Crystal Structures of the Acid Salts of Some Monobasic Acids. Part XVI.[1] Potassium Hydrogen Bis-*m*-chlorobenzoate

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The title compound crystallises in space group $C2/c$ with $Z = 4$ in a cell of dimensions: $a = 32{\cdot}55$, $b = 3{\cdot}83$, $c = 11{\cdot}45$ Å, $\beta = 94{\cdot}6°$. It proves to be a Type *A* acid salt with a crystal structure surprisingly similar to that of potassium hydrogen di-*p*-chlorobenzoate. Structure analysis was based on 1283 non-zero *X*-ray reflexion intensities obtained by diffractometer measurements and *R* was 5·9%. There is a hydrogen bond across a centre of symmetry between equivalent chlorobenzoate residues, with O · · · H · · · O 2·437(6) Å. This may be another example of a genuinely symmetrical hydrogen bond.

ACID potassium salts of chloro- and bromo-benzoic acids were described by Farmer[2] and Smith.[3] Some years ago[4] we determined the crystal structure of KHX_2 (HX = *p*-chlorobenzoic acid) from visually estimated *X*-ray intensities. We became interested in the corresponding acid salt, where HX = *m*-chlorobenzoic acid, by reason of its unexpectedly similar unit-cell dimensions. This structure has now been solved and refined by use of diffractometer data, which led to a more precise analysis.

RESULTS AND DESCRIPTION OF THE STRUCTURE

Table 1 shows the close resemblance between the lattice parameters of the acid potassium salts of *p*- and *m*-chlorobenzoic acids. The Figure compares the two structures as seen in their *b*-axial projections, and explains how they achieve such similarity despite having molecules of different shapes.

As was expected from the i.r. spectrum [which is of Hadži's Type (ii)[5]] and from the presence of four KHX_2 units in a cell of the eighth-order space group No. 15, this is a Type *A* acid salt.[6] The potassium ion lies on a two-fold axis; the acidic hydrogen atom lies, effectively, at a centre of symmetry; two *m*-chlorobenzoate residues are related by this centre and linked by a very short O · · · H · · · O bond.

The more important interatomic distances and angles, within and between the acid residues, are listed in Table 2. The numbering of atoms is specified in the Figure (b). Besides the atoms of the crystal-chemical unit (CCU) at x, y, z, other symmetry-related units necessary for the description of the structures are denoted as follows: I $-x, -y, -z$; IV $-x, y, \frac{1}{2} - z$; V $x, 1 + y, z$; VI $x, 1 - y, \frac{1}{2} + z$; VII $-x, 1 + y, \frac{1}{2} - z$; VIII $-x, 1 - y, -z$; IX $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (these Roman numerals are

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[1] Part XV, M. Currie, *J.C.S. Perkin II*, 1972, 832.

[2] R. C. Farmer, *Proc. Chem. Soc.*, 1903, **83**, 1440.

[3] N. Smith, Ph.D. Thesis, University of Sheffield, 1949.

[4] H. H. Mills and J. C. Speakman, *J. Chem. Soc.*, 1963, 4355.

[5] D. Hadži, *Pure Appl. Chem.*, 1965, **11**, 435.

[6] M. Currie and J. C. Speakman, *J. Chem. Soc.* (*A*), 1970, 1923; see also *Structure and Bonding*, 1972.

chosen to agree with those used in our report on potassium hydrogen bis-*p*-chlorobenzoate).

In general the dimensions of the HX_2^- anion agree with those found in the *p*-chlorobenzoate (see Figure 2 of ref. 4), though the results of the present analysis are more accurate.

TABLE 1

Comparison of crystal data for the acid potassium salts of *m*- and *p*-chlorobenzoic acids

	m-Cl	*p*-Cl [a]
M	351·2	351·2
a (Å)	32·551(8)	33·205
b (Å)	3·831(10)	3·846
c (Å)	11·450(6)	11·212
β/deg.	94·63(6)	90·09
U/Å^3	1427·8	1431
D_m	1·63	1·62
Z	4	4
D_c	1·634	1·629
Space group	$C2/c$	$C2/c$
μ(Mo-K_α)/cm^{-1}	7·51	

[a] From ref. 4.

