The Crystal Structures of the Acid Salts of some Monobasic Acids. Part IV. Ammonium Hydrogen Disalicylate Hydrate.*

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Acid salicylates of ammonium, potassium, and rubidium have been prepared, and studied by *X*-ray crystallographic methods. The compounds are isomorphous, and the structure of the ammonium salt has been fully investigated. This structure proves these salts to be monohydrates of the formula $MC_7H_5O_3,C_7H_6O_3,H_2O$ (M = NH_4, K, Rb), though the first two are probably identical with substances that had previously been described as anhydrous. The crystals are monoclinic, with four molecules of the above formula in a unit cell belonging to the space-group $P2_1/c$. The structural plan differs from that common to the acid salts described in the earlier papers of this series: the two salicylate residues are crystallographically distinct, and no apparently symmetrical hydrogen bonds are involved.

Acid salts of salicylic acid were first described by E. Hoffmann (*Arch. Pharm.*, 1878, **57**, 226; *Jahresber.*, 1878, 759), who prepared sodium, potassium, lithium, and ammonium compounds, gave the formula of the first as $NaC_7H_5O_3,C_7H_6O_3$, and implied that the formulæ of the others corresponded. Farmer (*J.*, 1903, **83**, 1444) also prepared the potassium salt and reported an analysis which supported the formula $KC_7H_5O_3,C_7H_6O_3$. Continuing our structural studies of acid salts (Part I, *J.*, 1949, 3357; Part II, *J.*, 1951, 185; Part III, *loc. cit.*), we have prepared potassium and ammonium hydrogen disalicylates which appear to be identical with the substances prepared by the earlier workers, and also a rubidium salt. These three compounds are isomorphous, and the crystal structure of the ammonium salt has been examined in detail. As with the acid salt described in Part II (*loc. cit.*), the structure shows that the compounds are in fact hydrated, *viz.*, (NH_4, K, Rb)$C_7H_5O_3,C_7H_6O_3,H_2O$. Because these acid salts crystallise incongruently from aqueous solutions containing a large excess of the neutral salt, it is difficult to purify them, so the results of analysis carried out in the usual way are not above suspicion. A detailed and exact study of the ternary phase diagram is therefore needed to establish their compositions by chemical means. Preliminary work on the system salicylic acid–potassium salicylate–water has been reported by N. Smith (Thesis, Sheffield, 1949), and further work is in progress. Hoitsema (*Z. physikal. Chem.*, 1898, **27**, 312) studied the ternary system involving sodium salicylate, and reported the " double salt " as $NaC_7H_5O_3,C_7H_6O_3$; but his work was not carried to the point when it could provide any definite evidence as to the hydration.

The acid salts studied in Parts I—III (*locc. cit.*) had structures based on a common plan. The structures of these acid salicylates prove to be quite different.

Experimental

Preparation of Materials.—Potassium hydrogen disalicylate is much more difficult to prepare than the other acid salts studied in this series. Attempts at preparation by the methods described by Hoffmann and Farmer were not successful: very often the crystals separating consisted of salicylic acid (which could easily be recognised by its oblique, 42°, extinction in polarised light), and under slightly different conditions a microcrystalline product of uncertain identity resulted. Suitable crystals of the acid salt (which shows straight extinction) were ultimately made by warming 1 g. of potassium carbonate and slightly over 2 g. of salicylic acid with about 8 c.c. of water or dilute aqueous alcohol. (These proportions correspond to a neutral salt, rather than to an acid one.) After the solution had cooled and been set aside, the free acid sometimes crystallised out first, but fine needles of the acid salt appeared later. The product had an equivalent that was a little high (320—340), but this was attributed to impurity due to the method of preparation. Purification by recrystallisation from alcohol was un-

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* Part III, *J.*, 1954, 180.

trustworthy because of the likelihood of salicylic acid's separating out. However, single crystals of a size suitable for *X*-ray study could be obtained without great difficulty from the original preparation. In general, the material consisted of very fine needles, or bundles of needles, elongated in the direction of the *b*-axis. The only faces to be well developed were {001}, and there was ready cleavage parallel to (100). As the structure analysis proceeded, it became clear that the substance was potassium hydrogen disalicylate hydrate.

