

## Neutron Diffraction Studies of Potassium Hydrogen Difformate, $\text{KH}(\text{HCOO})_2$ , at 120 and 295 K

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(Received 5 April 1983; accepted 9 June 1983)

**Abstract.**  $M_r = 130.144$ , orthorhombic,  $Pbca$ ,  $Z = 8$ ; at 120 K  $a = 17.705$  (8),  $b = 7.349$  (4),  $c = 7.302$  (3) Å,  $V = 950.1$  (8) Å<sup>3</sup>,  $D_x = 1.820$  (1) g cm<sup>-3</sup>; at 295 K  $a = 17.7079$  (9),  $b = 7.5096$  (4),  $c = 7.3774$  (4) Å,  $V = 981.05$  (9) Å<sup>3</sup>,  $D_x = 1.7623$  (2) g cm<sup>-3</sup>. The crystal structure has been investigated by neutron diffraction at 120 K ( $\lambda = 0.7228$  Å) and 295 K ( $\lambda = 1.210$  Å); final  $R(F^2)$  values are 0.041 (1418 reflections) and 0.065 (1365 reflections), respectively. The short intermolecular O...O hydrogen bond [2.437 (1) Å at 120 K] is found to be asymmetrical [O—H 1.167 (1), H...O 1.270 (1) Å] even though the bonding situations around the two formate groups are quite similar.

**Introduction.** The main purpose of this investigation is to study the geometry and electron density in the very short intermolecular hydrogen bond [O...O: 2.437 (1) Å at 120 K] between the two formate groups in  $\text{KH}(\text{HCOO})_2$ . The crystal structure was determined previously from room-temperature single-crystal X-ray data by Larsson & Nahrngbauer (1968). Most of the very short hydrogen bonds investigated by diffraction methods are either of an intramolecular type or they have a symmetry restriction on the bond, which makes it difficult to distinguish between a disordered non-centred bond and a centred bond with a large proton thermal vibration. This is not the case in potassium hydrogen difformate, where the two formate ions, hydrogen-bonded to form a dimer, are crystallographically non-equivalent. In the present paper neutron diffraction studies at 120 and 295 K will be presented. The deformation electron density distribution at 120 K will be described in a later publication.

**Experimental.** *Crystal growth:*  $\text{KH}(\text{HCOO})_2$  was prepared from formic acid and potassium hydroxide and recrystallized several times from an aqueous solution containing a small amount of formic acid. A large crystal was grown in a quartz-glass tube ( $\varnothing \sim 3.5$  mm) with the zone-melting technique. A cylinder-shaped

crystal with the  $c$  axis approximately along the cylinder axis was cut to a length of 7.9 mm. The melting point was measured and found to be 381.8 K (*cf.* Kendall & Adler, 1921). The crystal easily loses formic acid and is sensitive to air humidity; thus, it was sealed in a thin-walled quartz-glass bulb. The same crystal was used for both data collections. During the transportation to Grenoble (for the 120 K data collection) a small part of the crystal was destroyed so that the length of the crystal was reduced to 5.6 mm. For the absorption correction the cylinder was described with 16 faces of the type  $+h, +k, 0$  (*i.e.* parallel to the  $c$  axis) and two faces perpendicular to the  $c$  axis.

*Data collections for both data sets:* see Table 1; Lehmann & Larsen (1974) profile analysis; Lorentz and absorption corrections: at 295 K linear absorption coefficient determined experimentally, at 120 K linear absorption coefficient calculated from experimental value at 1.210 Å assuming  $\mu$  to be proportional to  $\lambda$  (*cf.* Bacon, 1975).

*Refinements:* the quantity minimized in the full-matrix least-squares refinements was  $\sum w(F_o^2 - F_c^2)^2$ , where  $w^{-1} = \sigma_c^2(F_o^2) + k^2 F_o^4$ ;  $\sigma_c^2$  was based on Poisson counting statistics and  $k$  was set to 0.02 and 0.03, for the 120 K and 295 K data sets, respectively.

