

**Hydrogen Bond Studies.**  
**XCI.\* Disorder in  $(\text{HCO}_3)_2^{2-}$  and  $(\text{DCO}_3)_2^{2-}$  Dimers: A Neutron**  
**Diffraction Study of  $\text{KHCO}_3$  and  $\text{KDCO}_3$**

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Three-dimensional single-crystal neutron-diffraction data sets have been collected for  $\text{KHCO}_3$  and  $\text{KDCO}_3$  at 298 K. Both unit cells are monoclinic, space group  $P2_1/a$ , containing four formula units. The cell dimensions are, for  $\text{KHCO}_3$ :  $a = 15.1725$  (11),  $b = 5.6283$  (5),  $c = 3.7110$  (4) Å,  $\beta = 104.631$  (6)°,  $V = 306.62$  Å<sup>3</sup>; and for  $\text{KDCO}_3$ :  $a = 15.1948$  (9),  $b = 5.6307$  (3),  $c = 3.7107$  (3) Å,  $\beta = 104.567$  (5)°,  $V = 307.27$  Å<sup>3</sup>. The structures comprise  $\text{K}^+$  ions and centrosymmetric  $(\text{HCO}_3)_2^{2-}$  dimers. Contrary to earlier X-ray findings, the H (and D) atoms of the dimers occupy two possible sites in the hydrogen bonds in the rough proportions 4:1; the dimers as a whole must therefore also be subject to the same degree of disordering. The conventional  $R$  values for the final refinements of a model in which only the H (and D) atoms occupy disordered sites are 0.033 and 0.040, respectively. The corresponding O...O hydrogen-bond lengths within the  $(\text{HCO}_3)_2^{2-}$  and  $(\text{DCO}_3)_2^{2-}$  dimers are 2.587 (1) and 2.607 (2) Å, respectively.

### Introduction

An earlier analysis of the results of isotope effect studies of simple hydrogen-bonded compounds (Thomas, 1972) suggested that even simpler systems should be examined for the effect of isotropic substitution to be satisfactorily isolated. It was to this end that the hydrogen-bond situation within the  $(\text{HCO}_3)_2^{2-}$  dimers occurring in  $\text{KHCO}_3$  was studied by X-ray diffraction methods at both room and low temperatures (Thomas, Tellgren & Olovsson, 1974). This work appeared to dispel the earlier suspicion that disorder existed in the structure (Hamilton & Ibers, 1968). A neutron diffraction study of  $\text{KHCO}_3$  and  $\text{KDCO}_3$  was therefore undertaken to obtain precise structural information on the effect of deuterating a simple hydrogen-bonded system. As will be seen from the following, the investigation provided information of a more unexpected nature.

### Crystal data

Potassium hydrogen carbonate,  $\text{KHCO}_3$ , F.W. 100.12. Monoclinic,  $P2_1/a$  (equivalent to  $P2_1/c$ , No. 14),  $a = 15.1725$  (11)†,  $b = 5.6283$  (5),  $c = 3.7110$  (4) Å,  $\beta = 104.631$  (6)°,  $V = 306.62$  Å<sup>3</sup> at 298 K;  $Z = 4$ ,  $D_x = 2.169$  g cm<sup>-3</sup>.

Potassium deuterium carbonate,  $\text{KDCO}_3$ , F.W. 101.13. Monoclinic,  $P2_1/a$ ,  $a = 15.1948$  (9),  $b = 5.6307$  (3),  $c = 3.7107$  (3) Å,  $\beta = 104.567$  (5)°,  $V = 307.27$  Å<sup>3</sup> at 298 K;  $Z = 4$ ,  $D_x = 2.186$  g cm<sup>-3</sup>.

\* Part XCI: *Acta Chem. Scand.* (1974). 28. In the press.  
 † Numbers in parentheses are the estimated standard deviations on the least significant digits.

### Experimental

Suitably large single crystals of  $\text{KHCO}_3$  were grown without difficulty in the same way as the X-ray crystals (Thomas *et al.*, 1974). The crystal used for data collection had a volume of 62.7 mm<sup>3</sup>.

Somewhat smaller  $\text{KDCO}_3$  crystals (>95% D) were obtained, again as described earlier; the largest (volume: 9.3 mm<sup>3</sup>) was used for the data collection after being sealed in a thin-walled quartz tube. Both crystals had four pairs of parallel faces; their separations are given in Table 1.

Table 1. *Dimensions of the crystals used*

Rational boundary planes	Separation (in mm)	
	$\text{KHCO}_3$	$\text{KDCO}_3$
(100), ( $\bar{1}00$ )	3.92	1.05
(40 $\bar{1}$ ), ( $\bar{4}01$ )	2.12	1.83
( $\bar{1}10$ ), ( $\bar{1}\bar{1}0$ )	6.16	3.66
(110), ( $\bar{1}\bar{1}0$ )*	6.16	3.84

\* ( $\bar{1}\bar{1}0$ ) face almost degenerate in  $\text{KDCO}_3$ .

Both data sets were collected at the Swedish Atomic Energy R2 reactor at Studsvik using a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer. A double-monochromator system as described by Stedman, Almqvist, Raunio & Nilsson (1969) was used to produce a very low-background neutron beam with a flux of  $\sim 10^6$  neutrons cm<sup>-2</sup> s<sup>-1</sup> at the crystal ( $\lambda = 1.210$  Å). The diffractometer  $\chi$  and  $\phi$  angles for the  $h00$ ,  $0k0$  and  $00l$  reflexions in  $\text{KHCO}_3$  were: 2.20, -171.28; 87.80, 6.17 and 0.65, 113.33°, respectively (symmetrical  $A$ -setting: Arndt & Willis,

1966). The corresponding angles for  $\text{KDCO}_3$  were:  $-1.08$ ,  $-141.72$ ;  $88.88$ ,  $-126.15$  and  $0.02$ ,  $142.85^\circ$ . All reflexions of type  $(h, k, \pm l)$  were collected out to  $\sin \theta/\lambda = 0.693 \text{ \AA}^{-1}$  using an  $\omega-2\theta$  step-scan mode. In all, 881 independent reflexions were measured for  $\text{KHCO}_3$  of which 752 had intensities greater than  $3\sigma_{\text{count}}$  and were used subsequently in the refinements. The corresponding numbers for  $\text{KDCO}_3$  were 885 and 683. The intensities of three reflexions were monitored at regular intervals throughout each of the data collections. Only small random fluctuations ( $\sim \pm 3\sigma_{\text{count}}$  for the least stable reflexion) were registered, implying that no systematic corrective measures were called for.

The data sets were corrected for Lorentz and absorption effects, the latter employing experimentally determined linear absorption coefficients ( $\text{KHCO}_3$ :  $0.75 \text{ cm}^{-1}$ ;  $\text{KDCO}_3$ :  $0.31 \text{ cm}^{-1}$ ). The value for  $\text{KHCO}_3$  corresponds to an incoherent scattering cross-section for hydrogen of 55 b; the value for  $\text{KDCO}_3$  includes the effect of absorption in the quartz tube. The transmission factors resulting from the absorption corrections were in the range  $0.738$ – $0.869$  for  $\text{KHCO}_3$ , and  $0.922$ – $0.972$  for  $\text{KDCO}_3$ . In making the absorption correction, a mean path-length and six geometrical factors were calculated and saved for each reflexion for use in the subsequent refinement of a correction for secondary extinction (see below).

