

Asymmetric hydrogen bonds in centrosymmetric environment. II. Neutron study of very short hydrogen bonds in potassium hydrogen dichloromaleate at 90 K and 170 K

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In our earlier neutron diffraction study of the title compound at 30 K and 295 K an unconventional strategy in the refinement of hydrogen was applied and the same procedure has now been followed in the present investigation at 170 K and 90 K. There are two short O···H···O hydrogen bonds [2.437 (2) Å and 2.442 (2) Å at 30 K] and the ‘heavy-atom’ structure is centrosymmetric ($P\bar{1}$) with centres of symmetry in the middle of the O···O bonds. However, statistical significance tests clearly show that an asymmetric location of both H atoms gives the most satisfactory description of the structure at all temperatures. The shift of hydrogen from the centre of symmetry is 0.15, 0.14, 0.15 and 0.15 Å for H2 at 30, 90, 170 and 295 K, respectively, and 0.15, 0.15, 0.15 and 0.12 Å for H4 ($\sigma = 0.01$ Å). Furthermore, the behaviour of H2 is very interesting: at 295 K and 170 K it is located on one side of the symmetry centre but at 90 K and 30 K it is located on the other side. A detailed determination of the unit-cell parameters by X-ray diffraction in the whole temperature range from 30 K to 295 K has revealed that the data points of the cell parameters as a function of temperature fall on two different straight lines with a sudden change in the slope around 135 K. It appears likely that the change in the location of H2 as the temperature is lowered is related to this behaviour. At 170 K, $R(F) = 0.029$ for 1236 reflections; at 90 K, $R(F) = 0.030$ for 1457 reflections.

1. Introduction

The structure was first determined by X-rays at room temperature by Golic *et al.* (1976). In our previous paper the structure was studied by neutron diffraction at 295 K and 30 K (Olovsson *et al.*, 2001). There are two crystallographically independent H atoms in two very short hydrogen bonds, 2.437 (2) and 2.442 (2) Å at 30 K. Several different types of refinements were applied in our previous investigation, including an unconventional model with all atoms except hydrogen constrained in $P\bar{1}$, but with hydrogen allowed to refine without any constraints in $P1$. Standard deviations and significance tests clearly showed that the ‘heavy-atom’ structure is best described as centrosymmetric. However, even when the heavy-atom structure was constrained to be perfectly centrosymmetric, the protons still refined to off-centred positions. This structure was described as ‘pseudo-centrosymmetric with non-centred protons’.

Another remarkable feature was that the proton distribution was found to be different at 295 K and 30 K, although no phase transition was observed on lowering the temperature: at 295 K one H atom (H2) was closer to one of the maleate ions (M), whereas the other one (H4) was closer to maleate ion M^1 (related to M by a centre of symmetry). At 30 K both H atoms were closer to molecule M^1 ; for details see below and previous

work (Olovsson *et al.*, 2001). The heavy-atom structure was practically identical at the two temperatures and there seemed to be no obvious reason for this difference in the proton distribution. In order to investigate if any abnormal changes could be detected at some intermediate temperature the unit-cell parameters have now been determined in great detail by X-ray diffraction in the whole temperature range from 30 K to 295 K. The data points of the cell parameters as a function of temperature have been found to fall on two different straight lines with a sudden change in the slope around 135 K. Attempts have been made to observe some phase change at this temperature by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) analysis but the results are negative. It appears likely that the difference in proton distribution at 30 K and 295 K observed in our earlier investigation is related to the sudden change in the slope of the unit-cell parameters with temperature at 135 K. It therefore seemed very interesting to determine the hydrogen distribution at temperatures closer to the transition point, 135 K, and the structure has now been determined with neutron diffraction at two intermediate temperatures, 90 K and 170 K.

