

Crystal Structure of the Acid Salts of Some Dibasic Acids. Part IX.¹ Potassium Hydrogen *meso*-Tartrate: a Neutron Diffraction Study

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Kroon and Kanters (1972) determined the crystal structure of the title compound with *X*-rays at 113 K: there are four $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$ units in the triclinic ($P\bar{1}$) cell. The structure has now been studied by neutron diffraction at room temperature, and refined to R 0.063 for 1 511 reflexions. In general the geometry found by *X*-rays is confirmed, though the hydrogen atoms are more precisely located. Thermal motion of the *meso*-tartrate residues is much enhanced at room temperature, and some of the longer $\text{K}^+ \cdots \text{O}$ contacts are significantly lengthened; these findings may be connected.

The structure contains two very short $\text{O} \cdots \text{H} \cdots \text{O}$ bonds, between carboxy-groups, which lie across centres of symmetry. One of them had been found to be anomalous in several structural details, and an electron-density 'difference' synthesis had revealed twin peaks which might be interpreted in terms of a hydrogen atom disordered between sites *ca.* 0.4 Å on either side of the bond centre. The neutron analysis does not support this possibility, though there is probably disorder of a subtler kind affecting this particular bond [$\text{O} \cdots \text{O}$ 2.483(2) (*X*-rays) and 2.474(8) Å neutrons]. The other short hydrogen bond [2.452(2) and 2.440(8) Å] is an ordinary Type A $\text{O} \cdots \text{H} \cdots \text{O}$ bond, and its proton probably vibrates in a flattened, single-minimum potential-energy well at the centre.

A PRECISE *X*-ray analysis of the crystal structure of potassium hydrogen *meso*-tartrate, $\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$, was reported² by Kroon and Kanters (K/K). It was based on some 5 300 independent reflexions measured at 113(2) K (subsequently referred to as LNT, *i.e.* liquid-nitrogen temperature). In the K/K paper, as well as in earlier preliminary communications,^{3,4} attention was drawn to a remarkable type of electron-density 'difference' map, in the region of one of the two short, and crystallographically symmetrical, $\text{O} \cdots \text{H} \cdots \text{O}$ bonds. (This map is reproduced here as part of Figure 2.) Taken at its face value, it implies that the bonding hydrogen atom is disordered between alternative sites, separated by *ca.* 0.75 Å across a centre of symmetry, and each nearer to its oxygen neighbour than would be acceptable in an unperturbed hydroxy-group. A similar result has been reported at other short, symmetrical $\text{O} \cdots \text{H} \cdots \text{O}$

bonds.^{5,6} It has been termed the Kroon-Kanters-McAdam (KKM) effect.^{7,8} Occurring, as it does, after precise *X*-ray analyses, it cannot be explained away as due to gross errors in intensity data.

For this reason in particular we deemed it useful to study this structure by neutron diffraction (ND). Our work has been done at room temperature [RT, estimated to be 292(2) K].

EXPERIMENTAL

A large single crystal of potassium hydrogen *meso*-tartrate was grown at Utrecht: its mass was 0.032 g and its dimensions (mm) were *ca.* $5 \times 3 \times 2$; the longest dimension was nearly parallel to the *b*-axis, about which the crystal was mounted, the equatorial forms present were {001} and {10 $\bar{1}$ }, and the crystal was capped by (010), ($\bar{1}$ 10), (01 $\bar{1}$), and ($\bar{1}$ 11), with corresponding faces beneath. Intensity measurements

⁵ A. McAdam, M. Currie, and J. C. Speakman, *J. Chem. Soc. (A)*, 1971, 1994.

⁶ J. O. Thomas, *Acta Cryst.*, 1973, **B29**, 1767.

⁷ A. L. Macdonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 825.

⁸ 'Chemical Crystallography,' ed. J. M. Robertson, M.T.P. International Review of Science, Physical Chemistry, Vol. 11, Butterworths, London, 1972, p. 25.

¹ Part VIII, J. Blain, J. C. Speakman, L. A. Stamp, Lj. Golić, and I. Leban, *J.C.S. Perkin II*, 1973, 706.

² J. Kroon and J. A. Kanters, *Acta Cryst.*, 1972, **B28**, 714.

³ J. Kroon, J. A. Kanters, and A. F. Peerdeman, *Nature*, 1971, **229**, 121.

