3. Selected distances and angles are given in Table 4 and hydrogen-bonding geometry in Table 5. The C—C distances in the dichloromaleate anion remain the same within 0.001 Å as the temperature changes from 30 to 295 K. The C—O distances are, however, significantly shortened (0.005–0.012 Å) at 295 K due to the larger thermal motion of the O atoms at higher temperature (the 'terminal' O atoms are more free to move than the 'internal' C atoms; the displacement parameters are approximately 50% larger for oxygen than for carbon, Table 3). The average value of the C(1)—C(2) and C(3)—C(4) (single bond) distances is 1.512 (2) Å and of the C(2)—C(3) (double bond) distance 1.342 (1) Å, in close agreement with the values in other maleates (cf. Olovsson et al., 1984). The average value of the single and double bond
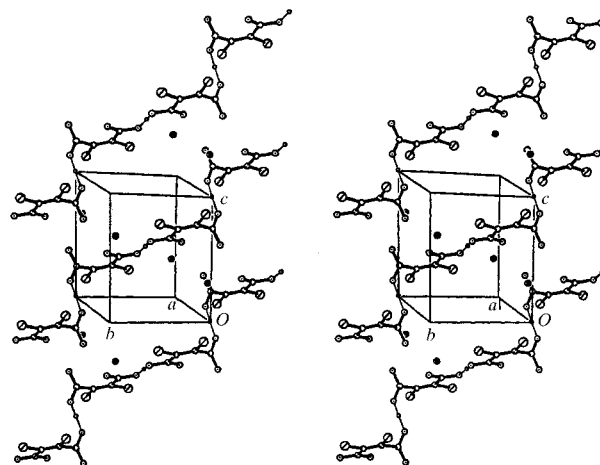

Figure 2
Stereoscopic picture of the final pseudocentrosymmetric structure of potassium hydrogen dichloromaleate with non-centred protons, refinement II (cf. Fig. 3).
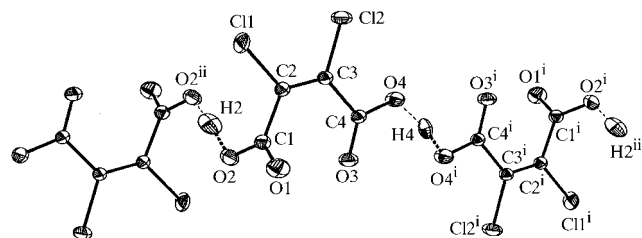

Figure 3
The hydrogen bonds and numbering of the atoms in the hydrogen-bonded network. The H atoms are off-centred in a centrosymmetric heavy-atom environment; at 295 K (as shown) the H2 atom is closer to molecule M, but H4 is closer to molecule M^i (M^i is related to M by a centre of symmetry; atoms are denoted O4^i, O3^i etc.); at 30 K both H atoms are closer to molecule M^i. Symmetry codes: (i) $-x - 1$, $-y - 1$, $-z + 1$; (ii) $-x$, $-y$, $-z$; (iii) $x - 1$, $y - 1$, $z + 1$.

Table 4
Selected geometric parameters (Å, °).

295 K			
K—O1	2.728 (3)	O3—C4	1.227 (2)
Cl1—C2	1.713 (2)	O4—C4	1.284 (2)
Cl2—C3	1.720 (1)	C1—C2	1.517 (1)
O1—C1	1.223 (2)	C2—C3	1.342 (1)
O2—C1	1.277 (2)	C3—C4	1.508 (2)
O1—C1—C2	120.1 (1)	C3—C4—O4	114.4 (1)
O2—C1—C2	116.6 (1)	O3—C4—O4	125.8 (1)
O1—C1—O2	123.3 (1)	H2—O2—C1	113.1 (6)
C3—C4—O3	119.8 (1)	H4—O4—C4	119.9 (5)
30 K			
K—O1	2.699 (2)	O3—C4	1.229 (1)
Cl1—C2	1.716 (1)	O4—C4	1.287 (1)
Cl2—C3	1.721 (1)	C1—C2	1.513 (1)
O1—C1	1.229 (1)	C2—C3	1.341 (1)
O2—C1	1.287 (1)	C3—C4	1.510 (1)
O1—C1—C2	120.1 (1)	C3—C4—O4	114.2 (1)
O2—C1—C2	116.3 (1)	O3—C4—O4	126.0 (1)
O1—C1—O2	123.5 (1)	H2—O2—C1	116.9 (6)
C3—C4—O3	119.7 (1)	H4—O4—C4	113.2 (6)

Table 5
Hydrogen-bonding scheme at 295 K (first entry) and 30 K (second entry).

$A \cdots H \cdots B$	$A \cdots H$	$H \cdots B$	$A \cdots B$	$A \cdots H \cdots B$
O2···H2···O2[i]	1.214 (15)	1.259 (15)	2.453 (2)	166 (1)
	1.268 (12)	1.185 (12)	2.437 (2)	167 (1)
O4···H4···O4[ii]	1.327 (13)	1.129 (13)	2.445 (2)	169 (1)
	1.253 (15)	1.201 (15)	2.442 (2)	169 (1)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x-1, -y-1, -z+1$.

distances in the carboxyl groups [1.258 (15) Å at 30 K and 1.253 (14) Å at 295 K] is close to the average value of 1.26 Å normally observed in the carboxyl group, irrespective of the degree of ionization (*cf.* Olovsson *et al.*, 1984).