### Refinements

The full-matrix least-squares refinements made are summarized in Table 2. In all refinements the function minimized was  $\sum w(|F_o|^2 - |F_c|^2)|^2$ , where  $w = 1/\sigma^2(F_o^2)$  and  $\sigma^2(F_o^2) = \sigma_{\text{count}}^2(F_o^2) + (kF_o^2)^2$ . Values for  $k$  between  $0.01$  and  $0.04$  were tested: a value of  $0.025$  was used in the final refinements for  $\text{KHCO}_3$  and  $0.040$  for  $\text{KDCO}_3$ . The agreement factors quoted are defined by the expressions:

$$R(F^2) = \sum [ |F_o|^2 - |F_c|^2 ] / \sum |F_o|^2$$

and

$$R_w(F^2) = [ \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^4 ]^{1/2}.$$

### $\text{KHCO}_3$

The refinements can be analysed most conveniently in three sections.

(a) *Ordered model* (refinement 1). Using the final room-temperature non-hydrogen atom positions from the earlier X-ray investigation (Thomas *et al.*, 1974) as starting values, a series of refinements was made assuming an ordered structure. No evidence for believing that this was not the case had materialized from the earlier X-ray work, even at low temperatures. However, inspection of the difference Fourier synthesis maps following the 'final' refinement (number 1 in Table 2) revealed a concentration of remnant scattering

Table 2. *Summary of the refinements*

$R(F^2)$  and  $R_w(F^2)$  are defined in the text.

Refinement number	Model refined	Numbers of parameters refined	$\text{KHCO}_3$		$\text{KDCO}_3$	
			$R(F^2)$	$R_w(F^2)$	$R(F^2)$	$R_w(F^2)$
1	Ordered model: one scale factor, positional and anisotropic thermal parameters for six atoms, isotropic extinction	56*	0.105	0.131	0.097	0.127
2	As 1 but H (and D) refined as two independent fractional atoms. Occupation numbers $\alpha[\text{H}]$ and $\alpha[\text{H}']$ guessed from difference maps and fixed	65	0.089	0.092	—	—
3	As 2 but $\alpha[\text{H}]$ and $\alpha[\text{H}']$ refined independently	67	0.088	0.092	—	—
4	As 3 but anisotropic (type 1) extinction	72	0.067	0.083	0.069	0.090
5	As 4 but $\alpha[\text{H}] + \alpha[\text{H}']$ constrained to unity and $\alpha[\text{H}]$ refined	71	0.067	0.083	—	—
6	As 5 but $\beta[\text{H}']$ 's constrained to follow $\beta[\text{H}]$ 's	65	0.067	0.084	0.069	0.091†
7	As 6 but weighting scheme modified	65	0.066	0.078†	—	—
8	Extended disordered model. Occupation and anisotropic (type 1) extinction parameters fixed from 6 and 7 (see text)	55	0.082	0.147	0.079	0.115

\* 57 in  $\text{KDCO}_3$  as  $\alpha[\text{D}]$  also refined.

† Final models chosen.

power in the form of a peak of height  $\sim 0.3$  protons  $\text{\AA}^{-3}$  lying roughly along the  $\text{O}\cdots\text{O}$  hydrogen-bond direction and  $\sim 0.7$   $\text{\AA}$  from the acceptor oxygen O(2). The refinements were thus extended to examine this apparent fractional disorder effect.

(b) *Limited disorder model* (refinements 2–7). It is clear that if the hydrogen atoms of the  $(\text{HCO}_3)_2^{2-}$  dimer are subject to a disordering effect then the non-hydrogen atoms must be equally involved. In this next series of refinements, however, a scattering model will be assumed in which only the hydrogen-atom sites are affected by the disorder.

In refinement 3 the occupation number of the dominant hydrogen-atom site ( $\alpha[\text{H}]$ ) and of the weaker hydrogen-atom site ( $\alpha[\text{H}']$ ) are refined independently. The sum of the refined occupation numbers,  $\alpha[\text{H}] + \alpha[\text{H}']$ , was 0.98 (9); the constraint  $\alpha[\text{H}] + \alpha[\text{H}'] = 1.0$  was thus applied in all subsequent refinements. A further constraint, that the thermal vibration ellipsoid for H' should follow that for H (*i.e.*  $\beta_{ii}[\text{H}] = \beta_{ii}[\text{H}']$ ,  $\beta_{12}[\text{H}] = -\beta_{12}[\text{H}']$ ,  $\beta_{13}[\text{H}] = \beta_{13}[\text{H}']$ , and  $\beta_{23}[\text{H}] = -\beta_{23}[\text{H}']$ ), was tested in refinement 6. Application of a significance test (Hamilton, 1965; Pawley, 1970) to the  $R_w(F^2)$  values from refinements 5 and 6 indicated that this was a physically significant constraint.

(c) *Extended disorder model* (refinement 8). An attempt was finally made to resolve in a refinement the manner in which the non-hydrogen atoms of the  $(\text{HCO}_3)_2^{2-}$  dimer are involved in the disorder. The problem is immediately clear. The only overt evidence for disorder in the structure is associated with the hydrogen atoms; the disordered non-hydrogen atoms approximately superpose to produce apparently

ordered sites. Refinement of such a situation must necessarily involve considerable correlation difficulties.

In refinement 8 a model is refined (see Fig. 1) in which *all* atom-sites of the dimer are disordered. The model comprises a more and a less dominant 'fractional' dimer, related by a twofold rotation about an axis parallel to the  $b$  axis and passing through the centre of symmetry of each dimer. Crude starting values for the positions of O(2) and O(3) were calculated assuming that the 'real' C–O(2) and C–O(3) bonds (unbiased by disorder) were of length 1.26 and 1.35  $\text{\AA}$ , respectively, but in the same directions with respect to C as the C–O(2) and C–O(3) bonds refined earlier (in refinement 7). The starting positions for C and O(1) were obtained by applying small arbitrary shifts to the  $y$  coordinates derived in refinement 7; the  $x$  and  $z$  coordinates were left unchanged. The occupation numbers associated with [C, O(1), O(2), O(3)] and [C', O(1'), O(2'), O(3')] were constrained to follow the occupation numbers for H and H', respectively: *i.e.*  $\alpha[\text{H}] = \alpha[\text{C}] = \alpha[\text{O}(1)] = \alpha[\text{O}(2)] = \alpha[\text{O}(3)]$  and  $\alpha[\text{H}'] = \alpha[\text{C}'] = \alpha[\text{O}(1')] = \alpha[\text{O}(2')] = \alpha[\text{O}(3')]$ . Furthermore, the constraint  $\alpha[\text{H}] + \alpha[\text{H}'] = 1.0$  was applied and the value of  $\alpha[\text{H}]$  fixed to the value obtained from refinement 7. Finally the thermal vibration ellipsoids for the 'weaker' fractional atoms were constrained to follow those of their more dominant counterparts, *e.g.*  $\beta_{ii}[\text{C}] = \beta_{ii}[\text{C}']$ ,  $\beta_{12}[\text{C}] = -\beta_{12}[\text{C}']$ ,  $\beta_{13}[\text{C}] = \beta_{13}[\text{C}']$  and  $\beta_{23}[\text{C}] = -\beta_{23}[\text{C}']$ , *etc.*