⁴ J. Kroon, J. A. Kanters, A. F. Peerdeman, and A. Vos, *Nature*, 1971, **232**, 107.

were made on the Hilger and Watts diffractometer of the Atomic Energy Establishment, Harwell, with neutron wavelength 1.181 Å (118.1 pm), and an ω -2 θ scan. Over 4 000 reflexions were measured out to ca. 45° (a spacing of 0.85 Å), though for instrumental reasons coverage of the reciprocal-lattice hemisphere was not complete. Reflexions with intensities $< 3\sigma$ being omitted, a set of 1 511 independent terms was used in least-squares refinement. The neutron absorption coefficient was 1.18 cm⁻¹, this being virtually due to hydrogen alone, for which the incoherent scattering cross-section was taken to be 37×10^{-24} cm². No absorption corrections were made; errors from this will be small, though perhaps not quite negligible.

TABLE 1

Fractional co-ordinates by ND ($\times 10^5$, with standard deviations in parentheses)

	<i>x</i>	<i>y</i>	<i>z</i>
K(1)	22 369(88)	43 531(83)	13 041(73)
α Residue			
O(3)	-7 381(53)	-8 978(45)	75 614(45)
O(4)	1 457(52)	12 904(47)	88 598(44)
O(5)	4 799(54)	22 303(51)	55 595(47)
O(6)	32 214(61)	41 164(51)	49 021(47)
O(7)	39 296(49)	32 717(44)	89 343(49)
O(8)	47 344(53)	25 824(48)	66 204(52)
C(15)	5 304(42)	6 595(37)	82 250(34)
C(16)	26 240(40)	16 200(36)	81 780(32)
C(17)	27 780(42)	17 952(37)	65 289(34)
C(18)	21 182(44)	27 909(38)	56 040(34)
K(2)	25 577(98)	85 035(83)	27 040(73)
β Residue			
O(9)	41 352(50)	26 861(48)	20 525(43)
O(10)	51 868(55)	17 964(49)	41 934(43)
O(11)	83 071(56)	26 904(55)	3 269(46)
O(12)	56 512(55)	8 753(51)	11 624(48)
O(13)	77 472(53)	50 651(51)	16 546(43)
O(14)	105 035(57)	46 008(51)	30 880(51)
C(19)	54 549(41)	27 210(38)	30 584(34)
C(20)	75 520(42)	40 485(37)	29 341(33)
C(21)	84 495(41)	32 673(38)	28 529(33)
C(22)	74 507(43)	22 397(37)	13 078(34)
Hydrogen atoms (co-ordinates $\times 10^4$)			
H(3)	-2 112(10)	-1 508(9)	7 663(8)
H(6)	5 000	5 000	5 000
H(7)	4 161(10)	3 159(9)	10 031(9)
H(8)	4 741(10)	2 317(10)	5 673(11)
H(16)	3 048(9)	844(8)	8 786(8)
H(17)	1 718(9)	498(8)	5 941(8)
H(12)	5 000	0	0
H(13)	7 381(13)	5 737(11)	1 709(9)
H(14)	11 206(11)	4 310(10)	3 872(9)
H(20)	8 450(9)	4 878(9)	4 009(8)
H(21)	8 186(10)	2 367(10)	3 794(8)

Refinement, by the CRYLSQ program of the 'X-Ray 70' system (University of Maryland), started from the K/K parameters for potassium, carbon, and oxygen. Hydrogen nuclei were easily located from a 'difference' synthesis. The total number of parameters, when anisotropic vibration of the hydrogen atoms was allowed, was too large for full-matrix operation, so two full-matrix blocks were used, comprising 16 and 17 atoms. The neutron-scattering amplitudes of potassium, carbon, oxygen, and hydrogen were taken, respectively, to be 3.50, 6.61, 5.88, and -3.78 fermi ($= 10^{-15}$ m). The least-squares weight was $w = (|F_o|/40)^2$ if $F_o > 40$, else $w = (40/|F_o|)^2$. Convergence was reached

* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

after twelve cycles, with R 6.3% and R' ($= \{\sum w \Delta^2 / \sum w |F_o|^2\}^{1/2}$) 5.6%. Final parameters are listed in Tables 1 and 2, whilst an agreement analysis is in Table 3. A structure-factor table has been deposited as Supplementary Publication No. SUP 21 446 (5 pp., 1 microfiche).*

TABLE 2

Vibrational parameters: components (10^{-4}Å^2) of tensors representing mean-square amplitudes; X-ray values, at liquid-nitrogen temperature, are listed below each neutron value, for room temperature