Ammonium hydrogen disalicylate hydrate was made in a similar way, concentrated ammonia solution being used instead of potassium carbonate. The substitution of rubidium carbonate led to rubidium hydrogen disalicylate hydrate, which was recognised to be such by its isomorphism with the other two. Several other crystalline substances, whose compositions were not investigated, were obtained with rubidium carbonate, and it appears that the system salicylic acid–rubidium salicylate–water may be fairly complex. It is just possible that the hydrated compound studied in this work may be a metastable phase.

Crystals of each of the three acid salts were examined by single-crystal rotation, oscillation and moving-film photographs, using Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}54_2$ Å). Intensity data were obtained as described in Parts I—III, and similarly treated to give structure amplitudes.

Results.—Crystal data. The crystals belonged to the monoclinic prismatic class, and were closely isomorphous, with the following unit-cell dimensions:

	a, Å	*b*, Å	*c*, Å	β
$NH_4C_7H_5O_3,C_7H_6O_3,H_2O$	17·28 ± 0·05	3·89 ± 0·02	22·33 ± 0·05	98·8° ± 0·5°
$KC_7H_5O_3,C_7H_6O_3,H_2O$	16·90 ± 0·15	3·88 ± 0·05	22·40 ± 0·15	96·0° ± 1·0°
$RbC_7H_5O_3,C_7H_6O_3,H_2O$	17·13 ± 0·10	3·99 ± 0·02	22·74 ± 0·10	98·5° ± 0·5°

Further data for the ammonium compound were: $M = 311{\cdot}3$; vol. of unit cell $= 1483$ Å^3; *d* (found) 1·37, *d* (calc. by assuming four molecules of the above formula per unit cell) 1·39; F(000) $= 656$, absorption coefficient for Cu-$K\alpha$ *X*-rays $= 10{\cdot}97$ cm.$^{-1}$.

Absent spectra for all three substances were: *h*0*l* when *l* is odd; 0*k*0 when *k* is odd. The space-group is thereby uniquely indicated to be $P2_1/c$ (C^5_{2h}). No molecular symmetry is required, and all atoms are in general positions. Centrosymmetry of the structure as a whole was confirmed by the Wilson (*Acta Cryst.*, 1949, **2**, 318) and the Rogers (*ibid.*, 1950, **3**, 210) test.

Structure amplitudes for the three principal zones of the ammonium compound are given in Tables 2 and 3.

Structure analysis. The very short *b*-axis suggested that the structure analysis could best be approached by way of the (*h*0*l*) projection. The potassium salt was first available, and a Patterson projection was calculated. The result was disappointing, as it did not even indicate the position of the " heavy " atom. A corresponding projection was then made for the rubidium salt; the highest peak, apart from that at the origin, did, in fact, signify the Rb–Rb vector, but, since this peak was only a little higher than some others, the result was felt to be uncertain until confirmed by carrying out a third projection with only the higher-order terms.

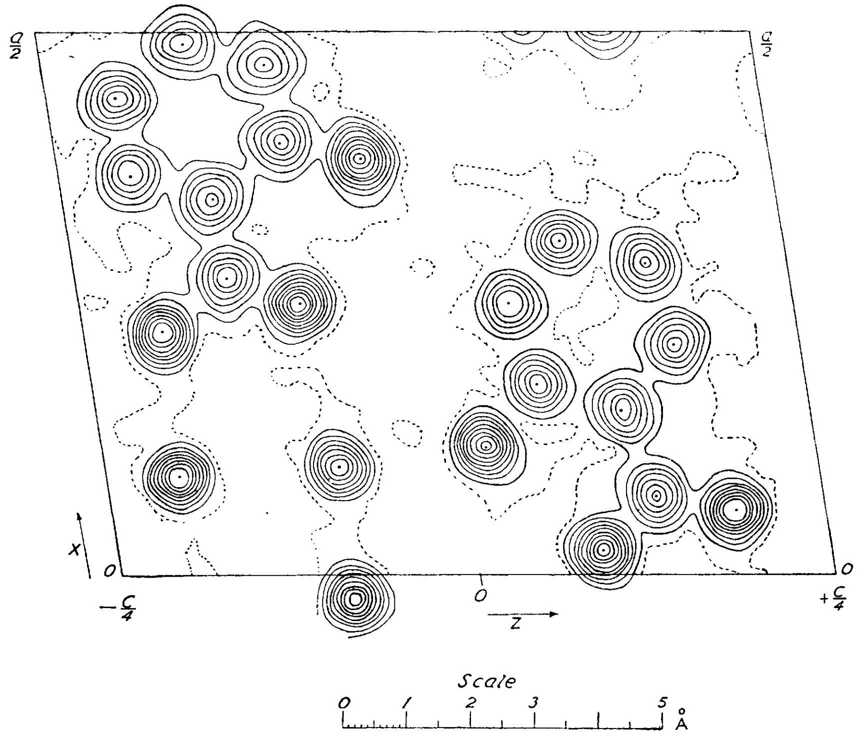
The *x*- and *z*-co-ordinates of the rubidium atoms now being known, it became possible to calculate their contributions to the structure factors, and hence to assess the possible signs of 223 terms. These were used to calculate an electron-density projection. Despite some blemishes, this projection could have led to the correct structure. It did not, in fact, do so because of the presence of a large peak, due to the water molecule, which could not be interpreted at the time.