2. Unit-cell parameters as a function of temperature

The unit-cell parameters were determined at 33 different temperatures (70 independent measurements) from 30 K to 295 K on a four-circle single-crystal Huber diffractometer, using graphite (002)-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, the average value being $(2\alpha_1 + \alpha_2)/3$; the crystal size was $0.3 \times 0.1 \times 0.1$ mm. The diffractometer was equipped with a two-stage closed-cycle helium refrigerator Aracor system (Samson *et al.*, 1980). The cell parameters were determined both on lowering and increasing the temperature and the results were identical. To allow the crystal to reach equilibrium, the temperature was kept constant at each step for at least 1 h and after that the cell parameters were determined from 26 reflections in the 2θ interval 12° – 24° at each temperature by least-squares refinement. The standard uncertainty (σ) is 0.004 Å for the unit-cell axes and 0.04° for the angles. In addition the cell parameters were determined at 30, 90, 170 and 295 K from 32 α_1 reflections in the 2θ interval 50° – 60° (using λ Mo $K\alpha_1 = 0.70930$ Å). These cell parameters agree within 1σ with the values obtained in the above measurements. The cell parameters are plotted in Figs. 1(a)–1(g). The data points appear to fall on two different straight lines, the best fit of which is shown; all data have been given equal statistical weights. A sudden change in the slope occurs around 135 K, which is particularly noticeable for the unit-cell axes b and c , the angle β and the volume V . It is clear that the structure undergoes some change at this temperature but evidently that change is so slight that the structure still remains a good single crystal on passing through 135 K; note that the crystal was given considerable time to attain equilibrium at each temperature both on lowering and increasing the temperature. It might be suggested that the crystal undergoes a phase transition of second order at 135 K but, as

mentioned above, DTA and DSC analysis did not reveal any abnormal features at this temperature. There is no essential difference in the IR spectrum at room temperature and 100 K and the spectra are typical for very short hydrogen bonds with broad continuous absorption and without stretching bands in the 3000 – 2000 cm^{-1} region. Evidently any small structural changes would be hidden under this strong continuous absorption band.

3. Crystal structures at 90 K and 170 K

The same single crystal as in the previous investigation was used. The neutron diffraction data were collected at 90 K and 170 K 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 is equipped with the same type of two-stage closed-cycle helium refrigerator as in the X-ray work (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 $\Delta\theta = 0.10^\circ$, 40 steps, minimum time 10 s per step. Average instability constants were 0.0073 and 0.013 at 90 K and 170 K, respectively. Owing to insufficient reactor time 200 reflections less were measured at 170 K than at 90 K. The reactor was run at half power during the data collection at 90 K and the measurement time was then twice as long but with correspondingly better statistics. The unit-cell dimensions have been taken from the single-crystal X-ray study; cell dimensions determined from the single-crystal neutron diffraction data, 16 reflections in the 2θ interval 40° – 60° , are not significantly different but, as the precision in the X-ray cell dimensions is significantly better, the X-ray results have been used in the present neutron investigation. Background corrections following Lehmann & Larsen (1974) and Lorentz corrections have been applied. An absorption correction has been applied by Gaussian integration (Coppens *et al.*, 1965). The computer programs used are described by Lundgren (1982).

3.1. Refinements

Experimental and 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 -0.3739×10^{-12} cm, respectively, taken from Sears (1992). The following weighting scheme was used: $w = 1/[\sigma^2(F_o^2) + k^2F_o^4]$, where k was fixed at 0.06. 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 the previous neutron study, were used as starting values.

The refinements were performed in the same way as in the earlier study (Olovsson *et al.*, 2001). The structure could be refined successfully in the centrosymmetric space group $P\bar{1}$, with anisotropic refinement of the H atoms located at the centres of symmetry (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$: refinement I. The R and S values after refinement I are given in Table 2.

As in the previous study, refinements were also performed in space group $P\bar{1}$ with H atoms slightly shifted away from the