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	147(27)	259(31)	236(30)	86(25)	98(22)	36(25)
	97	159	129	59	53	9
K(2)	305(33)	241(32)	195(29)	196(29)	36(24)	-4(25)
	180	148	138	116	21	4
O(3)	134(19)	129(17)	315(20)	40(15)	78(15)	-26(14)
	96	94	165	38	56	-2
O(4)	199(18)	231(18)	285(19)	141(16)	89(15)	28(15)
	131	134	155	91	62	18
O(5)	170(19)	271(19)	314(21)	153(16)	38(15)	65(16)
	127	157	157	95	28	27
O(6)	236(23)	243(19)	274(20)	139(17)	86(15)	119(16)
	146	122	151	77	58	60
O(7)	125(17)	171(17)	180(22)	58(14)	26(14)	-13(15)
	99	101	84	46	21	-3
O(8)	176(18)	245(19)	240(32)	134(16)	101(15)	48(16)
	108	157	117	84	52	16
C(15)	145(14)	128(14)	193(14)	93(13)	86(12)	37(11)
	102	94	108	57	40	25
C(16)	117(13)	107(13)	133(14)	75(12)	45(11)	41(11)
	92	88	88	51	33	16
C(17)	104(13)	136(13)	137(13)	64(12)	27(10)	8(11)
	96	109	92	60	35	15
C(18)	161(16)	134(13)	137(14)	77(13)	33(11)	4(11)
	124	100	83	62	21	5
O(9)	109(16)	270(19)	248(18)	105(15)	37(13)	41(15)
	94	144	123	71	35	21
O(10)	245(19)	269(20)	224(18)	161(17)	131(15)	69(16)
	160	143	109	99	73	41
O(11)	173(18)	331(21)	248(19)	48(16)	86(15)	-139(16)
	124	202	143	60	55	-52
O(12)	191(19)	209(19)	282(23)	59(17)	89(16)	-57(19)
	104	112	147	33	41	-41
O(13)	233(18)	184(17)	233(19)	150(16)	119(14)	26(15)
	143	119	122	96	65	41
O(14)	123(18)	266(20)	252(21)	115(17)	-18(16)	-57(16)
	75	133	125	62	-1	-18
C(19)	121(14)	166(14)	133(14)	79(13)	56(11)	18(12)
	105	99	91	60	37	-2
C(20)	127(14)	127(14)	106(15)	80(12)	26(12)	-12(12)
	98	95	84	57	27	2
C(21)	110(14)	152(14)	133(15)	90(12)	-8(11)	-34(13)
	91	98	89	58	14	-5
C(22)	135(15)	138(14)	169(14)	82(13)	17(12)	-52(12)
	91	103	106	67	22	-14

Hydrogen atoms, tensor components as 10^{-3}Å^2

H(3)	21(3)	26(3)	45(4)	13(3)	12(3)	2(2)
H(6)	70(10)	78(9)	29(5)	62(9)	-14(5)	-14(5)
H(7)	31(4)	34(4)	26(4)	19(3)	7(3)	-3(3)
H(8)	33(4)	53(5)	39(5)	30(4)	21(3)	10(4)
H(16)	31(3)	33(3)	34(3)	26(3)	6(2)	10(3)
H(17)	30(3)	23(3)	39(4)	16(3)	7(3)	-6(3)
H(12)	27(5)	32(5)	58(8)	17(4)	19(5)	6(6)
H(13)	62(5)	43(4)	47(4)	45(5)	19(4)	12(3)
H(14)	32(4)	50(5)	27(4)	30(4)	-8(3)	-11(3)
H(20)	28(3)	31(4)	29(4)	12(3)	7(3)	-14(3)
H(21)	39(4)	43(4)	24(3)	30(3)	4(3)	5(3)

Crystal Data.—RT lattice parameters, determined at Utrecht (from angular measurements on 22 reflexions by a Nonius three-circle diffractometer, using Mo-radiation: $\lambda = 0.7107$ Å), were used in our ND study: $C_4H_5KO_8$, $M = 188.2$, Triclinic, $a = 9.324(2)$, $b = 10.402(2)$, $c = 9.079(1)$

\AA , $\alpha = 80.73(1)^\circ$, $\beta = 108.47(5)^\circ$, $\gamma = 131.11(2)^\circ$, $u_c = 627.9 \text{\AA}^3$, $Z = 4$, $D_c = 1.990 \text{ g cm}^{-3}$. These should be compared with the LNT values:² $a = 9.33$, $b = 10.29$, $c = 9.09 \text{\AA}$, $\alpha = 80.71^\circ$, $\beta = 108.77^\circ$, $\gamma = 130.95^\circ$, $u_c = 622.6$

TABLE 3
Analysis of the weighting scheme

$ F_o $ range	N^*	R	Mean $w\Delta^2$	Sin θ range	N^*	R	Mean $w\Delta^2$
0—10	34	0.41	0.8	0.0—0.1	5	0.03	0.5
10—20	421	0.18	1.4	0.1—0.2	69	0.08	5.7
20—30	345	0.07	1.6	0.2—0.3	178	0.07	2.4
30—40	296	0.04	1.9	0.3—0.35	133	0.07	2.3
40—50	185	0.03	1.8	0.35—0.4	194	0.06	2.1
50—80	215	0.04	3.5	0.4—0.45	240	0.05	1.8
80—100	14	0.11	23	0.45—0.5	262	0.06	1.8
>100	1	0.15	36	0.5—0.55	295	0.07	2.0
				>0.55	135	0.05	1.6

* N is the no. of reflexions in each set.