Another approach was more successful. Experience with similar compounds had suggested a *ratio* of about 1·8 between the average structure amplitudes for rubidium and potassium isomorphs; and knowing the position of the cation and assuming it to be exactly the same in both cells, the *difference*, on an absolute scale, between individual pairs of structure factors could be calculated. Hence, by considering statistically a large number of terms for which this difference was significant, it was possible to place both sets of data on an approximately absolute scale. The scheme could then be extended to the ammonium salt, so as to put its structure factors on to the same scale and to decide the signs of 75 of them. A Fourier synthesis was made, and the resulting map could be interpreted without difficulty; the indication of the presence of an unexpected water molecule was now unmistakable. This view of the structure was refined by repeated syntheses until the final electron-density map, shown in Fig. 1, was achieved. The interpretation of this map and the numbering of the atoms are indicated in Fig. 2(*a*).

The peak attributed to the ammonium ion is only a little lower than that attributed to the water molecule, and the assignment might well have been in doubt. However, a similar electron-density projection was made for the potassium compound, and it was unequivocal in placing the potassium ion in a position equivalent to that of the ammonium in Fig. 2(*a*).

All the atoms (apart from hydrogen) are well resolved in Fig. 1, and the co-ordinates derived

FIG. 1. *Ammonium hydrogen disalicylate hydrate: electron-density projected along* b-*axis.*



(Contour-line scale: 1 electron per sq. Å; line of unit electron-density broken.)

TABLE 1. *Atomic co-ordinates.* [See Fig. 2(*a*) for numbering of atoms. Origin at a centre of symmetry; *x*, *y*, and *z* as fractions of the cell-edges; *X′*, *Y*, and *Z′* in Å, and referred to orthogonal axes, with *X′* parallel to *x*.]

	x	*y*	*z*	*X′*	*Y*	*Z′*
NH_4^+	0·0992	0·000	−0·0863	2·02	0·00	−1·91
H_2O	0·0906	−0·380	−0·1994	2·25	−1·48	−4·41
O(1)	0·2237	0·243	−0·1949	4·54	0·95	−4·31
O(2)	0·2491	0·2925	−0·0951	4·64	1·14	−2·10
O(3)	0·3834	0·069	−0·0366	6·76	0·27	−0·81
O(4)	0·0587	0·650	0·1878	0·37	2·53	4·14
O(5)	0·0208	0·500	0·0892	0·06	1·95	1·97
O(6)	0·1163	0·530	0·0187	1·95	2·06	0·41
C(1)	0·2740	0·189	−0·1439	5·23	0·74	−3·18
C(2)	0·3475	0·033	−0·1445	6·51	0·13	−3·19
C(3)	0·3678	−0·067	−0·2007	7·05	−0·27	−4·43
C(4)	0·4398	−0·222	−0·2023	8·29	−0·87	−4·47
C(5)	0·4893	−0·272	−0·1490	8·97	−1·06	−3·29
C(6)	0·4702	−0·174	−0·0937	8·45	−0·68	−2·08
C(7)	0·3976	−0·018	−0·0915	7·18	−0·08	−2·03
C(8)	0·0718	0·604	0·1327	0·79	2·35	2·93
C(9)	0·1505	0·676	0·1177	2·20	2·63	2·60
C(10)	0·1753	0·643	0·0621	2·82	2·50	1·37
C(11)	0·2497	0·716	0·0505	4·14	2·79	1·12
C(12)	0·3073	0·825	0·0939	4·99	3·21	2·07
C(13)	0·2862	0·865	0·1513	4·43	3·37	3·34
C(14)	0·2115	0·794	0·1624	3·10	3·09	3·58

TABLE 2. *Observed structure amplitudes and calculated structure factors for h0l.* (In each set of three columns, the first lists values of *h*, the second |F_O|, and the third F_C.)