The application of these constraints had the effect that no pair of refined parameters were correlated by more than 58% in the subsequent refinement. Al-

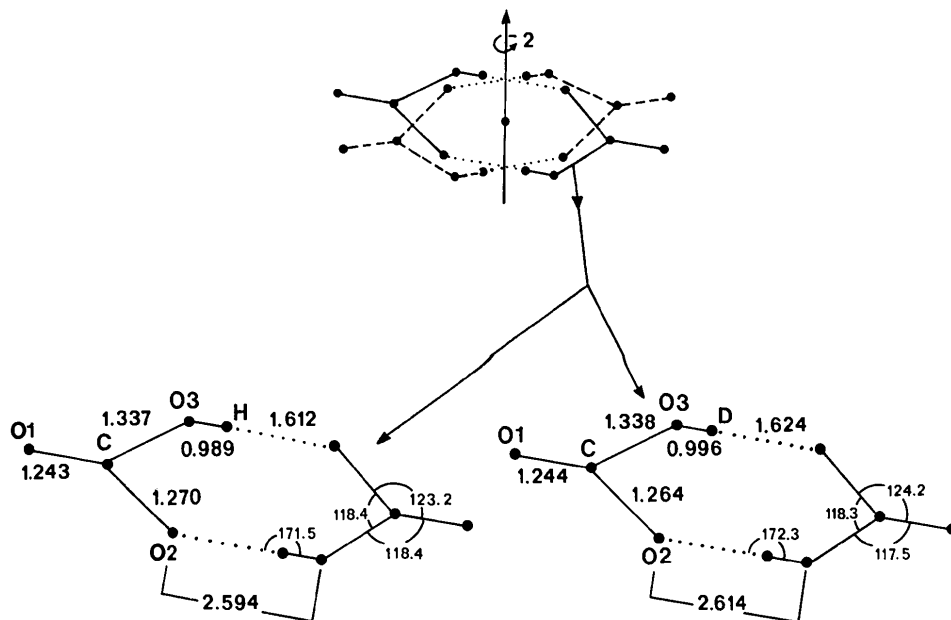


Fig. 1. A schematic representation of the disorder model investigated in refinement 8 (see Table 2). The upper figure depicts the overlapping of the two fractional dimers related by a twofold rotation. The lower figures show the internal geometries of the individual dimers in  $\text{KHCO}_3$  (left) and  $\text{KDCO}_3$  (right).

though the refinement converged satisfactorily, we see from Table 2 that the agreement factor worsened significantly. Final parameters from this refinement are therefore not provided here. Nevertheless, in view of the fact that the internal geometry of the identical 'fractional' dimers was realistic, the resulting bond distances and angles are included in Fig. 1.

The simple model suggested here is thus inadequate for describing the detail of the disorder in the structure. No more sophisticated model was investigated to resolve the disorder. The positional and thermal parameters from refinement 7 were therefore taken as the most appropriate representation of the structure. These are given in Tables 3 and 4. The final observed and calculated structure factors are given in Table 5. The treatment of extinction is discussed later.

### KDCO<sub>3</sub>

Only features of the refinement procedure which differ significantly from those of KHCO<sub>3</sub> will be mentioned here.

By way of further confirmation of the disorder found in KHCO<sub>3</sub>, a peak of height  $\sim 0.2$  deuterons  $\text{\AA}^{-3}$  was found after refinement 1 in essentially the same position as the peak found in KHCO<sub>3</sub>. This indicates that a similar type of disorder also affects KDCO<sub>3</sub>.

Uncertainty as to the degree of deuteration of the crystal demanded greater caution in applying the occupation constraint. It was found, however, that following refinement 4 the value of  $\alpha[D] + \alpha[D']$  was 1.00 (8), suggesting that even here the constraint  $\alpha[D] + \alpha[D'] = 1.0$  was justified in the final refinement (num-

ber 6). Resulting parameters are again given in Tables 3 and 4; final observed and calculated structure factors are given in Table 5.

Refinement of the more extended disorder model (number 8) again provided an inadequate description of the disorder in the structure (see Table 2). The internal geometry derived for the individual dimers is again included in Fig. 1, however.

In both the KHCO<sub>3</sub> and KDCO<sub>3</sub> refinements, isotropic and anisotropic (type 1 and type 2) models were investigated to describe secondary extinction effects in the data (Coppens & Hamilton, 1970). An anisotropic (type 1) model was found to produce a significant improvement in the refinements compared with an isotropic model. The final values of the six extinction parameters are given in Table 6. A successful refinement using a type 2 model was only possible after the removal of several reflexions ( $\sim 50$  for KDCO<sub>3</sub>) from the data-sets. This model was therefore rejected as being unrealistic.

In all refinements the values assumed for the neutron coherent scattering amplitudes for K, H, D, C and O were 3.7, -3.74, 6.67, 6.65 and 5.80 fm, respectively (Bacon, 1972).

### Computer programs

All programs used during this investigation have been described by Lundgren (1974). The calculations were carried out using an IBM 370/155 computer at the Uppsala University Data Center, and the departmental IBM 1800 computer.

Table 3. *Atomic coordinates* ( $\times 10^5$ ) at 298 K

For the non-hydrogen atoms the three rows are, from the top, the neutron coordinates, the X-ray coordinates and the differences between the neutron and X-ray coordinates.

	KHCO <sub>3</sub> (refinement 7)			KDCO <sub>3</sub> (refinement 6)		
	x	y	z	x	y	z
K	16534 (8)	2279 (19)	29524 (30)	16544 (13)	2876 (38)	29631 (51)
	16533 (3)	2177 (10)	29533 (13)	16540 (3)	2850 (9)	29583 (14)
	1 (9)	102 (22)	-9 (32)	4 (13)	26 (39)	48 (53)
H(D)	1618 (14)	68990 (28)	-44970 (52)	1649 (12)	69130 (27)	-44827 (43)
	(Occupation: 0.804 (7))			(Occupation: 0.877 (5))		
H'(D')	-2110 (61)	68091 (121)	-56163 (229)	-2391 (101)	67813 (205)	-56904 (349)
	(Occupation: 0.196 (7))			(Occupation: 0.123 (5))		
C	11952 (4)	51630 (10)	-14418 (16)	11990 (6)	52115 (19)	-14341 (26)
	11967 (14)	51500 (13)	-14363 (68)	12005 (15)	51990 (37)	-14296 (66)
	-15 (15)	130 (17)	-55 (70)	-15 (16)	125 (42)	-45 (68)
O(1)	19342 (5)	52999 (14)	9465 (21)	19358 (8)	53868 (27)	9426 (36)
	19329 (11)	52915 (27)	9482 (55)	19350 (11)	53839 (31)	9399 (54)
	13 (12)	84 (31)	-17 (59)	8 (14)	29 (41)	27 (65)
O(2)	8230 (5)	32072 (13)	-27325 (21)	8327 (8)	32640 (25)	-27232 (32)
	8221 (9)	31998 (31)	-27353 (42)	8330 (10)	32577 (30)	-27233 (47)
	9 (11)	74 (34)	28 (47)	-3 (13)	63 (40)	1 (57)
O(3)	7748 (5)	71816 (13)	-27376 (22)	7718 (8)	72298 (26)	-27289 (33)
	7761 (9)	71772 (27)	-27448 (43)	7721 (11)	72337 (29)	-27330 (47)
	-13 (11)	44 (30)	72 (49)	-3 (14)	39 (39)	41 (58)

## Discussion

*General.* A general stereoscopic view of the  $\text{KHCO}_3$  structure derived from refinement 7 is given in Fig. 2.