\AA^3 , $D_c = 2.007 \text{ g cm}^{-3}$. The contraction over this range (amounting to 0.28% linear) is far from isotropic, and we shall discuss its possible origin later.

RESULTS AND DISCUSSION

The space group being $P\bar{1}$ (No. 2), the asymmetric unit consists of two different sets of $C_4H_5O_6K$, each duplicated

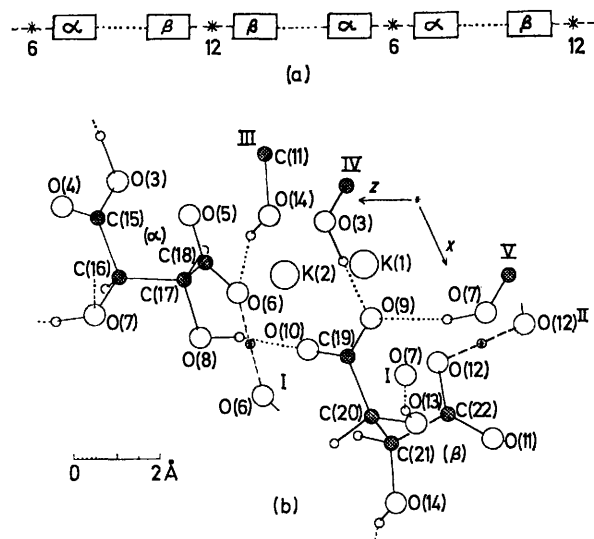


FIGURE 1 (a) Topological representation of the infinite chains of α and β meso-tartrate residues, linked by hydrogen bonds. [Centres of symmetry are marked by asterisks; symmetrical hydrogen bonds are represented by broken lines, others by dotted lines. The numerals 6 and 12 denote the bonds between O(6) and O(12) atoms respectively]. (b) The crystal structure as seen projected along the Y' axis, an orthogonal set of axes having been set up with Z' parallel to c and X' parallel to a^* . (The smallest circles represent hydrogen atoms, which are numbered as the carbon or oxygen atom to which they are attached. For coding of symmetry-related units see text)

by a different centre of symmetry. Including antimers, there are four distinct meso-tartrate residues, each dissymmetric. This meso-tartrate structure is a racemate.

⁹ H. N. Shrivastava and J. C. Speakman, *J. Chem. Soc.*, 1961, 1151; M. Currie and J. C. Speakman, *J. Chem. Soc. (A)*, 1970, 1923.

A basis for description and discussion is provided by Figure 1, in which (a) suggests schematically how the anions are linked by hydrogen bonds between their carboxy-groups, and (b) pictures the situation in more realistic detail. The numbering of atoms, also shown in (b), is that used by K/K except that we now use α and β , rather than (I) and (II), to specify the independent meso-tartrate residues. Roman numerals are reserved for symmetry-related units according to the following code:

CCU x, y, z		V $x, y, -1 + z$
I $1 - x, 1 - y, 1 - z$		VI $x, 1 + y, z$
II $1 - x, -y, -z$		VII $1 - x, 1 - y, -z$
III $-1 + x, y, z$		VIII $-x, 1 - y, 1 - z$
IV $-x, -y, 1 - z$		

The meso-tartrate residues are linked into infinite, but tortuous, chains by $O \cdots H \cdots O$ bonds, their sequence being sketched in Figure 1(a). These bonds are of three sorts. Two of them lie across crystallographically different centres of symmetry and connect, respectively, pairs of α and β units. These are hydrogen bonds of Type A.⁹ The third bond is unsymmetrical and links an α to a β unit, the former being the proton donor. Characteristically for intermolecular bonds between carboxy-groups, the unsymmetrical bond is longest. The structure is further stabilised, and complicated for description, by four other hydrogen bonds involving the hydroxy-groups. Three of the oxygen atoms do not participate in hydrogen bonding: O(4), O(5), and O(11). Location of the protons by ND enables us to give the fuller description of the hydrogen bonding contained in Table 4.