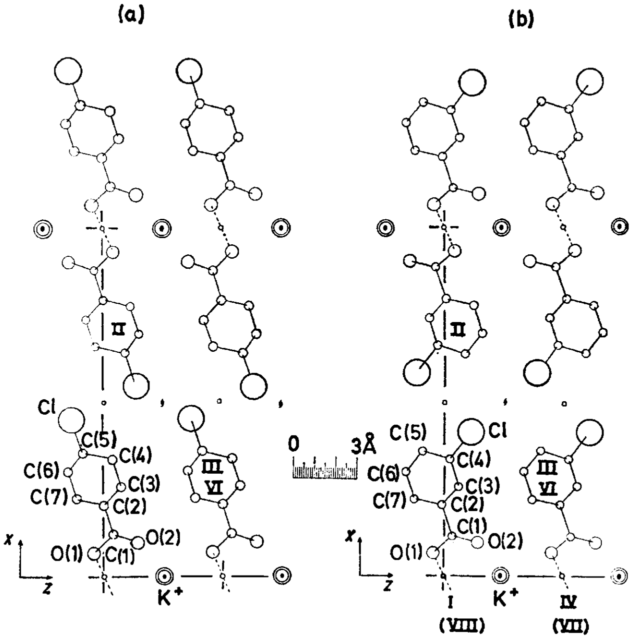

FIGURE Crystal structures of the acid salts (KHX_2) of (a) HX = *p*-chlorobenzoic acid, and (b) HX = *m*-chlorobenzoic acid (to bring out the similarity of the two structures, the β-angles are drawn here as 90°, though indeed they differ by *ca.* 4°)

The carbon atoms of the benzenoid ring do not deviate significantly from their mean plane, which is defined by the equation,* $0{\cdot}1891X' - 0{\cdot}9130Y + 0{\cdot}3614Z' = -0{\cdot}0912$ Å. Nor do the individual C–C distances differ significantly from their mean [1·388(3) Å]. On the other hand, though the internal C–C–C angles necessarily total 720·0°, the angle at C(4), which carries the chlorine substituent, is significantly extended to 122·4 (0·4)°. A similar extension [to 121·6 (0·7)°], was found in the *p*-chlorobenzoate, though it was, in that case, of questionable validity. It may be attributed to directionally non-equivalent hybridisation at the substituted carbon atom.[7,8]

The chlorine atom is only 0·026 Å from the mean plane of the ring. The deviation was five times larger in the *p*-compound, where it was explained as being due to a third Cl · · · Cl contact, of 3·70 Å, with another molecule, related by a centre of symmetry, in addition to a pair of Cl · · · Cl contacts, of 3·58 Å, across a screw axis. In the *m*-compound, only the latter two contacts are operative; the chlorine atoms related by the centre are more than 4 Å apart.

The atoms C(1), C(2), O(1), and O(2) are coplanar, according to the equation: $0{\cdot}1851X' - 0{\cdot}9574Y + 0{\cdot}2218Z' = -0{\cdot}1288$ Å. The angle between this plane and that of the ring is 8½°, substantially the same as in the *p*-compound. Though required to be parallel, the planes of the two carboxy-groups in the HX_2^- anion are significantly separated, by 0·26 Å. The presumptive site of the proton is therefore 0·13 Å from each plane.

The environment of the potassium ion is essentially the same as in the *p*-compound. There are three pairs of digonally related oxygen atoms belonging to six different chlorobenzoate units, and nine independent O · · · K$^+$ · · · O angles. Details are in Table 3. No other intermolecular contacts call for special mention.

TABLE 2

Bond-lengths (Å) and angles (deg.) within, and between, the acid-anions, with standard deviations in parentheses

C(4)–Cl	1·744(4)	C(3)–C(4)–Cl	119·8(3)
		C(5)–C(4)–Cl	117·8(3)
C(1)–O(1)	1·290(6)	C(2)–C(1)–O(1)	114·4(4)
C(1)–O(2)	1·223(6)	C(2)–C(1)–O(2)	121·8(4)
		O(1)–C(1)–O(2)	123·8(4)
C(1)–C(2)	1·503(6)	C(1)–C(2)–C(3)	119·5(4)
C(2)–C(3)	1·392(6)	C(1)–C(2)–C(7)	120·5(4)
C(3)–C(4)	1·386(6)	C(2)–C(3)–C(4)	118·4(4)
C(4)–C(5)	1·378(6)	C(3)–C(4)–C(5)	122·4(4)
C(5)–C(6)	1·395(6)	C(4)–C(5)–C(6)	118·7(4)
C(6)–C(7)	1·381(6)	C(5)–C(6)–C(7)	120·1(4)
C(7)–C(2)	1·394(6)	C(6)–C(7)–C(2)	120·4(4)
C(3)–H(3)	0·87(6)	C(7)–C(2)–C(3)	120·0(4)
C(4)–H(4)	[1·10](17)		
C(6)–H(6)	0·91(7)	Sum of angles in ring	720·0
C(7)–H(7)	0·94(6)		
O(1) · · · O(1^{VIII})	2·437(6)	C(1)–O(1) · · · O(1^{VIII})	111·6(3)