**120 K data:** isotropic secondary-extinction parameter (Becker & Coppens, 1974) refined to an insignificant value (see also Table 1) and no extinction correction applied in subsequent refinements. All reflections included in the final refinement of one scale factor and positional and anisotropic thermal parameters for all ten atoms (91 parameters in all).  $R_w(F^2) = 0.053$ ,  $R(F^2) = 0.041$ ,  $S = 1.27$  for all 1418 reflections.  $R_w(F^2) = 0.047$ ,  $R(F^2) = 0.032$ ,  $S = 1.29$  for 1095 reflections with  $F_o^2 > 3\sigma(F_o^2)$ .

**295 K data:** the refinement included an isotropic extinction parameter as well, which was refined to 1340 (229) within an isotropic type I extinction model with Lorentzian mosaic-spread distribution (Becker & Coppens, 1974). Six reflections which were weakened between 17 and 26% due to extinction were excluded

from this refinement. Moreover, three reflections with large  $|F_o^2 - F_c^2|/\sigma(F^2)$  values and improper background correction due to overlap of reflections along the  $a^*$  axis were removed from the 295 K data set.  $R_w(F^2) = 0.088$ ,  $R(F^2) = 0.065$ ,  $S = 1.29$  for all 1365 reflections.  $R_w(F^2) = 0.073$ ,  $R(F^2) = 0.048$ ,  $S = 1.40$  for 845 reflections with  $F_o^2 > 3\sigma(F_o^2)$ .

The scattering lengths employed were 3.70, 5.80, 6.65 and  $-3.74$  fm for K, O, C and H, respectively (Koester & Steyerl, 1977). The largest features in the  $F_o - F_c$  residual maps calculated after the last cycles of refinement correspond to a scattering density of  $<2\%$  of the maximum peak height for C in the  $F_c$  synthesis maps. The computer programs used have been described by Lundgren (1982).

**Discussion.** Positional parameters are listed in Table 2.†

#### Effects of temperature on thermal parameters and distances

The results from a 'rigid-bond test' (Hirshfeld, 1976) for the C—O bonds are given in Table 3, where the validity of the thermal parameters is indicated by the very good agreement between the m. s. amplitudes of vibration in the bond direction for two (non-hydrogen) atoms connected by a covalent bond. Along the C—H bonds the H-atom m. s. amplitudes are larger than those of C. In all cases the differences are consistent with the amplitude expected for an H atom participat-

† Lists of structure factors and anisotropic thermal parameters obtained at 120 and 295 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38663 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Details of the data collections and reductions

	120 K	295 K
Reactor	ILL, Grenoble	R2, Studsvik
Diffraction	D9, four-circle	Hilger & Watts, four-circle
Flux at sample ( $\text{n cm}^{-2}\text{s}^{-1}$ )	$3.0 \times 10^6$	$1.3 \times 10^6$
$\lambda$ (Å)	0.7228	1.210
Temperature (K)	$120 \pm 0.5$	$295 \pm 1$
Cooling device	Displex CS-1003 closed-cycle cryostat	
$(\sin\theta/\lambda)_{\text{max}}$ (Å $^{-1}$ )	0.692	0.693
Scanning mode	$\omega-2\theta$	$\omega-2\theta$
Scanning range in $\theta$ (°)	1.5	2.0
No. of test reflections	2	3
No. of reflections measured (including extinct reflections)	1669	2022
No. of unique reflections	1418	1373
No. of reflections with $F_o^2 > 3\sigma(F_o^2)$	1095	858
Crystal volume ( $\text{mm}^3$ )	47.4	66.9
$\mu$ ( $\text{cm}^{-1}$ )	0.72 (calc)	1.20 (5) (obs)
Transmission	0.815–0.825	0.713–0.803
Extinction level	$j^* < 1.00$ for 1 reflection	$j^* < 0.95$ for 22 reflections
$F_o^2/\sigma(F_o^2)_{\text{uncorr.}}$		
$F_o^2/\sigma(F_o^2)_{\text{ext.corr.}}$		

ing in an harmonic C—H stretching mode at a wavenumber around  $2900 \text{ cm}^{-1}$  (Spinner, 1982), i.e.  $\sim 0.005 \text{ \AA}^2$ .