Table 5 lists the ND bond lengths, and some of the angles, within the two tartrate residues, and compares the former with the X-ray results of K/K. Though angles agree well enough, there is a systematic and highly significant discrepancy between the two sets of intramolecular distances, the mean difference (ND — X) being -0.010\AA . The parameters in Table 2 indicate that our ND amplitudes of vibration are much greater than those of K/K. This is due to the large temperature difference. However, unpublished RT X-ray work has also been done at Utrecht. The averaged U_{ij} for all atoms except hydrogens are as follows: (X, RT) 0.032; (X, LNT) 0.012; and (ND, RT) 0.019 \AA^2 . Thus the apparent amplitudes found at RT by X-rays are substantially larger than those found by ND, as is commonly observed. The results imply that, despite the elaborate hydrogen bonding, the anions undergo considerable molecular vibration at RT, but that this is much reduced at LNT.

We have therefore applied, to our ND results, the Schomaker-Trueblood method¹⁰ for studying the rigid-body vibration of the two anions, and we have corrected our atomic co-ordinates for 'shrinkage' or 'foreshortening' due to libration. For the α residue the root-mean-square difference between observed U_{ij} and those calculated for rigid-body vibration was 0.0024\AA^2 . The translational tensor had eigenvalues of 0.0163, 0.0112, and 0.0093\AA^2 , corresponding to root-mean-square amplitudes

¹⁰ V. Schomaker and K. N. Trueblood, *Acta Cryst.*, 1968, **B24**, 63.

of 0.13, 0.11, and 0.10 Å. The librational tensor had eigenvalues of 0.0056, 0.0024, and 0.0016 rad², corresponding to root-mean-square amplitudes of 4.2, 2.8, and 2.3°; the axis of maximum libration made angles of *ca.* 54, 86, and 137° with the positive directions of *a*, *b*, and *c* respectively. For the β residue, corresponding results were 0.0028 Å²; 0.13, 0.11, and 0.08 Å; 4.8, 3.3, and 2.3°; and *ca.* 37, 96, and 119°.

there may still be a significant residual difference. This might be attributed to an underestimate of the librational corrections, to the asphericity effect,^{11,12} or possibly to a real change of structure at low temperature upon which we speculate later.

A formal consequence of correcting co-ordinates for rigid-body libration is to diminish intermolecular distances. As has been stressed,^{13,10} such emendations are

TABLE 4

Hydrogen bonds. (Distances Å, angles deg., standard deviations in parentheses; O...O distances found by X-rays at liquid-nitrogen temperature are also shown for comparison)

Bond	O...O (X-Rays)	O...O (ND)	O-H	H...O	O-H...O
C(6)···H···C(6 ^I)	2.483(2)	2.474(8)	(1.237)	(1.237)	(180)
O(12)···H···O(12 ^{II})	2.452(2)	2.440(8)	(1.220)	(1.220)	(180)
O(3 ^{IV})-H···O(9)	2.543(1)	2.521(5)	1.019(8)	1.514(8)	168.7(7)
O(8)-H···O(10)	2.720(1)	2.706(6)	0.948(10)	1.776(9)	166.4(8)
O(7 ^V)-H···O(9)	2.768(1)	2.771(6)	0.955(9)	1.826(9)	170.0(7)
O(14 ^{III})-H···O(6)	2.838(2)	2.855(5)	0.961(9)	1.941(9)	158.2(7)
O(13)-H···O(7)	2.877(1)	2.906(5)	0.970(10)	1.977(10)	159.7(7)

TABLE 5

Intramolecular distances and some angles. (Distances Å, angles deg., with standard deviations in parentheses; distances found by X-rays at liquid-nitrogen temperature are compared with those by ND at room temperature, and libration-corrected values of the latter are also listed)