*h*00

1	(?)	+35·7
2	26·0	−26·4
4	5·9	+1·9
5	34·7	−34·0
6	59·1	−65·6
7	46·8	−43·6
8	34·1	+37·1
9	8·3	−9·7
11	13·5	+16·5
13	14·4	+13·2
15	15·0	−10·4
21	7·0	−3·0

*h*02

$\overline{22}$	6·4	−6·0
$\overline{20}$	8·4	+11·6
$\overline{18}$	5·5	+6·1
$\overline{17}$	16·0	+14·5
$\overline{16}$	9·8	+15·0
$\overline{15}$	3·3	+4·0
$\overline{14}$	26·9	−33·8
$\overline{13}$	27·4	−23·2
$\overline{12}$	6·2	−7·4
$\overline{10}$	23·1	+31·3
$\bar{9}$	35·1	−33·2
$\bar{8}$	92·4	+107·9
$\bar{7}$	96·0	+115·9
$\bar{6}$	25·1	+22·5
$\bar{5}$	9·1	−5·6
$\bar{4}$	7·6	+8·9
$\bar{3}$	29·8	−44·1
$\bar{2}$	52·6	+93·0
$\bar{1}$	(?)	−14·7
0	(?)	−13·0
1	27·2	+25·1
2	66·8	−115·5
3	22·4	+27·1
4	60·0	−62·5
5	8·1	+20·4
7	30·0	−27·6
8	7·2	−13·9
9	12·6	+17·4
10	3·3	−4·3
12	12·4	+11·8
13	17·9	+16·5
14	45·7	−40·4
16	8·6	+5·0
18	14·8	−13·0
19	5·5	−6·4
20	8·4	−11·4
21	2·6	−5·4

*h*04

$\overline{22}$	4·3	−6·6
$\overline{20}$	7·6	−7·4
$\overline{18}$	4·5	+7·9
$\overline{17}$	11·9	+11·0
$\overline{16}$	12·4	+7·7
$\overline{15}$	10·0	+4·4
$\overline{14}$	16·2	+11·6
$\overline{13}$	5·7	+5·0
$\overline{12}$	10·0	+11·8
$\overline{11}$	9·1	−6·2
$\overline{10}$	22·9	+28·2
$\bar{9}$	35·7	+41·6
$\bar{8}$	7·4	−4·9
$\bar{7}$	15·3	+18·3
$\bar{6}$	29·1	−33·6
$\bar{5}$	15·1	+16·3
$\bar{4}$	65·1	−74·5
$\bar{3}$	36·3	−45·5
$\bar{2}$	29·8	+27·4
$\bar{1}$	33·2	+47·8
0	101·1	−136·1
1	34·9	−38·8
3	7·9	+11·1
4	48·4	−44·2
5	37·2	+49·1
6	10·2	−4·2
7	22·2	−21·3
8	17·4	+16·9
9	14·1	+10·2
10	14·6	−18·5
11	9·3	+5·0
12	42·7	−39·7
13	15·1	−12·3
14	29·3	−28·4
15	17·4	−17·4
16	20·1	+20·2
17	9·3	−7·6
18	4·8	+6·6
20	4·3	−3·5
21	8·4	+11·9