Relevant bond distances and angles for both  $\text{KHCO}_3$  and  $\text{KDCO}_3$  are given in Table 7 and the geometries of the  $(\text{HCO}_3)_2^{2-}$  and  $(\text{DCO}_3)_2^{2-}$  dimers are illustrated in Fig. 3 together with the corresponding values from

Table 4. *Anisotropic thermal parameters* ( $\times 10^4$ )

The form of the temperature factor is:  $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{12}hk + \dots)]$ . For the non-hydrogen atoms the three rows are, from the top, the neutron parameters, the X-ray parameters and the differences between the neutron and X-ray parameters. The r.m.s. components ( $R_i \times 10^3 \text{ \AA}$ ) of thermal displacement from the neutron study (first row) are also given along with the X-ray values for comparison.

(a)  $\text{KHCO}_3$ 

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1$	$R_2$	$R_3$
K	27 (1)	167 (3)	358 (7)	1 (1)	9 (1)	-1 (3)	149 (2)	164 (2)	184 (1)
	26 (1)	163 (3)	412 (9)	2 (1)	15 (1)	2 (1)	158 (1)	162 (1)	177 (1)
	1 (2)	4 (4)	-54 (11)	-1 (2)	-6 (2)	-3 (3)			
H	31 (1)	180 (4)	623 (15)	1 (1)	0 (3)	17 (5)	168 (2)	174 (2)	226 (2)
	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-
H'	31 (1)*	180 (4)	623 (15)	-1 (1)	0 (3)	-17 (5)	168 (2)	174 (2)	226 (2)
	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-
C	19 (1)	144 (2)	337 (5)	-1 (1)	9 (1)	-4 (2)	138 (1)	152 (1)	160 (1)
	19 (1)	144 (7)	384 (24)	0 (1)	26 (3)	5 (6)	140 (3)	152 (3)	159 (5)
	0 (2)	0 (7)	-47 (25)	-1 (2)	-17 (3)	-9 (6)			
O(1)	22 (1)	225 (3)	478 (6)	-1 (1)	-11 (1)	-14 (3)	139 (1)	190 (1)	205 (1)
	21 (1)	220 (6)	576 (18)	1 (1)	0 (3)	-8 (6)	146 (3)	187 (3)	209 (3)
	1 (2)	5 (7)	-98 (19)	-2 (2)	-11 (3)	-6 (7)			
O(2)	27 (1)	142 (2)	490 (6)	2 (1)	-11 (1)	-11 (2)	149 (1)	151 (1)	212 (1)
	26 (1)	143 (5)	554 (15)	2 (1)	-1 (2)	-13 (5)	151 (3)	157 (2)	211 (2)
	1 (2)	-1 (5)	-64 (16)	0 (2)	-10 (2)	2 (5)			
O(3)	26 (1)	142 (2)	525 (6)	-2 (1)	-10 (1)	3 (2)	150 (1)	152 (1)	214 (1)
	25 (1)	140 (5)	618 (16)	-3 (1)	-2 (1)	8 (6)	149 (3)	157 (2)	219 (2)
	1 (2)	2 (5)	-93 (17)	1 (2)	-8 (2)	-5 (6)			

(b)  $\text{KDCO}_3$ 

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1$	$R_2$	$R_3$
K	30 (1)	174 (7)	400 (12)	1 (2)	13 (3)	-2 (7)	158 (3)	167 (3)	189 (2)
	26 (1)	129 (2)	463 (7)	2 (1)	6 (1)	-1 (2)	144 (1)	157 (1)	192 (1)
	4 (2)	45 (7)	-63 (14)	-1 (2)	7 (3)	-1 (7)			
D	33 (1)	171 (5)	629 (12)	2 (1)	6 (3)	-3 (5)	165 (2)	178 (3)	223 (2)
	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-
D'	33(1)*	171 (5)	629 (12)	-2 (1)	6 (3)	3 (5)	165 (2)	178 (3)	223 (2)
	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-
C	21 (1)	145 (4)	357 (7)	-1 (1)	12 (1)	-8 (3)	144 (2)	153 (2)	164 (1)
	19 (1)	125 (7)	385 (23)	-1 (2)	16 (3)	-2 (7)	141 (4)	145 (4)	162 (4)
	2 (2)	20 (8)	-28 (24)	0 (2)	-4 (3)	-6 (7)			
O(1)	25 (1)	220 (5)	495 (9)	1 (1)	-8 (2)	-21 (5)	148 (2)	187 (2)	209 (2)
	21 (1)	198 (6)	588 (18)	1 (2)	-12 (3)	-14 (6)	140 (3)	178 (3)	219 (3)
	4 (2)	22 (8)	-93 (20)	0 (2)	4 (4)	-7 (8)			
O(2)	29 (1)	150 (5)	517 (9)	1 (1)	-5 (2)	-10 (5)	155 (2)	158 (2)	212 (2)
	27 (1)	110 (5)	611 (16)	1 (1)	-5 (3)	-11 (6)	132 (3)	158 (3)	222 (3)
	2 (2)	40 (7)	-94 (19)	0 (2)	0 (4)	1 (8)			
O(3)	28 (1)	141 (4)	561 (10)	-1 (1)	-8 (2)	-1 (5)	150 (2)	157 (2)	220 (2)
	25 (1)	104 (5)	666 (16)	-3 (1)	-12 (1)	0 (6)	129 (3)	153 (3)	232 (3)
	3 (2)	37 (7)	-105 (19)	2 (2)	4 (4)	-1 (8)			

\* Values constrained to follow those for H (and D); see text.

Table 5. Observed and calculated structure factors for (a) KHCO<sub>3</sub> and (b) KDCO<sub>3</sub> at 298 K

The five columns are, in order: *k*, *l*, 100|*F*<sub>o</sub>|, 100|*F*<sub>c</sub>| and 100 *E*. Reflexions for which *F*<sup>2</sup> < 3σ(*F*<sup>2</sup>) are marked with an asterisk; these were given zero weight in the refinement. *E* is the extinction correction factor multiplying *F*<sub>c</sub>.