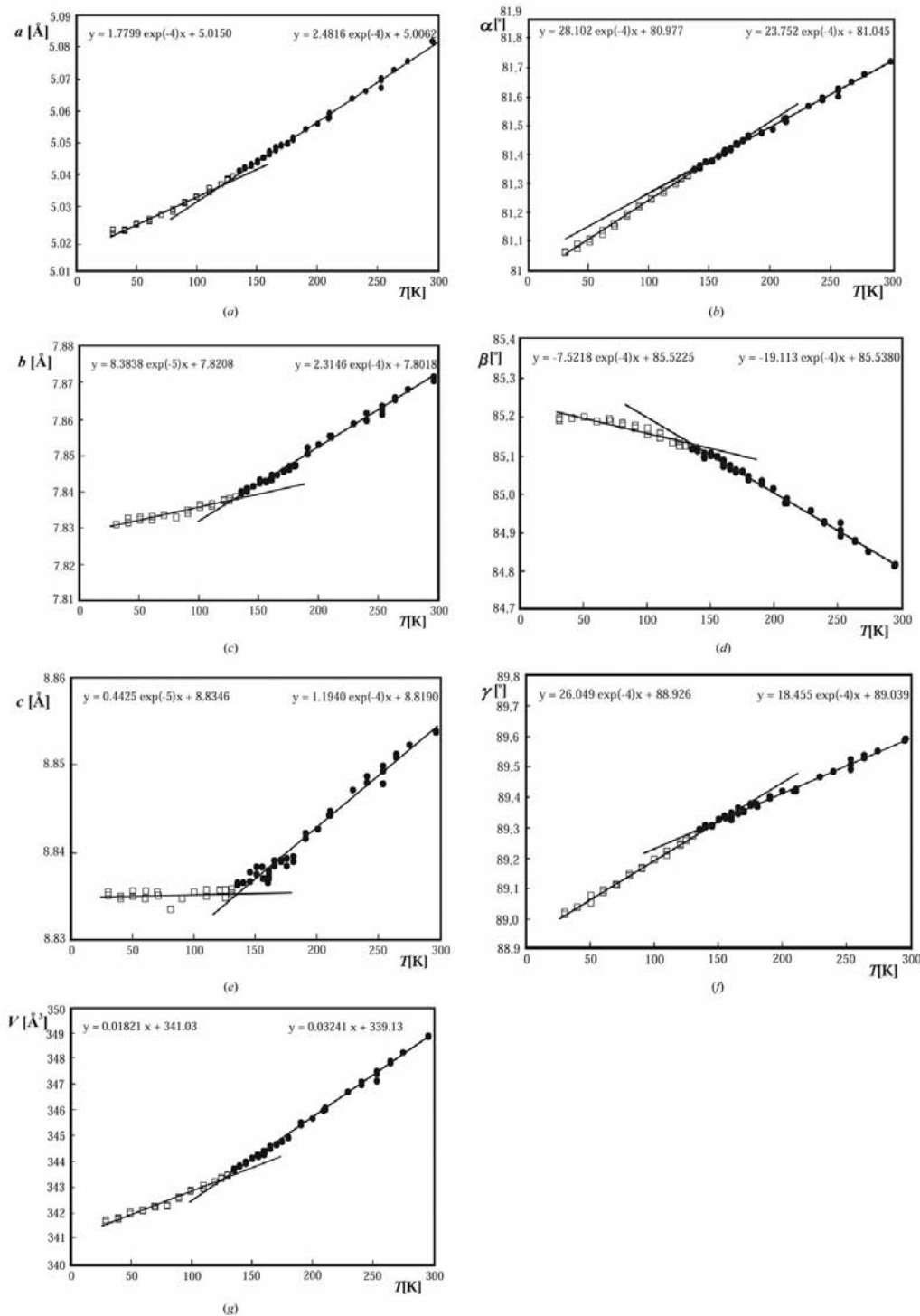


Figure 1
Unit-cell parameters as a function of temperature. The straight lines have been fitted to the data points by least-squares (with equal weights) methods.

two centres of symmetry, with partially occupied positions on either side of the centres (original shifts from the centres of symmetry: $\Delta x = 0.04$, $\Delta y = 0.02$, $\Delta z = 0.02$; individual occupation factors refined). The refinements proceeded without difficulties but the H atoms moved back to the centres of symmetry after several cycles.

independently of the direction of shift, hydrogen moved back to the same position as in refinement II. Refinements with shifts larger than 0.05 \AA diverged. Naturally, more complicated types of disorder are still possible.

The statistical significance of the constraints on all atoms to centrosymmetry (I) and only on heavy atoms (II) was esti-

The possibility that the structure is only pseudo-centrosymmetric and that the H bonds are in fact asymmetric was subsequently investigated: refinement II. All atoms except hydrogen were constrained in $P\bar{1}$ (corresponding to a pseudo-centrosymmetric structure) whereas the H atoms were allowed to refine without any constraints. In practise this was done in such a way that 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.

At 90 K the thermal ellipsoids of H2 and H4 were quite elongated which might be an indication of some disorder between two positions (around the final position from refinement II); at 170 K they were more normal (as well as at 30 K and 295 K in the earlier study). However, to test the possibility of disorder in any of these cases the following series of refinements were performed separately for H2 and H4 at both temperatures: hydrogen was split in two positions (each with occupancy one half) shifted about 0.02 \AA in different directions from the final position obtained in refinement II. However,

Table 1

Experimental details.