*h*06

$\overline{21}$	3·1	+4·8
$\overline{18}$	44·6	+30·6
$\overline{16}$	9·8	−12·3
$\overline{15}$	10·0	−9·7
$\overline{14}$	3·3	−2·9
$\overline{13}$	6·0	+4·1
$\overline{12}$	15·8	−15·9
$\overline{11}$	19·3	−18·7
$\bar{9}$	23·8	+21·6
$\bar{8}$	3·4	−3·8
$\bar{7}$	32·0	−30·9
$\bar{6}$	37·7	−33·9
$\bar{5}$	5·5	−9·6
$\bar{4}$	6·2	−0·4
$\bar{3}$	56·7	−55·6
$\bar{2}$	1·7	−1·4
$\bar{1}$	21·0	−24·8
0	6·7	−3·3
1	20·0	+15·5
2	32·9	−28·2
3	46·3	+37·4
4	17·2	−17·6
5	29·1	−29·7
6	10·0	+12·6
7	35·4	−35·8
8	16·2	−16·1
9	27·1	−21·0
10	6·4	+1·1
11	4·8	+6·2
12	28·1	−27·7
13	30·6	−29·8
14	71·0	+66·6
15	24·6	+18·3
16	10·1	+11·2
18	7·2	+7·5
20	6·9	−9·3

*h*08

$\overline{19}$	10·0	−11·3
$\overline{17}$	5·2	−7·5
$\overline{16}$	10·0	−11·6
$\overline{15}$	7·2	+7·6
$\overline{14}$	6·7	+6·9
$\overline{13}$	9·5	−11·9
$\overline{11}$	10·2	−10·1
$\bar{9}$	20·3	−22·5
$\bar{8}$	24·8	−31·8
$\bar{7}$	12·9	−19·4
$\bar{5}$	11·4	+6·6
$\bar{4}$	33·9	−39·6
$\bar{3}$	10·1	+14·1
$\bar{2}$	51·8	+49·5
$\bar{1}$	37·9	+39·3
0	57·1	−57·5
1	65·0	−62·8
2	56·0	−42·4
3	13·4	−11·9
4	11·2	+9·8
5	74·0	−73·8
6	46·8	+46·3
7	68·5	+72·3
8	44·8	+47·3
9	5·5	+4·5
10	4·3	−1·1
12	8·3	−3·1
13	8·8	−9·3
14	9·5	+7·7
15	16·7	+18·0
16	3·8	−0·9
17	5·2	+6·9
18	4·0	−2·9

*h*0,10

$\overline{18}$	7·4	−8·7
$\overline{15}$	11·2	−11·1
$\overline{14}$	11·2	−14·6
$\overline{13}$	22·9	+27·4
$\overline{12}$	15·0	−5·2
$\overline{11}$	11·6	−9·9
$\overline{10}$	8·3	+8·0
$\bar{9}$	26·5	+36·3
$\bar{8}$	18·6	−23·5
$\bar{7}$	34·6	−34·8
$\bar{6}$	65·0	−70·9
$\bar{4}$	19·8	−16·6
$\bar{3}$	18·4	+20·2
$\bar{2}$	67·3	+76·3
$\bar{1}$	40·6	+35·8
0	55·0	+54·1
1	39·2	+29·5
2	11·7	+3·1
3	19·3	−18·5
5	12·2	+5·6
6	9·8	+5·2
7	23·8	+22·1
8	15·5	+10·7
9	31·4	+28·7
13	7·9	+10·4
14	9·3	−8·9
15	10·0	−11·1
18	8·8	−7·1

*h*0,12

$\overline{20}$	9·1	+12·0
$\overline{19}$	5·2	+7·8
$\overline{18}$	3·6	−4·7
$\bar{1}$	8·8	+9·8
$\overline{16}$	9·1	−11·8
$\overline{15}$	5·3	+6·2
$\overline{14}$	34·9	−35·1
$\overline{13}$	21·2	−22·9
$\overline{11}$	8·1	−5·2
$\overline{10}$	31·0	+32·9
$\bar{9}$	21·0	+19·4
$\bar{8}$	16·0	+14·7
$\bar{7}$	42·9	+40·7
$\bar{6}$	4·3	−1·6
$\bar{5}$	29·6	−31·6
$\bar{4}$	71·6	+69·6
$\bar{3}$	26·4	+21·8
$\bar{2}$	14·5	+10·2
$\bar{1}$	13·4	−16·1
1	30·5	+30·2
3	12·6	−15·2
4	7·9	−0·6
5	9·5	+11·4
6	27·4	+25·8
8	9·8	−8·7
11	10·7	−8·6
12	15·5	−4·2
13	5·2	−1·3
14	6·2	+5·4
16	5·5	−5·4
17	5·5	+4·7