(a)

<i>k</i>	<i>l</i>	100  <i>F</i> <sub>o</sub>	100  <i>F</i> <sub>c</sub>	100 <i>E</i>
0	0	100	100	1.00
0	1	100	100	1.00
0	2	100	100	1.00
0	3	100	100	1.00
0	4	100	100	1.00
0	5	100	100	1.00
0	6	100	100	1.00
0	7	100	100	1.00
0	8	100	100	1.00
0	9	100	100	1.00
0	10	100	100	1.00
0	11	100	100	1.00
0	12	100	100	1.00
0	13	100	100	1.00
0	14	100	100	1.00
0	15	100	100	1.00
0	16	100	100	1.00
0	17	100	100	1.00
0	18	100	100	1.00
0	19	100	100	1.00
0	20	100	100	1.00
0	21	100	100	1.00
0	22	100	100	1.00
0	23	100	100	1.00
0	24	100	100	1.00
0	25	100	100	1.00
0	26	100	100	1.00
0	27	100	100	1.00
0	28	100	100	1.00
0	29	100	100	1.00
0	30	100	100	1.00
0	31	100	100	1.00
0	32	100	100	1.00
0	33	100	100	1.00
0	34	100	100	1.00
0	35	100	100	1.00
0	36	100	100	1.00
0	37	100	100	1.00
0	38	100	100	1.00
0	39	100	100	1.00
0	40	100	100	1.00
0	41	100	100	1.00
0	42	100	100	1.00
0	43	100	100	1.00
0	44	100	100	1.00
0	45	100	100	1.00
0	46	100	100	1.00
0	47	100	100	1.00
0	48	100	100	1.00
0	49	100	100	1.00
0	50	100	100	1.00
0	51	100	100	1.00
0	52	100	100	1.00
0	53	100	100	1.00
0	54	100	100	1.00
0	55	100	100	1.00
0	56	100	100	1.00
0	57	100	100	1.00
0	58	100	100	1.00
0	59	100	100	1.00
0	60	100	100	1.00
0	61	100	100	1.00
0	62	100	100	1.00
0	63	100	100	1.00
0	64	100	100	1.00
0	65	100	100	1.00
0	66	100	100	1.00
0	67	100	100	1.00
0	68	100	100	1.00
0	69	100	100	1.00
0	70	100	100	1.00
0	71	100	100	1.00
0	72	100	100	1.00
0	73	100	100	1.00
0	74	100	100	1.00
0	75	100	100	1.00
0	76	100	100	1.00
0	77	100	100	1.00
0	78	100	100	1.00
0	79	100	100	1.00
0	80	100	100	1.00
0	81	100	100	1.00
0	82	100	100	1.00
0	83	100	100	1.00
0	84	100	100	1.00
0	85	100	100	1.00
0	86	100	100	1.00
0	87	100	100	1.00
0	88	100	100	1.00
0	89	100	100	1.00
0	90	100	100	1.00
0	91	100	100	1.00
0	92	100	100	1.00
0	93	100	100	1.00
0	94	100	100	1.00
0	95	100	100	1.00
0	96	100	100	1.00
0	97	100	100	1.00
0	98	100	100	1.00
0	99	100	100	1.00
0	100	100	100	1.00

(b)

<i>k</i>	<i>l</i>	100  <i>F</i> <sub>o</sub>	100  <i>F</i> <sub>c</sub>	100 <i>E</i>
0	0	100	100	1.00
0	1	100	100	1.00
0	2	100	100	1.00
0	3	100	100	1.00
0	4	100	100	1.00
0	5	100	100	1.00
0	6	100	100	1.00
0	7	100	100	1.00
0	8	100	100	1.00
0	9	100	100	1.00
0	10	100	100	1.00
0	11	100	100	1.00
0	12	100	100	1.00
0	13	100	100	1.00
0	14	100	100	1.00
0	15	100	100	1.00
0	16	100	100	1.00
0	17	100	100	1.00
0	18	100	100	1.00
0	19	100	100	1.00
0	20	100	100	1.00
0	21	100	100	1.00
0	22	100	100	1.00
0	23	100	100	1.00
0	24	100	100	1.00
0	25	100	100	1.00
0	26	100	100	1.00
0	27	100	100	1.00
0	28	100	100	1.00
0	29	100	100	1.00
0	30	100	100	1.00
0	31	100	100	1.00
0	32	100	100	1.00
0	33	100	100	1.00
0	34	100	100	1.00
0	35	100	100	1.00
0	36	100	100	1.00
0	37	100	100	1.00
0	38	100	100	1.00
0	39	100	100	1.00
0	40	100	100	1.00
0	41	100	100	1.00
0	42	100	100	1.00
0	43	100	100	1.00
0	44	100	100	1.00
0	45	100	100	1.00
0	46	100	100	1.00
0	47	100	100	1.00
0	48	100	100	1.00
0	49	100	100	1.00
0	50	100	100	1.00
0	51	100	100	1.00
0	52	100	100	1.00
0	53	100	100	1.00
0	54	100	100	1.00
0	55	100	100	1.00
0	56	100	100	1.00
0	57	100	100	1.00
0	58	100	100	1.00
0	59	100	100	1.00
0	60	100	100	1.00
0	61	100	100	1.00
0	62	100	100	1.00
0	63	100	100	1.00
0	64	100	100	1.00
0	65	100	100	1.00
0	66	100	100	1.00
0	67	100	100	1.00
0	68	100	100	1.00
0	69	100	100	1.00
0	70	100	100	1.00
0	71	100	100	1.00
0	72	100	100	1.00
0	73	100	100	1.00
0	74	100	100	1.00
0	75	100	100	1.00
0	76	100	100	1.00
0	77	100	100	1.00
0	78	100	100	1.00
0	79	100	100	1.00
0	80	100	100	1.00
0	81	100	100	1.00
0	82	100	100	1.00
0	83	100	100	1.00
0	84	100	100	1.00
0	85	100	100	1.00
0	86	100	100	1.00
0	87	100	100	1.00
0	88	100	100	1.00
0	89	100	100	1.00
0	90	100	100	1.00
0	91	100	100	1.00
0	92	100	100	1.00
0	93	100	100	1.00
0	94	100	100	1.00
0	95	100	100	1.00
0	96	100	100	1.00
0	97	100	100	1.00
0	98	100	100	1.00
0	99	100	100	1.00
0	100	100	100	1.00

the room-temperature X-ray study. The planarity of the dimer in  $\text{KHCO}_3$  and  $\text{KDCO}_3$  is summarized in Table 8.