	170 K	90 K
Crystal data		
Chemical formula	K ₂ Cl ₄ O ₈ C ₈ H ₂	K ₂ Cl ₄ O ₈ C ₈ H ₂
Chemical formula weight	446.1	446.1
Cell setting, space group	Triclinic, <i>P</i> 1	Triclinic, <i>P</i> 1
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.048 (3), 7.840 (4), 8.839 (4)	5.031 (3), 7.827 (4), 8.835 (5)
α , β , γ (°)	81.46 (5), 85.05 (5), 89.35 (5)	81.24 (4), 85.17 (4), 89.16 (4)
<i>V</i> (Å ³)	344.6 (3)	342.6 (2)
<i>Z</i>	1	1
<i>D_x</i> (Mg m ⁻³)	2.150	2.162
Radiation type	Neutron	Neutron
Wavelength (Å)	1.207	1.207
μ (mm ⁻¹)	0.087	0.088
Temperature (K)	170	90
Crystal form, colour	Plate with six faces, colourless	Plate with six faces, colourless
Crystal size (mm)	4.2 × 3.5 × 1.0	4.2 × 3.5 × 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
<i>T_{min}</i>	0.7004	0.7019
<i>T_{max}</i>	0.9173	0.9162
No. of measured, independent and observed reflections	1614, 1370, 1236	1880, 1580, 1457
Criterion for observed reflections	$F_o^2 > 3\sigma(F_o^2)$	$F_o^2 > 3\sigma(F_o^2)$
<i>R_{int}</i>	0.036	0.034
θ_{max} (°)	52	52
Range of <i>h</i> , <i>k</i> , <i>l</i>	0 → <i>h</i> → 6 –10 → <i>k</i> → 10 –11 → <i>l</i> → 11	0 → <i>h</i> → 6 –10 → <i>k</i> → 10 –11 → <i>l</i> → 11
No. and frequency of standard reflections	3 every 33 reflections	3 every 33 reflections
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 3\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.0549, 0.0746, 1.0116	0.0544, 0.0801, 1.0846
No. of reflections and parameters used in refinement	1236, 119	1457, 119
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
(Δ/σ) _{max}	0.05	0.05
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (nucleons Å ⁻³)	0.04, –0.04	0.04, –0.04
Extinction method	Lorentzian type I isotropic (Becker & Coppens, 1974, 1975)	Lorentzian type I isotropic (Becker & Coppens, 1974, 1975)
Extinction coefficient	6580.1	7038.3

mated from a comparison with the ratio R_w^c/R_w^u . The usual *R*-factor definitions are used.

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

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

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

Pawley (1972) has empirically suggested the use of $R' = (R_w^c/R_w^u - 1)/(R_\alpha^{c/u} - 1)$ when comparing the results of similar constrained refinements: if $R' < 3.0$ 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. We conclude that the centro-

symmetric structure (I) should be rejected. [In the earlier study all atoms were also refined without constraints in *P*1. These refinements resulted in hydrogen positions quite close to those obtained in the constrained refinements (II) but the $R_\alpha^{c/u}$ and R' tests clearly showed that this refinement was not significant in comparison with refinement II.]

The positional and displacement parameters for the final ‘pseudo-centrosymmetric’ structure with non-centred protons (refinement II) have been deposited as well as the structure factors.¹

4. Results and discussion

A stereoscopic picture and selected geometrical parameters at 295 K and 30 K were presented in the earlier paper. The numbering and bonding scheme is illustrated in Fig. 2 (the symmetry-related atoms are denoted O4ⁱ, O3ⁱ etc.). Comparison of the distances at 30, 90, 170 and 295 K gives the following result: the C–Cl and C–C distances in the dichloromaleate anion remain the same within 1σ as the temperature changes from 30 K to 295 K. The C–O distances are, however, successively shortened (0.002–

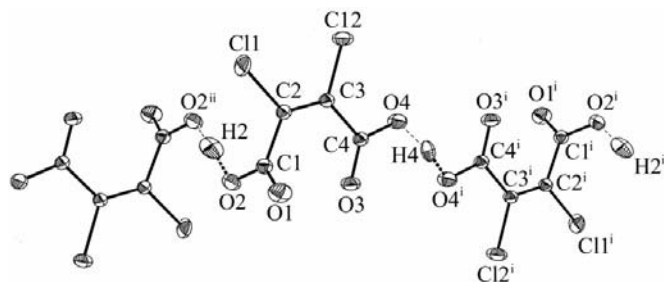


Figure 2

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 and 170 K (as shown) atom H2 is closer to molecule *M* but H4 is closer to molecule *M'* (*M'* is related to *M* by a centre of symmetry; atoms are denoted O4ⁱ, O3ⁱ etc.); at 90 K and 30 K both H atoms are closer to molecule *M'*. Symmetry codes: (i) $-x - 1, -y - 1, -z + 1$; (ii) $-x, -y, -z$; (iii) $x - 1, y - 1, z + 1$.