4.1. Conformation

With the exception of O1 and O2 the dichloromaleate ion is close to planar: the dihedral angle between the least-squares plane defined by C1, C2, C3, C4 and the plane of the carboxylic group defined by O3, C4, O4 is only 0.5°. The other carboxylic group is almost perpendicular to the rest of the ion: the dihedral angle between the least-squares plane defined by O1, C1, O2 and the carbon least-squares plane is 82.3° at both temperatures. It is noteworthy that in the present compound intermolecular hydrogen-bonded chains are formed, whereas in most other hydrogen maleates studied so far close to planar ring structures are formed, with very short intramolecular hydrogen bonds (2.40–2.45 Å); for references see Olovsson *et al.* (1984). Compare for instance with potassium hydrogen difluoromaleate: is the stronger interaction of potassium with chlorine in comparison to fluorine the reason for the formation of a chain instead of a ring structure? Potassium hydrogen monochloromaleate also forms intramolecular hydrogen bonds: is the interaction of potassium with *two* Cl atoms responsible for this difference? (The K—Cl in potassium hydrogen monochloromaleate is 3.58 Å; in the present case K—Cl1 3.97 Å and K—Cl2 3.22 Å.) Some strain must be imposed on the bonds in forming a close to planar ring structure; this point is discussed in detail by Olovsson *et al.* (1984) and the reader is referred to this paper for a list of distances and angles in other hydrogen maleates with ring structures. This strain leads to an opening of the C—C—C bond angles in the ring, *e.g.* in sodium hydrogen maleate trihydrate (*loc. cit.*): here the two angles are 130.4 and 130.6° compared with 122.5 (1) and 125.5 (1)° in the present

compound, where the strain is released as one of the carboxyl groups is turned perpendicular to the plane of the other carboxyl group.

4.2. Hydrogen bonds

In the present investigation it appears to be established that the two protons are asymmetrically located in the short hydrogen bonds [*cf.* (i) in §1]. This may seem surprising as standard deviations and statistical significance tests clearly show that the 'heavy-atom' structure is best described as centrosymmetric. The geometry of the hydrogen bonds is shown in Table 5. It may seem remarkable that even when the heavy-atom structure is constrained to be perfectly centro-symmetric the protons still refine to off-centred positions. In similar situations in earlier published structures (*cf.* Olovsson & Jönsson, 1976) one has not attempted to refine the protons unconstrained and the protons have then been reported either as perfectly centred or as distributed among two partially occupied positions around a centre of symmetry (see, however, Thomas, 1995).

The shifts from the centres of symmetry are 0.15 (1) Å for H2 and 0.12 (1) Å for H4 at 30 K, 0.15 (1) Å for both H2 and H4 at 295 K. It is interesting to note a difference in the proton distribution: at 295 K the H2 atom is closer to *M*, but H4 is closer to molecule *M*[i], whereas at 30 K both H atoms are closer to molecule *M*[i] (*M*[i] is related to *M* by a centre of symmetry, *cf.* Fig. 3). This result did not depend on where H2 and H4 were placed at the beginning of the refinements. The distribution of the H atoms will be further studied at inter-mediate temperatures.

References

Avbelj, F., Orel, B., Klanjsek, M. & Hadzi, D. (1985). *Spectrochim. Acta A*, **41**, 75–87.
Baran, J., Pawlukojc, A., Majerz, I., Malarski, Z., Sobczyk, L. & Grech, E. (2000). *Spectrochim Acta A*, **56**, 1801–1812.
Bartoszak, E., Dega-Szafran, Z., Grunwald-Wyspianska, M., Jaskolski, M. & Szafran, M. (1993). *J. Chem. Soc. Faraday. Trans.* **89**, 2085–2094.

Becker, P. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.

Becker, P. & Coppens, P. (1975). *Acta Cryst.* A**31**, 417–425.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Fillaux, F., Leygue, N., Tomkinson, J., Cousson, A. & Paulus, W. (1999). *Chem. Phys.* **244**, 387–403.

Hadzi, D. (1965). *Pure Appl. Chem.* **11**, 435–453.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

Lundgren, J.-O. (1982). *Crystallographic Computer Programs*, Report UUIC-B13-4–05. Institute of Chemistry, University of Uppsala, Sweden.

Olovsson, I. & Jönsson, P.-G. (1976). *The Hydrogen Bond – Recent Developments in Theory and Experiments*, edited by P. Schuster, G. Zundel and C. Sandorfy, pp. 426–433. Amsterdam: North-Holland.

Olovsson, G., Olovsson, I. & Lehmann, M. S. (1984). *Acta Cryst.* C**40**, 1521–1526.

Pawley, G. S. (1972). *Advances in Structure Research by Diffraction Methods*, edited by W. Hoppe and R. Mason, Vol. 4, pp. 1–64. Oxford: Pergamon Press.

Samson, S., Goldish, E. & Dick, C. F. (1980). *J. Appl. Cryst.* **13**, 425–432.

Sears, V. F. (1992). *Neutron News*, **3**, 26–37.

Thomas, J. (1995). *Solid State Ion.* **77**, 275–279.

Tomkinson, J., Braid, I. J., Howard, J. & Waddington, T. C. (1982). *Chem. Phys.* **64**, 151–157.