It will be noted from Table 3 that the X-ray- and neutron-determined non-hydrogen atom positions agree well; although the maximum disagreement is

$\sim 7\sigma$  [in  $\gamma(\text{C})$  for  $\text{KHCO}_3$ ], the average difference is only  $1.3\sigma$ . Discrepancies of this magnitude are no more than are to be expected in view of the fundamental difference between the X-ray and neutron diffraction methods (see Coppens, 1970). The slightly larger discrepancies between the anisotropic thermal param-

Table 6. Refined anisotropic (type 1) extinction parameters ( $Z'_{ij}$ ) as defined by Coppens & Hamilton (1970)

	$Z'_{11}$	$Z'_{22}$	$Z'_{33}$	$Z'_{12}$	$Z'_{13}$	$Z'_{23}$
$\text{KHCO}_3$	1.05 (17)	0.42 (5)	1.52 (20)	1.05 (16)	-0.07 (29)	-0.04 (16)
$\text{KDCO}_3$	30.3 (4.9)	9.4 (1.2)	22.7 (4.0)	16.5 (4.2)	-12.3 (6.6)	-4.1 (3.3)

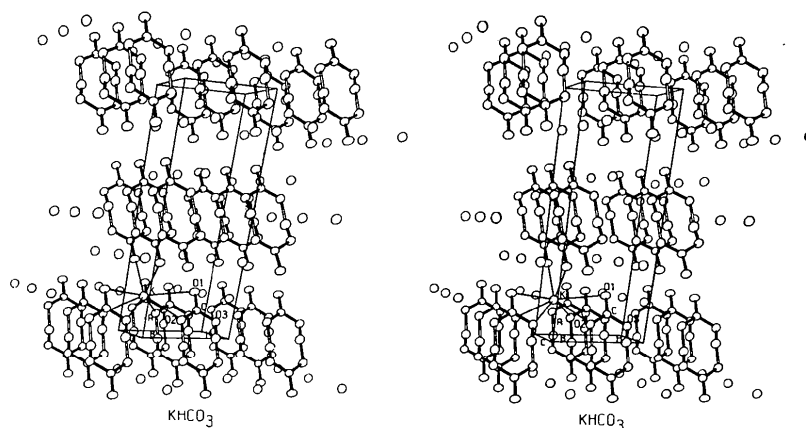


Fig. 2. A stereoscopic illustration of the  $\text{KHCO}_3$  structure. Note that only the 'dominant' hydrogen atom site is shown here. The thermal vibration ellipsoids are drawn to include 50% probability.

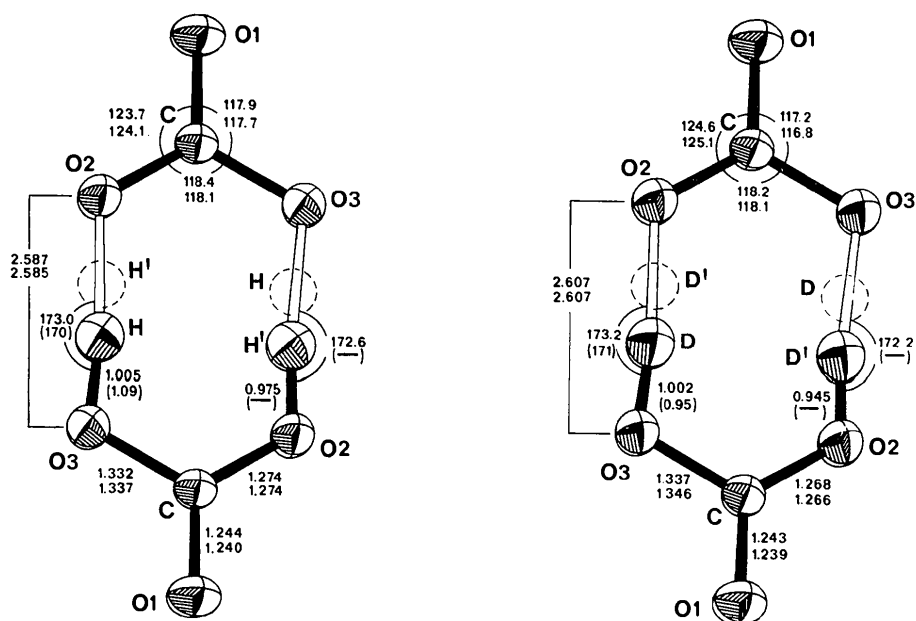


Fig. 3. The internal geometries of the disordered  $(\text{HCO}_3)_2^-$  and  $(\text{DCO}_3)_2^-$  ions as obtained from refinements 7 ( $\text{KHCO}_3$ ) and 6 ( $\text{KDCO}_3$ ). The X-ray values (Thomas *et al.*, 1974) are also included for comparison below the neutron values. The figure has been simplified by drawing the centrosymmetrically related H and D atoms as dashed circles. The thermal vibration ellipsoids for the atoms are otherwise drawn to include 50% probability.

eters (Table 4) observed with X-rays and neutrons (maximum:  $\sim 7\sigma$ , mean:  $2.0\sigma$ ) are again no more than an expression of the differences in the methods. Similar discrepancies were found in the case of  $\alpha$ -glycine (Almlöf, Kvik & Thomas, 1973). A point to observe here is that the greatest disagreement is found in the  $\beta_{33}$  values, with the X-ray values systematically larger. This is probably a consequence of the X-ray data being collected about the  $c$  axis using a Weissenberg diffractometer.

We can conclude therefore that, as far as the non-hydrogen atoms are concerned, neither the neutron

Table 8. *The planarity of the  $(\text{HCO}_3)_2^{2-}$  dimer; values obtained from the X-ray study are included for comparison*

The parallel planes through the oxygen atoms of each  $\text{HCO}_3^-$  ion are taken as references; the notation is defined in the following schematic figure:

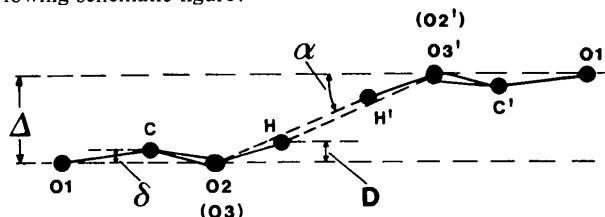


Table 7. *Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) at 298 K*

The X-ray-determined values are included for comparison. The first three digits of the identifying suffices on atoms not in the asymmetric unit refer to a lattice translation, *e.g.* 564 implies the operation  $(x, y+1, z-1)$ ; the fourth digit specifies one of the symmetry operations:

- 1:  $x, y, z$
- 2:  $\frac{1}{2} + x, \frac{1}{2} - y, z$
- 3:  $-x, -y, -z$
- 4:  $\frac{1}{2} - x, \frac{1}{2} + y, -z$

(a)  $\text{K}^+$  ion

	$\text{KHCO}_3$		$\text{KDCO}_3$	
	Neutron	X-ray	Neutron	X-ray
$\text{K} \cdots \text{O}(1)$	3.008 (1)	3.008 (2)	3.025 (2)	3.024 (2)
$\text{K} \cdots \text{O}(1)_{5451}$	2.931 (1)	2.929 (2)	2.919 (2)	2.919 (2)
$\text{K} \cdots \text{O}(1)_{5454}$	2.873 (1)	2.875 (2)	2.873 (2)	2.873 (2)
$\text{K} \cdots \text{O}(1)_{5464}$	2.696 (1)	2.697 (2)	2.696 (2)	2.699 (2)
$\text{K} \cdots \text{O}(2)$	2.740 (1)	2.742 (2)	2.738 (2)	2.735 (2)
$\text{K} \cdots \text{O}(2)_{5561}$	2.825 (1)	2.826 (2)	2.817 (2)	2.816 (2)
$\text{K} \cdots \text{O}(3)_{5451}$	2.784 (1)	2.784 (2)	2.793 (2)	2.790 (2)
$\text{K} \cdots \text{O}(3)_{5461}$	2.890 (1)	2.885 (2)	2.898 (2)	2.895 (2)
$\text{K} \cdots \text{O}$	2.843	2.843	2.845	2.844