The average r.m.s. amplitudes of vibration are listed in Table 2. The thermal motion is distinctly anisotropic. The general form and orientation of the ellipsoids are very similar at the two temperatures for all atoms. The increase in vibrational motion on going from 120 to 295 K can be expressed by the ratios  $U_{ii}^{295}/U_{ii}^{120}$  which all lie in the range 2.51–2.92 for non-H atoms and 1.79–2.34 for H atoms. It is expected that the temperature dependence of the thermal parameters of H atoms is less than that for non-H atoms due to the larger contribution of high-frequency vibrational modes to the motion of the H atoms.

Table 2. Atomic coordinates ( $\times 10^5$ ) and equivalent isotropic thermal parameters (expressed as average r.m.s. amplitudes)

The upper row refers to the 120 K data, the lower row to the 295 K data.

	x	y	z	$\bar{U}$ (Å $^2$ )
K	46296 (5)	43978 (13)	28616 (14)	0.113
	46293 (9)	43738 (27)	28418 (27)	0.190
O(1)	15724 (4)	42723 (10)	57962 (10)	0.132
	15656 (6)	42339 (21)	57950 (21)	0.218
O(2)	5426 (3)	28371 (8)	48365 (10)	0.126
	5456 (6)	28218 (19)	48461 (20)	0.208
O(3)	29221 (4)	5253 (11)	1742 (11)	0.152
	29205 (7)	5772 (27)	1981 (25)	0.246
O(4)	40124 (3)	12504 (9)	14627 (10)	0.131
	40073 (6)	12590 (20)	14481 (23)	0.218
C(1)	12217 (3)	32020 (7)	47150 (8)	0.113
	12231 (5)	31677 (14)	47640 (15)	0.186
C(2)	33202 (3)	12488 (8)	14357 (8)	0.118
	33200 (5)	12530 (16)	14321 (17)	0.196
H(1)	15579 (7)	25820 (22)	36138 (22)	0.197
	15674 (14)	25450 (54)	37166 (49)	0.289
H(2)	30022 (8)	19063 (27)	25435 (24)	0.223
	30042 (15)	18713 (70)	25108 (52)	0.328
H(3)	22758 (7)	6320 (19)	4700 (19)	0.175
	22764 (13)	6727 (39)	4888 (38)	0.246

Table 3. M.s. amplitudes (Å $^2$ ) along the covalent bonds for the H(HCOO) $_2$  group

Bond	Atom	M.s. amplitude (Å $^2$ )	
		120 K	295 K
C(1)—O(1)	C(1)	0.0125 (2)	0.0328 (4)
	O(1)	0.0121 (4)	0.0335 (4)
C(1)—O(2)	C(1)	0.0119 (2)	0.0296 (3)
	O(2)	0.0114 (2)	0.0299 (7)
C(2)—O(3)	C(2)	0.0144 (2)	0.0392 (8)
	O(3)	0.0146 (5)	0.0420 (8)
C(2)—O(4)	C(2)	0.0104 (2)	0.0289 (3)
	O(4)	0.0102 (2)	0.0282 (7)
C(1)—H(1)	C(1)	0.0128 (2)	0.0350 (4)
	H(1)	0.0186 (8)	0.0420 (25)
C(2)—H(2)	C(2)	0.0125 (2)	0.0357 (8)
	H(2)	0.0185 (11)	0.0454 (26)

Within the harmonic approximation, the theoretical upper limit for the ratio of the vibrational m. s. amplitudes is equal to the temperature ratio (see, for example, Cyvin, 1968), *i.e.* 2.46, in the present case. The ratios in  $\text{KH}(\text{HCOO})_2$  are larger, which may indicate that the harmonic approximation is not completely valid here (this is also seen by the presence of a thermal expansion between 120 and 295 K).

The thermal motion is particularly large for the atoms O(3), H(1) and H(2) with r.m.s. amplitudes at 295 K equal to 0.322 (2), 0.381 (3) and 0.462 (5) Å, respectively, along their largest principal axes which are directed normal to the respective formate plane. On cooling, the thermal ellipsoids of these atoms show a decrease which is consistent with the behaviour of the other atoms and with the expected decrease of the vibrational atomic motion; this would not have been the case if the large ellipsoids were caused by disorder.