α Residue				β Residue			
	X-Ray	ND	ND (corr.)		X-Ray	ND	ND (corr.)
C(15)-O(3)	1.324(1)	1.315(5)	1.320	C(19)-O(9)	1.271(1)	1.260(5)	1.266
C(15)-O(4)	1.219(2)	1.206(5)	1.210	C(19)-O(10)	1.255(1)	1.256(5)	1.261
C(18)-O(5)	1.231(2)	1.213(5)	1.216	C(22)-O(11)	1.229(1)	1.214(5)	1.218
C(18)-O(6)	1.297(1)	1.278(5)	1.280	C(22)-O(12)	1.297(1)	1.278(5)	1.282
C(16)-O(7)	1.419(1)	1.416(5)	1.421	C(20)-O(13)	1.413(1)	1.409(5)	1.416
C(17)-O(8)	1.414(2)	1.402(5)	1.405	C(21)-O(14)	1.423(2)	1.407(5)	1.411
C(15)-C(16)	1.526(2)	1.511(4)	1.515	C(19)-C(20)	1.530(2)	1.510(4)	1.514
C(16)-C(17)	1.534(2)	1.520(4)	1.524	C(20)-C(21)	1.522(2)	1.522(4)	1.528
C(17)-C(18)	1.535(2)	1.545(5)	1.550	C(21)-C(22)	1.529(2)	1.525(4)	1.532
O(3)-H(3)	0.90(4)	1.019(8)		O(13)-H(13)	0.82(3)	0.970(10)	
O(7)-H(7)	0.76(3)	0.955(9)		O(14)-H(14)	0.79(3)	0.961(9)	
O(8)-H(8)	0.80(3)	0.948(10)					
C(16)-H(16)	0.95(3)	1.118(7)		C(20)-H(20)	0.94(3)	1.096(7)	
C(17)-H(17)	0.93(3)	1.108(7)		C(21)-H(21)	0.92(3)	1.114(8)	
O(3)-C(15)-O(4)		125.7(3)		O(9)-C(19)-O(10)		125.5(3)	
C(16)-C(15)-O(3)		112.9(3)		C(20)-C(19)-O(9)		117.2(3)	
C(16)-C(15)-O(4)		121.4(3)		C(20)-C(19)-O(10)		117.3(3)	
C(15)-C(16)-C(17)		112.6(2)		C(19)-C(20)-C(21)		112.5(2)	
C(16)-C(17)-C(18)		110.1(2)		C(20)-C(21)-C(22)		110.9(2)	
O(5)-C(18)-O(6)		121.7(4)		O(11)-C(22)-O(12)		124.1(4)	
C(17)-C(18)-O(5)		116.3(3)		C(21)-C(22)-O(12)		113.4(3)	
C(17)-C(18)-O(6)		122.0(3)		C(21)-C(22)-O(11)		122.4(3)	

Correction of the co-ordinates in Table 1 for the effects of these librations leads to the bond lengths listed in the fourth column of Table 5. The discrepancy (ND - X) is reduced to *ca.* one half; the mean, with its internal standard deviation, falls from -0.0100(20) to -0.0055(21) Å. Bearing in mind that our bond-length standard deviations are probably underestimated (because the X-ray analysis used block-diagonal refinement, and the ND used two blocks), differences between individual bond lengths are no longer significant. Overall however,

unrealistic, and we have ignored them so far as the hydrogen bonds are concerned.

Table 6 compares the K⁺...O distances around each potassium ion with those found by X-rays. There are some singularly large discrepancies. These are all in the sense that the RT values (by ND) are greater than those at LNT. (When, notwithstanding the objections just mentioned, we used libration-corrected co-ordinates for the oxygen atoms, the differences were a little diminished, but remained large.) Round K(1), which has nine oxygen atoms within 3.2 Å, the large discrepancies are confined to the longer, and weaker, K⁺...O contacts.

¹¹ P. Coppens and C. A. Coulson, *Acta Cryst.*, 1967, **23**, 718; P. Coppens in 'Chemical Crystallography,' ed. J. M. Robertson, M.T.P. International Review of Science, Physical Chemistry, Series 2, Vol. 11, Butterworths, London (to be published in 1975); P. Coppens, *Acta Cryst.*, 1974, **B30**, 255.

¹² See *e.g.* B. H. O'Connor, *Acta Cryst.*, 1973, **B29**, 1893.

¹³ W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

Round the other potassium ion, which has seven oxygen neighbours, one contact [K(2)⁺ ··· O(14^{III})] is inordinately divergent with (ND - X) 0.085 Å; this is not the longest contact, though it is rather long.

TABLE 6

Comparison of K⁺ ··· O distances (Å, with standard deviations in parentheses) round each potassium ion, as found by X-rays at liquid-nitrogen temperature and by ND at room temperature

	X-Ray		X-Ray		
	(LNT)	ND (RT)	K(2)	(LNT)	ND (RT)
O(13 ^{VII})	2.643(1)	2.660(7)	O(4 ^{VIII})	2.733(1)	2.735(7)
O(11 ^{III})	2.695	2.702(8)	O(11 ^{VIII})	2.775	2.776(7)
O(7 ^I)	2.763	2.762(7)	O(14 ^{III})	2.900	2.985(8)
O(14 ^{III})	2.766	2.764(7)	O(10 ^I)	2.948	2.968(7)
O(8 ^I)	2.860	2.900(8)	O(10 ^{VI})	2.949	2.968(8)
O(3 ^{IV})	2.957	3.007(7)	O(12 ^{VI})	2.950	2.939(8)
O(9)	3.029	3.081(7)	O(8 ^I)	3.053	3.080(7)
O(6)	3.127	3.117(7)			
C(4 ^V)	3.161	3.201(7)			

These very significant positive differences may be a genuine temperature effect, we suggest. When, as here, the vibration of the anions is greatly reduced at LNT, the more distant oxygen atoms can reasonably be envisaged as settling down nearer to their cation. This would be a real structural effect, distinct from errors in apparent positions due to libration. If our interpretation is true, the phenomenon should be general for crystals of this type. Four out of the five K⁺ ··· O contacts which show this effect prominently have a large component of their contraction in the *y* direction. The *b* axis is the only lattice translation which diminishes on cooling crystals from RT to LNT.