	$\text{KHCO}_3$		$\text{KDCO}_3$	
	Neutron	X-ray	Neutron	X-ray
$\Delta(\text{\AA})$	0.214 (1)	0.222 (3)	0.214 (1)	0.219 (3)
$D$	0.077 (2)	0.09 (3)	0.072 (2)	0.03 (3)
$(D')$	0.107 (9)	—	0.109 (16)	—
$\delta$	0.003 (1)	0.004 (3)	0.004 (1)	0.005 (3)
$\alpha(^\circ)^*$	4.7 (1)	4.9 (1)	4.7 (1)	4.8 (1)

\*  $\alpha$  is the angle between the plane defined by  $\text{O}(2), \text{O}(3), \text{O}(3'), \text{O}(2')$  and the reference plane through  $\text{O}(1), \text{O}(2), \text{O}(3)$  or  $\text{O}(1'), \text{O}(2'), \text{O}(3')$ .

nor the X-ray study has given any obvious indication of disorder. The non-hydrogen atom parameters clearly adjust to camouflage the disorder in the structure. The discovery of a fractional disorder can therefore be attributed entirely to the superior ability of the neutron to detect hydrogen (and to an even greater extent deuterium) atoms. This is an important point remembering that the majority of documented hydrogen-bonded structures are X-ray determined.

Table 7 (cont.)

(b)  $\text{CO}_3$  group

	$\text{KHCO}_3$		$\text{KDCO}_3$	
	Neutron	X-ray	Neutron	X-ray
$\text{C}-\text{O}(1)$	1.244 (1)	1.240 (3)	1.243 (1)	1.239 (3)
$\text{C}-\text{O}(2)$	1.274 (1)	1.274 (2)	1.268 (2)	1.266 (3)
$\text{C}-\text{O}(3)$	1.332 (1)	1.337 (2)	1.337 (2)	1.346 (3)
$\text{C}-\text{O}$	1.283	1.284	1.283	1.284
$\text{O}(1)-\text{C}-\text{O}(2)$	123.75 (6)	124.12 (17)	124.62 (12)	125.05 (20)
$\text{O}(1)-\text{C}-\text{O}(3)$	117.89 (6)	117.74 (16)	117.19 (12)	116.82 (19)
$\text{O}(2)-\text{C}-\text{O}(3)$	118.35 (6)	118.14 (18)	118.18 (11)	118.12 (20)

(c) Hydrogen bond

$\text{O}(3) \cdots \text{O}(2)_{5643}$	2.587 (1)	2.585 (2)	2.607 (2)	2.607 (2)
$\text{O}(3) \cdots \text{H}$	1.005 (2)	1.09 (3)	1.002 (2)	0.95 (4)
$\text{H} \cdots \text{O}(2)_{5643}$	1.587 (2)	1.50 (3)	1.610 (2)	1.66 (4)
$\text{O}(3) \cdots \text{H} \cdots \text{O}(2)_{5643}$	173.02 (15)	169.8 (5.7)	173.21 (17)	170.6 (4.4)
$\text{O}(2)_{5643} \cdots \text{H}'$	0.975 (9)	—	0.945 (15)	—
$\text{H}' \cdots \text{O}(3)$	1.617 (9)	—	1.668 (16)	—
$\text{O}(2)_{5643} \cdots \text{H}' \cdots \text{O}(3)$	172.61 (6)	—	172.21 (11)	—
$\text{C} \cdots \text{O}(3) \cdots \text{O}(2)_{5643}$	116.56 (5)	116.67 (12)	115.63 (9)	115.54 (13)
$\text{O}(3) \cdots \text{O}(2)_{5643} \cdots \text{C}_{5643}$	124.82 (5)	124.90 (12)	125.93 (10)	125.05 (14)
$\text{C} \cdots \text{O}(3) \cdots \text{H}$	112.32 (11)	110.8 (3.3)	111.50 (16)	110.6 (3.2)
$\text{H} \cdots \text{O}(2)_{5643} \cdots \text{C}_{5643}$	122.11 (8)	120.6 (2.4)	123.33 (12)	123.0 (1.8)
$\text{C}_{5643} \cdots \text{O}(2)_{5643} \cdots \text{H}'$	120.4 (4)	—	121.2 (7)	—
$\text{H}' \cdots \text{O}(3) \cdots \text{C}$	114.0 (3)	—	113.1 (4)	—
$\text{H} \cdots \text{H}'$	0.613 (9)	—	0.667 (14)	—



*The dimers.* The final refined values for the occupation numbers of H and D were 0.804 (7) and 0.877 (5), respectively. This would suggest that, although the  $(\text{HCO}_3)_2^-$  and  $(\text{DCO}_3)_2^-$  dimers are affected by the same general form of disordering, the degree of disordering is *different* in the two crystals studied. It is clearly a dubious extrapolation, however, to suggest that this is true for the  $\text{KHCO}_3$  and  $\text{KDCO}_3$  structures in general. Let us analyse the situation in a little more detail.

Intuitively we would expect the source of the disorder to be an orientational disordering of the entire  $(\text{HCO}_3)_2^-$  and  $(\text{DCO}_3)_2^-$  dimers in the lattice. The near-planar symmetrical shape of the dimer suggests that stacking 'mistakes' of this type could occur without introducing undue local strain into the crystal structure. The alternative disordering mechanism, synchronous proton jumps across the  $\sim 2.60$  Å hydrogen bonds within an individual dimer, must be regarded as highly unlikely in the present case. It is also relevant to recall the long-held suspicion that carboxyl dimers are susceptible to an insidious fractional disordering tendency. Currie, Speakman & Curry (1967) cite as evidence for this the observation that differences between C=O carbonyl and C-OH hydroxyl distances fall in the range 0.04–0.12 Å. More recently Bernstein & Leiserowitz (1972) have deduced that the structure of *trans,trans*-muconic acid contains a statistical disorder (not 50%–50%) within one of its carboxyl groups.