TABLE 3

Environment of the potassium ion (distances in Å, angles in deg.; mean standard deviations, respectively, $\nless \pm 0{\cdot}004$ Å and $\pm 0{\cdot}2°$)

K$^+$ · · · O(2), O(2^{IV})	2·750
K$^+$ · · · O(2^{V}), O(2^{VII})	2·926
K$^+$ · · · O(1^{VI}), O(1^{VIII})	2·799

	O(1^{VI})	O(1^{VIII})	O(2)	O(2^{IV})	O(2^{V})	O(2^{VII})
O(1^{VI}), O(1^{VIII})		138·1	113·2	94·0	84·4	66·3
O(2), O(2^{IV})				99·0	84·8	176·1
O(2^{V}), O(2^{VII})						91·3

The hydrogen bond has O · · · H · · · O 2·437(6) Å. It is another example of the set of very short bonds in Type *A* acid salts.[9] Including all the Type *A* acid salts of monocarboxylic acids which have been studied with any accuracy, the current mean (each of the values weighted according to its standard deviation) is 2·443(2) Å. We have given reasons for supposing that these may represent genuinely symmetrical O · · · H · · · O bonds, with the proton vibrating

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* X', Y, and Z' are orthogonal co-ordinates in Å; $X' = ax \sin\beta$, $Y = by$, and $Z' = ax\cos\beta + cz$.

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anharmonically in a symmetrical potential-energy well, with a single, flattened minimum.[10,11]

EXPERIMENTAL

Preparation and Crystal Data.—The material used was made accidentally. We were trying to make an acid potassium salt of *m*-chloroperbenzoic acid, which evidently decomposed during the experiment. Normally, potassium hydrogen bis-*m*-chlorobenzoate would be, and has been, prepared by dissolving chlorobenzoic acid (1 mol) and potassium hydroxide (0·5 mol) of KOH in hot 95% aqueous ethanol, and allowing the solution to cool or evaporate. The product can be recrystallised from the same medium.

Crystal data were first determined photographically, then refined by a least-squares treatment of the θ-values for some high-order reflexions, measured on a diffractometer with Mo-K_α-radiation ($\lambda = 0{\cdot}7107$ Å). The results are included in Table 1. The diffraction symbol [12] is C^*c: the space group shown (No. 15 of ref. 13) was chosen, initially, because it obtains in the virtually isomorphous crystals of potassium hydrogen bis-*p*-chlorobenzoate; it was supported by the Patterson function, and it is deemed to have been validated by the successful structure analysis.

Structure Analysis and Refinement.—Intensities were measured with a Hilger and Watts four-circle diffractometer, by use of Mo-K_α *X*-rays, from a crystal of dimensions $0{\cdot}56 \times 0{\cdot}34 \times 0{\cdot}08$ mm: 2067 independent reflexions were covered out to $\theta = 30°$, of which 1283 were significantly above background [$F > 3\sigma(F)$]. The structure was easily solved by Patterson and electron-density syntheses, and refined by full-matrix least-squares, with anisotropic vibrational parameters for the heavier atoms. Hydrogen atoms, with isotropic vibrations, were introduced at chemically reasonable positions. One hydrogen atom, H(5), did not refine satisfactorily, its position shifted to a site much too close to the chlorine atom, and its vibrational parameter became very large. For this atom we therefore report the calculated position, though all its standard deviations are given the large values resulting from the refinement. Evidently, our analysis has failed to find this atom, for reasons involving some minor errors in our intensity data and the close proximity of the chlorine atom.