Earlier, we mentioned a small residual discrepancy (ND - X negative) in the intramolecular distances, even after application of librational corrections. Just possibly it may result from the stronger pull exerted in closer K⁺ ··· O contacts.

Symmetrical Hydrogen Bonds and The KKM Effect.—The O(12) ··· H(12) ··· O(12^{VI}) bond [denoted 12 in Figure 1(a)] is a normal 'very short', symmetrical, Type A bond. By ND, O ··· O is 2.440(8), compared with 2.452(2) Å found by K/K. The angle C(22)-O(12) ··· H (equivalent, in this case, to C-O ··· O) is 108.3°; such an angle favours strong bonding, and is indeed mandatory for this sort of hydrogen bond.¹⁴

We are now in a position to study the vibrations of the proton relative to its propinquent O(12) atoms. When, in accordance with the 'riding' model,¹³ the vibrational parameters are transformed to orthogonal axes, with X' coincident with O ··· H ··· O, and with the origin at the

* This map has not been published; it closely resembles that reproduced in ref. 5.

¹⁴ J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

¹⁵ B. L. McGaw and J. A. Ibers, *J. Chem. Phys.*, 1963, **39**, 2677.

¹⁶ J. C. Speakman, *Chem. Soc. Specialist Periodical Reports, Molecular Structure by Diffraction Methods*, Vol. 3, 85.

¹⁷ J.-O. Lundgren and R. Tellgren, *Acta Cryst.*, 1974, **B30**, 1937.

centre (*U'*₁₁ is parallel to X'), we arrive at the following results:

	<i>U'</i> ₁₁	<i>U'</i> ₂₂	<i>U'</i> ₃₃	<i>U'</i> ₁₂	<i>U'</i> ₁₃	<i>U'</i> ₂₃
H(12)	0.0551	0.0500	0.0273	0.0007	0.0071	0.0123 (Å ²)
O(12)	0.0193	0.0381	0.0225	-0.0001	0.0030	-0.0102
Δ	0.0358	0.0119	0.0048	0.0008	0.0041	-0.0021

These results imply a root-mean-square amplitude of the proton, relative to its immediate environment, of 0.19 Å along the bond, and amplitudes of 0.12 and 0.07 Å in directions perpendicular to the bond and to each other. This behaviour is characteristic of Type A bonds,^{15,16} as well as of other very short O ··· H ··· O bonds.^{17,18} In particular, such a large amplitude (or effective amplitude) along the bond would be sufficient to carry the proton from one potential-energy minimum to the other, even were we to assume a double-minimum situation with the minima as far from the centre, and the intervening barrier as high, as is feasible.¹⁹ We therefore assume a symmetrical potential, effectively with a single minimum. The minimum will be broader and flatter than would correspond to a parabolic well. [Recent X-ray and ND studies of Ca(H₂PO₄)₂ have led to an independent²⁰ discovery of the type A bond, and to an interesting discussion with conclusions similar to our own.]

In apparent contradiction to our foregoing inferences, the electron-density difference map* in the region of O ··· H ··· O bond 12 had shown well separated double peaks, *ca.* 0.45 Å apart, though less dramatic than those for bond 6 reproduced in Figure 2(a). Other examples of the KKM effect continue to be reported, an excellent, recent example being in the undeuteriated form of hydrazinium hydrogen oxalate.⁶ A KKM effect, we conclude, is not necessarily valid evidence of a disordered hydrogen bond, with alternative proton sites well away from the centre. The X-ray result is anomalous and may be connected with the asphericity effect.^{7,11}

The O ··· H ··· O bond 6 is not of normal Type A. We have previously emphasised² the unique conformation of the participating carboxy-groups: and the C-C-O angles are anomalous. Amongst symmetrical O ··· H ··· O bonds between carboxy-groups, bond 6 is also unique in that the oxygen atom accepts a second proton from O(14^{III}). The geometry of this second hydrogen bond is given in Table 4; though fairly weak, it seems capable of weakening bond 6. A further nonconformity is that C(18)-O(6) ··· O(6^I) subtends 130.3(4)°, which is very unfavourable for strong bonding. Were the proton assumed to lie, not at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, but at one of the peaks of Figure 2(a), the C-O-H angle would be 123.9°, still too large, whilst O-H would be 0.89 Å, too small. The O(6) ··· O(6^I) distance is probably too long for a Type A bond.

¹⁸ A. Kvik, T. F. Koetzle, R. Thomas, and F. Takusugawa, *J. Chem. Phys.*, 1974, **60**, 3866.