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0089). Services for accessing these data are described at the back of this journal.

Table 2

Statistical significance tests.

(a) Experimental results. (b) Comparison between experimental R ratios and statistical estimates (for notations see the text). I – centrosymmetric refinement. II – pseudo-centrosymmetric refinement (heavy atoms in $P1$, H atoms in $P1$).

(a)	170 K		90 K	
	I	II	I	II
$R(F^2)$	0.0567	0.0549	0.0583	0.0544
$R_w(F^2)$	0.0788	0.0745	0.0865	0.0801
$R(F)$	0.0309	0.0294	0.0322	0.0299
S	1.0667	1.0116	1.1744	1.0846
n	113	119	113	119
N	1236	1236	1457	1457

(b)	I / II (170 K)	I / II (90 K)
R_w^c/R_w^u	1.058	1.080
$R_{0.005}^c/R_{0.005}^u$	1.009	1.007
R^c	6.7	11.4

0.010 Å) as the temperature increases from 30 K to 295 K, an artefact due to larger thermal motion of the O atoms at higher temperatures (the ‘terminal’ O atoms are more free to move than the ‘internal’ C atoms; the displacement parameters are about 50% larger for oxygen than for carbon).

The conformation of the dichloromaleate ion was discussed in some detail in the earlier paper; note that one of the carboxylic groups is almost perpendicular to the rest of the ion. A general survey of the conformation of maleate ions was also made in the previous paper.

4.1. Hydrogen bonds

The present investigation confirms the conclusions in our earlier study that the two protons are asymmetrically located in the short hydrogen bonds, although the ‘heavy-atom’ structure is best described as centrosymmetric. The protons are also shifted away from the O...O connecting lines (*cf.* Table 3). The distances between the proton positions and the centres of symmetry are 0.15, 0.14, 0.15 and 0.15 Å for H2 at 295, 170, 90 and 30 K, respectively, and 0.15, 0.15, 0.15 and 0.12 Å for H4 ($\sigma = 0.01$ Å). These two diffraction investigations illustrate that it is important also to apply unconventional strategies in the refinement of hydrogen in structures containing short hydrogen bonds. The results do not at all agree with our traditional ideas about the situation in short hydrogen bonds, where it is normally assumed that the hydrogen distribution adopts the same symmetry as the ‘heavy atoms’.

The geometry of the hydrogen bonds at all four temperatures is compared in Table 3. It is then very interesting to note a difference in the proton distribution, as was also observed in the previous investigation: at 295 K and 170 K atom H2 is

Table 3

Geometry of the hydrogen bonds (Å, °) at different temperatures (T in K).

A	H	B	A...H	H...B	A...B	A...H...B	T
O2	H2	O2 ⁱⁱ	1.214 (15)	1.259 (15)	2.453 (2)	166 (1)	295
			1.214 (11)	1.243 (11)	2.441 (2)	167 (1)	170
			1.320 (7)	1.127 (8)	2.437 (2)	169 (1)	90
			1.268 (12)	1.185 (12)	2.437 (2)	167 (1)	30
O4	H4	O4 ⁱ	1.327 (13)	1.129 (13)	2.445 (2)	169 (1)	295
			1.282 (10)	1.175 (11)	2.442 (2)	167 (1)	170
			1.358 (8)	1.087 (8)	2.442 (2)	175 (1)	90
			1.253 (15)	1.201 (15)	2.442 (2)	169 (1)	30

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

closer to M but H4 is closer to molecule M^i , whereas at 90 K and 30 K both H atoms are closer to molecule M^i (M^i is related to M by a centre of symmetry, *cf.* Fig. 2). This result does not depend on where H2 and H4 are placed at the beginning of the refinements. Evidently this difference is related to the behaviour of the unit-cell parameters as a function of temperature. As mentioned earlier there is a sudden change in the slopes of the straight lines at 135 K (Fig. 1).

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