Absorption [14] and extinction [15] corrections were made during the later cycles of refinement, which converged to *R* 0·059 for the 1283 observed terms with R' ($= \Sigma w\Delta^2/\Sigma w|F_o|^2$) 0·0061. Atomic-scattering functions were taken from ref. 13. The least-squares weighting scheme was based on: $w = [1 - \exp\{-p_1[(\sin\theta)/\lambda]^2\}]/(1 + p_2|F_o|)$, with, in the final cycles, p_1 5 and p_2 0·1. The positional and vibrational parameters are listed in Tables 4 and 5. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20438 (12 pp., 1 microfiche).* Table 6 gives an analysis of the agreement between observed and calculated structure amptitudes.

TABLE 4

Fractional co-ordinates ($x, y, z \times 10^5$), with absolute standard deviations (in 10^{-4} Å) in parentheses

	x	*y*	*z*
K^+	0	67,884(19)	25,000
Cl	21,205(13)	52,534(19)	16,239(16)
O(1)	3368(32)	6000(56)	−3490(33)
O(2)	5085(32)	21,280(44)	14,932(33)
C(1)	5982(42)	15,976(54)	4920(43)
C(2)	10,326(36)	19,781(46)	1531(40)
C(3)	13,329(39)	33,696(48)	9552(39)
C(4)	17,341(39)	35,749(46)	6382(44)
C(5)	18,439(42)	24,840(54)	−4406(47)
C(6)	15,406(42)	10,773(54)	−12,339(44)
C(7)	11,385(42)	8347(52)	−9384(43)
H(3)	12,521(578)	41,096(640)	16,167(611)
H(5)	21,008(1632)	66,981(1970)	15,350(1670)
H(6)	16,437(672)	3654(758)	−19,060(702)
H(7)	9497(529)	−3598(615)	−14,581(531)

TABLE 5

Vibrational parameters (10^{-4} Å^2) with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
K^+	531(9)	439(9)	363(7)	0	345(12)	0
Cl	275(4)	534(8)	410(6)	−193(12)	−87(7)	−38(11)
O(1)	276(14)	968(34)	332(16)	−97(39)	90(23)	−392(38)
O(2)	326(15)	580(23)	356(16)	−93(32)	197(24)	−33(32)
C(1)	271(18)	458(26)	309(19)	106(39)	104(28)	14(36)
C(2)	232(16)	281(19)	295(18)	26(32)	78(26)	−3(30)
C(3)	285(17)	322(21)	251(17)	39(33)	96(27)	62(32)
C(4)	250(17)	303(22)	351(19)	−74(34)	−2(28)	−36(30)
C(5)	262(18)	462(28)	360(21)	−82(39)	127(30)	−37(36)
C(6)	320(24)	462(29)	323(21)	−105(39)	213(31)	−39(36)
C(7)	317(19)	375(24)	314(19)	−30(35)	71(30)	−46(35)

	U_{iso}
H(3)	106(130)
H(5)	862(745)
H(6)	236(158)
H(7)	62(117)
H(0)	199(412)

TABLE 6

Analysis of agreement between $|F_o|$ and $|F_c|$, and a weighting analysis at the end of the refinement (*N* is the number of reflexions)

$\|F_o\|$ range	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	*N*	*R*	$\Sigma\|\Delta\|/N$
0—10	938	861	174	102	0·185	1·70
10—15	4057	3986	480	330	0·118	1·46
15—20	3753	3752	264	218	0·070	1·21
20—30	6853	6818	329	281	0·048	1·17
30—40	4274	4216	193	124	0·045	1·56
40—80	8967	9050	395	166	0·044	2·10
80—	6066	6086	268	54	0·044	4·9

$\|F_o\|$ range	*N*	$\Sigma w\Delta^2/N$
0—11	194	3·26
11—22	544	2·00
22—44	346	1·21
44—88	155	3·20
88—177	42	3·16
177—	2	13·9

(sin θ)/λ range)	*N*	$\Sigma w\Delta^2/N$
0·0—0·2	51	1·86
0·2—0·4	279	2·31
0·4—0·6	640	1·98
0·6—0·8	313	2·51
All	1283	2·18

We thank the S.R.C. for financial support to A. L. M., and acknowledge our indebtedness to the labours of many computer-programmers, in particular to Dr. J. G. Sime.

[2/706 *Received*, 27*th March*, 1972]

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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