Distances and angles are listed in Table 4. Ionic and hydrogen-bond distances are seen to increase with temperature; the K—O contacts increase by 0.017 (2)—0.072 (2) Å and the O(1)···O(3) bond by 0.007 (2) Å between 120 and 295 K. The covalent C—O and C—H bond distances are all seen to decrease; this result is an inadequacy of the vibrational model used (second-rank tensor). Inclusion of third-order cumulants (Johnson, 1969) for the atoms H(1) and H(2) of the 295 K structure caused an additional shortening of the C—H distances: a decrease of 0.023 (7) Å for the C(1)—H(1) distance and 0.022 (7) Å for C(2)—H(2). The second-rank thermal parameters were not significantly changed by this procedure. A shortening of the C—H bonds on inclusion of third-order cumulants is not unexpected; these describe asymmetric vibrational behaviour along the bond direction and the refined H position is shifted towards the C atom (Eriksson, 1983). Inclusion of fourth-order cumulants on H(1) and H(2) had no significant effect on the H positions, second-rank thermal parameters or third-order cumulants.

#### The structure

A detailed description of the structure was given by Larsson & Nahringsbauer (1968) where a stereoscopic illustration of the unit cell (without H atoms) was presented.

Fig. 1 displays the unit cell at 120 K. The structure contains infinite puckered layers of  $\text{K}^+$  ions located perpendicular to **a** at  $x = 0$  and  $x = \frac{1}{2}$ . The  $\text{H}(\text{HCOO})_2^-$  ions are located between these planes with the intermolecular hydrogen bond running roughly in the **a** direction. As shown in Fig. 2, the  $\text{K}^+$  ion is coordinated by eight O atoms.

#### The $\text{H}(\text{HCOO})_2^-$ ion and the hydrogen bond

The  $\text{H}(\text{HCOO})_2^-$  ion is shown in Fig. 3. The two formate groups are joined by a short H bond;

O(3)···O(1) is 2.437 (1) Å at 120 K with an H-bond angle very close to linear.

Both formate groups are planar; within each formate group the atoms deviate by less than 0.002 (2) Å from a least-squares plane through the group. Both the C(1)—O(1) and C(2)—O(3) bonds lie between the distances expected for a C—OH carboxyl bond (~1.31 Å) and a carboxylate C—O bond (~1.25 Å; see Borthwick, 1980). In fact, the C(1)—O(1) and the C(2)—O(3) distances are equal within one  $\sigma$  at both temperatures. The strong O(3)—H(3)···O(1) bond causes the H(3) atom to be more detached from the O(3) atom than in a weakly bonded or non-bonded carboxyl group.

The bonding situations around the two formate groups seem quite similar, even though important differences apparently exist, since the C(1)—O(2) and C(2)—O(4) bond lengths differ by 0.009 (1) Å at 120 K, and the H(3) atom is situated 0.103 (1) Å closer to O(3) than to O(1). Several examples in the literature (*e.g.* Kvick, 1974) have indicated that the potential of a short intramolecular hydrogen bond is very flat and sensitive to minor differences in the vicinity of the bond.

The skilled technical assistance by MM John Allibon, Hilding Karlsson and Sten Åhlin is gratefully acknowledged. This work has been supported by grants from the Swedish National Science Research Council and the French—Swedish Research Exchange Scheme; these grants are gratefully acknowledged.

Table 4. *Interatomic distances (Å) and angles (°)*

The upper row refers to the 120 K data, the lower row to the 295 K data.

(a) $\text{K}^+$ ion			
K—O(4)	2.754 (1)	K—O(2)	2.852 (1)
	2.782 (2)		2.874 (2)
K—O(1)	2.785 (1)	K—O(4)	2.887 (1)
	2.802 (2)		2.918 (2)
K—O(2)	2.795 (1)	K—O(2)	2.926 (1)
	2.815 (2)		2.998 (2)
K—O(4)	2.807 (1)	K—O(2)	3.017 (1)
	2.847 (2)		3.068 (2)
(b) $\text{H}(\text{HCOO})_2^-$ ion			
C(1)—O(1)	1.276 (1)	O(1)—C(1)—O(2)	124.28 (6)
	1.260 (2)		125.06 (12)
C(1)—O(2)	1.235 (1)	O(1)—C(1)—H(1)	116.40 (9)
	1.229 (1)		115.57 (19)
C(1)—H(1)	1.099 (2)	O(2)—C(1)—H(1)	119.31 (9)
	1.090 (4)		119.36 (20)
C(2)—O(3)	1.276 (1)	O(3)—C(2)—O(4)	124.36 (7)
	1.260 (2)		124.76 (14)
C(2)—O(4)	1.226 (1)	O(3)—C(2)—H(2)	115.61 (9)
	1.217 (1)		114.57 (20)
C(2)—H(2)	1.098 (2)	O(4)—C(2)—H(2)	120.04 (10)
	1.078 (4)		120.67 (21)
(c) Hydrogen bond			
O(3)···O(1)	2.437 (1)	O(3)—H(3)—O(1)	179.31 (14)
	2.444 (2)		179.39 (29)
O(3)—H(3)	1.167 (1)	C(2)—O(3)—H(3)	112.33 (10)
	1.163 (3)		113.13 (20)
H(3)···O(1)	1.270 (1)	C(1)—O(1)—H(3)	113.29 (9)
	1.281 (3)		113.66 (18)