*h*0,14

$\overline{16}$	5·5	−7·8
$\overline{15}$	10·2	+6·7
$\overline{14}$	26·8	+30·5
$\overline{13}$	35·1	−37·8
$\overline{12}$	25·5	+27·1
$\overline{11}$	47·0	+48·1
$\overline{10}$	30·6	+36·3
$\bar{9}$	7·4	−7·3
$\bar{8}$	17·9	−17·5
$\bar{7}$	8·8	+4·4
$\bar{6}$	14·8	+11·1
$\bar{5}$	26·7	−28·1
$\bar{4}$	9·3	+10·6
$\bar{3}$	7·4	−4·9
$\bar{2}$	4·3	−3·0
$\bar{1}$	5·0	+2·3
1	12·0	−10·6
4	9·8	−0·2
5	17·0	−9·2
6	5·0	+4·8
7	6·0	−1·0
8	4·8	+1·7
9	10·0	+10·4
10	18·4	−19·6
11	11·4	−8·4
12	6·4	−7·4
13	4·8	+3·0
15	8·8	−11·7
16	6·0	−5·4

*h*0,16

$\overline{19}$	8·8	+7·5
$\overline{18}$	18·6	+16·6
$\overline{17}$	9·3	+10·6
$\overline{15}$	9·3	−11·4
$\overline{14}$	7·4	+6·6
$\overline{11}$	13·6	+8·7
$\overline{10}$	15·8	−16·1
$\bar{9}$	7·9	−5·4
$\bar{8}$	13·8	−6·4
$\bar{7}$	7·2	−7·8
$\bar{6}$	7·4	−4·9
$\bar{5}$	9·8	−2·5
$\bar{4}$	4·8	−3·3
$\bar{3}$	15·8	−11·8
$\bar{2}$	5·7	+3·0
0	21·3	−26·3
1	45·4	+47·8
3	27·7	−17·0
4	15·8	−14·5
5	11·2	+9·8
6	8·6	−0·6
7	16·0	−13·3
8	32·0	−33·8
10	22·2	−20·3
11	8·6	−10·1
12	11·7	+11·3
13	3·3	+2·9
14	10·0	+11·8
15	5·3	+6·4

*h*0,18

$\overline{15}$	4·5	−2·9
$\overline{14}$	9·8	−7·1
$\overline{13}$	3·2	+4·6
$\overline{11}$	17·9	−14·6
$\overline{10}$	19·8	−27·5
$\bar{9}$	8·3	+5·8
$\bar{8}$	14·4	−17·5
$\bar{6}$	23·4	+20·4
$\bar{5}$	11·2	+15·0
$\bar{4}$	4·5	+1·4
$\bar{3}$	11·4	+13·6
$\bar{2}$	8·8	−12·6
$\bar{1}$	19·6	+17·8
0	46·5	−46·0
1	28·8	−28·1
2	23·1	−19·7
3	42·5	−41·7
4	16·0	+12·7
5	16·5	+7·7
6	12·4	+13·6
7	22·7	+24·8
9	12·4	−12·4
12	5·5	+4·3
13	4·5	−5·2
14	2·9	+1·4

*h*0,20

$\overline{17}$	10·4	−14·4
$\overline{15}$	7·6	−8·0
$\overline{13}$	6·7	+9·3
$\overline{12}$	9·3	+5·4
$\overline{11}$	16·2	+15·3
$\overline{10}$	7·2	−6·9
$\bar{9}$	6·2	+5·6
$\bar{7}$	25·8	−29·3
$\bar{6}$	16·0	−15·2
$\bar{5}$	15·5	−14·9
$\bar{3}$	5·7	+1·3
$\bar{2}$	11·0	−9·8
$\bar{1}$	13·1	+10·6
0	29·6	+34·6
1	35·8	−39·5
2	13·1	−9·2
3	10·0	+9·0
4	42·2	+32·2
5	9·1	+5·3
6	5·5	−3·6
7	9·8	+12·9
8	9·8	+12·0
10	4·1	+2·6

*h*0,22

$\overline{15}$	5·5	−6·3
$\overline{14}$	10·8	−10·9
$\overline{12}$	7·6	+6·7

TABLE 2. (*Continued.*)