Let us therefore make the simplifying assumption (the validity of which we have made no attempt to examine here) that the disorder in the dimers takes the form of a statistical overlap of just *two* differently oriented dimers, *i.e.* there exists one discrete dimeric orientation for each of the two observed H (and D) positions. It would therefore follow that, in the event of a 50%–50% disordering, the apparent C-O(2) and C-O(3) distances would be equal. The observation that (a) extremely consistent correspondence is found between X-ray- and neutron-determined C-O(2) and C-O(3) distances (see Table 7 and Fig. 3) in  $\text{KHCO}_3$  and  $\text{KDCO}_3$ , and (b) that these distances differ significantly (by  $\sim 0.07$  Å) would suggest a *general* tendency for each of the structures to comprise a superposition of a predominant and a subordinate orientation. From this experiment alone, however, it is of course not possible to establish that the significantly different degrees of disordering deduced for  $\text{KHCO}_3$  and  $\text{KDCO}_3$  have a more general significance, *e.g.* that the degree of ordering is related to the degree of deuteration in some systematic way. One point immediately suggests itself, however. It could well be that the small systematic structural differences between  $\text{KHCO}_3$  and  $\text{KDCO}_3$  observed at all three temperatures in the X-ray study (especially in the C-O(2) and C-O(3) bond lengths: see Fig. 4) were artifacts of a differing degree of disordering in the  $\text{KHCO}_3$  and  $\text{KDCO}_3$  crystals used. Differences of the same order of magnitude are

also found in the present room-temperature neutron study.

In the light of this possibility, it is clearly extremely difficult to ascertain the geometry of an individual dimer, if indeed a discrete characteristic geometry exists for an individual dimer in this type of situation. Nevertheless, an attempt was made (refinement 8) to discover how such a hypothetical dimer might look. The model refined was described earlier. Although satisfactory convergence was obtained and realistic internal geometries resulted (see Fig. 1), the poor agreement factors implied that the model was unsatisfactory in describing the detail of the disorder in the structure.

*Isotope effect.* It is inevitable from the above that doubts must be raised as to the meaningfulness of data obtained on the isotope effect in view of the presence of disorder in the structure. We observe that the change in  $\text{O}(2)\cdots\text{O}(3)$  length on deuteration (Table 7) [ $\Delta(\text{D}-\text{H}) = +0.020$  (2) Å] is in good agreement with the X-ray result of  $+0.022$  (3) Å at the same temperature.

Two conditions must be fulfilled, however, if the results obtained here and from the earlier X-ray study of the temperature dependence of the isotope effect can be taken as giving a representative picture or the 'true' situation within an individual dimer. The  $\text{O}\cdots\text{O}$

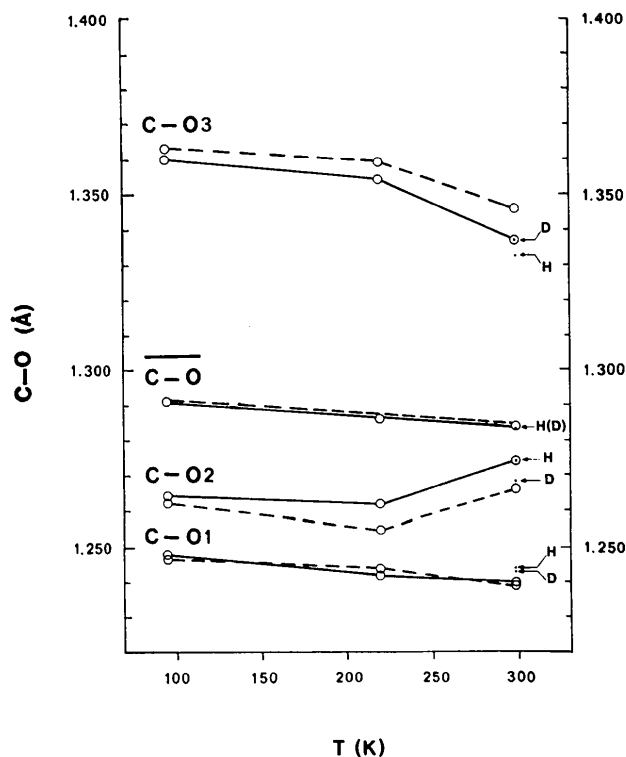


Fig. 4. The variation in the C-O distances in  $\text{KHCO}_3$  (solid lines) and  $\text{KDCO}_3$  (dashed lines) with temperature, as observed by X-ray diffraction. The room-temperature values obtained here are included for comparison.

bonds must superpose in the structure in such a way that a valid measure of the *difference* between O...O lengths in KHCO<sub>3</sub> and KDClO<sub>3</sub> is obtained. The degree of disordering must also be invariant with temperature. These would both appear reasonable assumptions if the disorder is of the form suggested above.

### Summary

Convincing evidence has thus emerged to indicate the presence of a roughly 4:1 statistical disordering of the (HCO<sub>3</sub>)<sub>2</sub><sup>-</sup> and (DCO<sub>3</sub>)<sub>2</sub><sup>-</sup> dimers. Despite the fact that the refined occupation numbers of the (assumed) two dimeric orientations indicated a significantly greater percentage of the more dominant orientation in KDClO<sub>3</sub>, it is not possible to ascertain from this work alone the extent to which the degree of disordering in each compound is specimen dependent. It is clear therefore that the present study can usefully be extended in several directions, *e.g.* low-temperature neutron diffraction studies, comparative studies using different crystals and different degrees of deuteration, disorder diffuse scattering studies (especially of KDClO<sub>3</sub> using neutrons).

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## Struktur des borreichen Borphosphids

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During the reduction of gaseous BBr<sub>3</sub> and PBr<sub>3</sub> with H<sub>2</sub> boron-rich boron phosphide with a variable content of phosphorus is deposited on a tantalum or boron nitride substrate at 900–1800°C. X-ray data of an untwinned single crystal with the formula B<sub>12</sub>(P<sub>1.36</sub>B<sub>0.64</sub>) show a rhombohedral cell, space group  $R\bar{3}m$  with  $a = 5.2310(3)$  Å,  $\alpha = 69^\circ 30' 36''$  ( $10''$ ) (hexagonal setting:  $a = 5.964$ ;  $c = 11.814$  Å),  $R$  value = 0.040, one formula unit in the cell. The structure derives from the  $\alpha$ -rhombohedral boron ( $a = 5.06$  Å;  $\alpha = 58.1^\circ$ ) with B<sub>12</sub> icosahedra on each corner. The long hole in the centre of the cell lies in line with the long cell diagonal, and is fully occupied with two single atoms, phosphorus and boron, in statistical distribution. The two single atoms have nearly ideal tetrahedral environments. Each is bonded to three B<sub>12</sub> icosahedra and to the other single atom. The model is not in accordance with the model of 'B<sub>13</sub>P<sub>2</sub>' (hex.:  $a = 5.984$ ;  $c = 11.850$  Å) with a three-atom chain P–B–P in the hole (Spinár & Wang, *Acta Cryst.* (1962). **15**, 1048–1049).

### Einleitung

In der Literatur wird verschiedentlich über borreiche Bor-Phosphorphasen berichtet, so von Matkovich (1961*a, b*) über B<sub>13</sub>P<sub>2</sub>, Matkovich & Giese (1965) und

Peng Nien Chao & Chin-chi Mo (1963) sowie Burmester & Green (1967) über B<sub>12</sub>P<sub>2</sub> bzw. B<sub>6</sub>P, ausserdem Gruber (1966) über B<sub>6</sub>...<sub>100</sub>P. Matkovich (1961*a, b*) erhielt das Borphosphid durch Zusammenschmelzen von amorphem Bor und Aluminiumphosphid bei 1400–