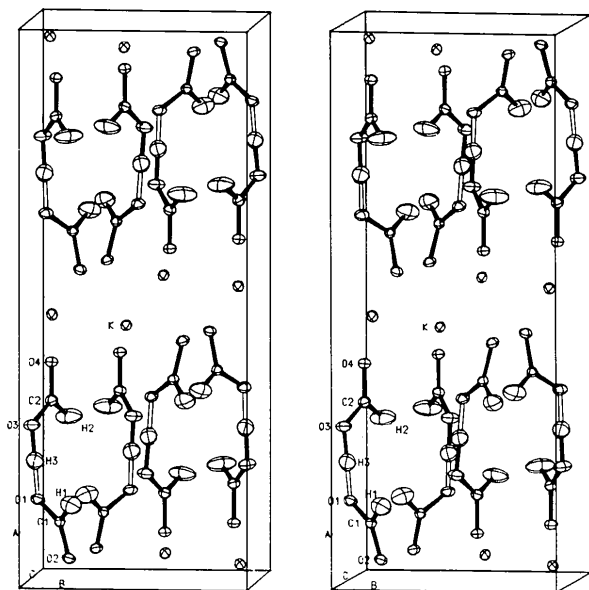


Fig. 1. A stereoscopic illustration of the unit cell in  $\text{KH}(\text{HCOO})_2$  at 120 K. The ellipsoids are drawn to include 50% probability.

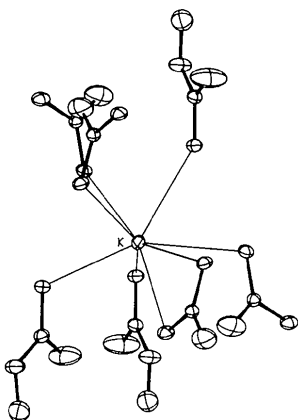


Fig. 2. The bonding situation around the  $\text{K}^+$  ion.

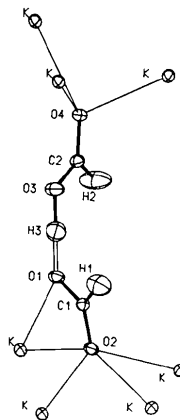


Fig. 3. The formate dimer with the nearest ionic contacts.

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## Diamminebis(dimethylglyoximato)cobalt(III) Tetracyanonickelate(II) Hexahydrate, $2\text{C}_8\text{H}_{20}\text{CoN}_6\text{O}_4^+\cdot\text{C}_4\text{N}_4\text{Ni}^{2-}\cdot 6\text{H}_2\text{O}$

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(Received 10 March 1983; accepted 7 July 1983)

**Abstract.**  $M_r = 917.3$ , triclinic,  $P\bar{1}$ ,  $a = 14.496$  (4),  $b = 10.542$  (4),  $c = 7.069$  (3) Å,  $\alpha = 90.18$  (2),  $\beta = 104.05$  (2),  $\gamma = 111.56$  (2)°,  $V = 969.5$  (10) Å<sup>3</sup>,  $Z = 1$ ,

$D_x = 1.57$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.339$  mm<sup>-1</sup>,  $F(000) = 478$ ,  $T = 295$  K. Final  $R = 0.074$  for 1861 observed reflections. The Co atom

0108-2701/83/111510-03\$01.50

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