¹⁹ R. D. Ellison and H. A. Levy, *Acta Cryst.*, 1965, **19**, 260; A. Sequeira, C. A. Berkebille, and W. C. Hamilton, *J. Mol. Structure*, 1967-1968, **1**, 283.

²⁰ B. Dickens, E. Prince, L. W. Schroeder, and W. E. Brown, *Acta Cryst.*, 1973, **B29**, 2057.

Analysis of the vibrational parameters for H(6) and O(6), as explained earlier, reveals a confused situation:

	U'_{11}	U'_{22}	U'_{33}	U'_{12}	U'_{13}	U'_{23}
H(6)	0.0787	0.0301	0.0512	-0.0208	0.0273	-0.0021 (\AA^2)
O(6)	0.0222	0.0192	0.0304	0.0041	0.0020	-0.0182
Δ	0.0565	0.0109	0.0208	-0.0249	0.0253	0.0161

Making the same assumptions, we find a longitudinal root-mean-square amplitude of *ca.* 0.24 \AA —larger than

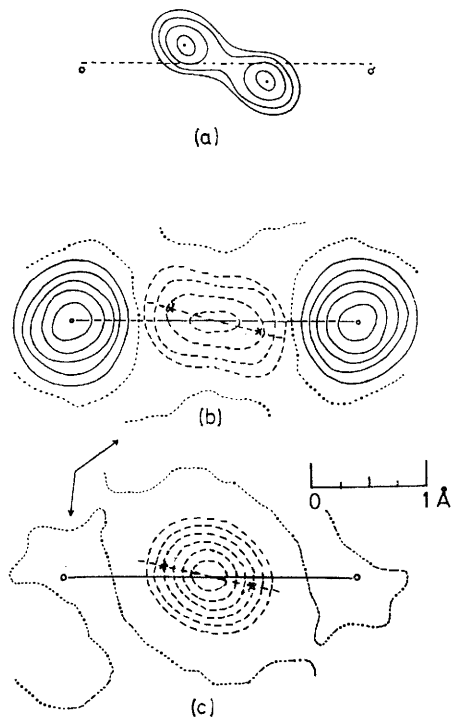


FIGURE 2 (a) The KKM effect: an electron-density difference map in the region of $\text{O} \cdots \text{H} \cdots \text{O}$ bond 6. (Contour scale: 0.20/0.05/0.35 $\text{e}\text{\AA}^{-3}$). (b) Neutron-scattering density in the same region. (Zero contours, dotted; negative contours, broken lines: scales -10/2/-4; 4/4/20 $\text{fermi}\text{\AA}^{-3}$). (c) Corresponding difference map. (Contour scale -3/-1/-8 $\text{fermi}\text{\AA}^{-3}$). [In (b) and (c) the positions corresponding to the peaks in (a) are marked with crosses]

for bond 12. In the plane perpendicular to the bond the maximum amplitude is improbably large (0.18 \AA), and the minimum corresponds to a negative value for the mean-square amplitude, which is unacceptable, and which implies either errors in our U_y or a failure of our model.

For comparison with the difference electron-density map in Figure 2(a) we show neutron-scattering density maps in (b) and (c), the latter being another 'difference' map with all nuclei taken out except H(6). These last two syntheses are in the plane $x, y, \frac{1}{2}$. They differ from (a) which was calculated in the plane containing O(6), the centre of symmetry and the middle of the difference peak. However O(6) and the peak are only 0.09 and 0.08 \AA from the $x, y, \frac{1}{2}$ plane, and this will make no perceptible difference to the relevant regions of maps (b) and (c). Both these maps suggest some smearing of the proton along a direction a little removed from the $\text{O}(6) \cdots \text{O}(6^I)$ line. But, if there is proton disorder along this direction, map (c) rules out the possibility that the alternative sites are 0.75 \AA apart, as was suggested by (a). So large a separation equals that between the proton sites in ice-Ih, and our resolution would have revealed it. X-rays are scattered by the electron density and, in refinement, we followed the almost universal custom of assuming this density to consist of spherical atoms. Neutrons are scattered by the atomic nuclei, which are virtually points.

Our conclusion on $\text{O} \cdots \text{H} \cdots \text{O}$ 6 is that this unique hydrogen bond is indeed affected by some form of proton disorder; but that the proton sites are not those suggested by a literal acceptance of Figure 2(a).

We are glad to record our use of programs developed by Prof. J. M. Stewart and his collaborators ('X-Ray' System), Dr. U. Shmueli (vibrational analysis), and Drs. P. H. Mallinson, K. W. Muir, and D. N. J. White (molecular geometry). Neutron-diffraction facilities were provided by the Atomic Energy Research Establishment at Harwell, with S.R.C. support.

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