	*h*0,22		$\bar{1}$	3·4	− 2·2	$\overline{13}$	6·0	+ 8·6	3	9·5	− 4·2	0	2·6	− 1·9
$\overline{11}$	3·6	+ 2·0	0	11·2	+ 8·4	$\overline{10}$	7·9	+ 7·7	4	10·8	−11·8	1	5·7	− 0·5
$\overline{10}$	5·2	− 5·6	1	6·7	+ 3·3	$\bar{8}$	4·1	− 5·6	5	4·3	+ 6·0	3	11·0	+10·8
$\bar{9}$	13·1	−14·3	2	6·0	+ 3·8	$\bar{6}$	5·0	+ 3·0	6	9·8	− 9·9	5	3·1	+ 2·8
$\bar{8}$	16·7	+14·4	3	8·8	+ 9·6	$\bar{5}$	12·2	+11·5	8	6·4	+ 5·1			
$\bar{6}$	16·0	−10·2	4	7·9	+ 5·3	$\bar{4}$	3·1	− 0·1					*h*0,28	
$\bar{5}$	10·5	− 7·6	8	6·4	− 6·7	$\bar{3}$	11·4	+ 9·2		*h*0,26		$\bar{3}$	5·7	+ 6·8
$\bar{4}$	15·6	+16·3				$\bar{2}$	8·4	+ 6·9	$\overline{10}$	6·0	+ 5·7	$\bar{1}$	5·0	− 4·7
$\bar{3}$	25·5	+22·5		*h*0,24		$\bar{1}$	3·8	+ 3·8	$\bar{9}$	6·4	+ 3·7	0	15·3	−16·9
$\bar{2}$	4·1	+ 7·0	$\overline{14}$	8·3	+ 9·1	1	7·2	− 4·2	$\bar{3}$	9·8	−11·0			

from it were corrected for termination-of-series errors by Booth's method (" Fourier Technique in X-Ray Organic Structure Analysis," Univ. Press, Cambridge, 1948, p. 100) to yield the *x* and *z*-co-ordinates listed in Table 1.

FIG. 2(*a*).

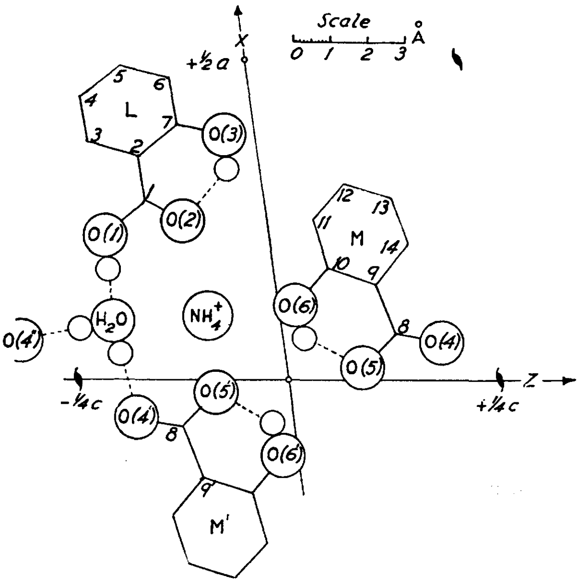


FIG. 2(*b*).

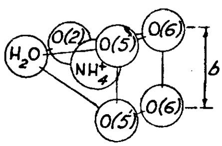


FIG. 2(*a*). *Ammonium hydrogen disalicylate hydrate : numbering of atoms and interpretation of Fig.* 1 (The centres of symmetry shown are at $y = 0$ and $\frac{1}{2}b$.)

FIG. 2(*b*). *Sketch of the immediate environment of the ammonium ion.*

In the earlier stages of the analysis, the atomic scattering factors used were those given in Part I, the factor for nitrogen being taken to be the same as that for oxygen. As the refinement proceeded, these factors were modified by a method essentially the same as that described by Luzzati (*Acta Cryst.*, 1953, **6**, 158), and the scattering functions which best fitted the data were as follows :

$2 \sin \theta$	0·00	0·25	0·50	0·75	1·00	1·25	1·50	1·75
f_C	(6·00)	5·02	3·63	2·37	1·54	1·04	0·76	0·57
f_N	(7·00)	6·53	4·94	3·14	1·89	1·44	1·09	0·79
f_O	(8·50)	6·61	4·99	3·55	2·40	1·64	1·14	0·79

By using these factors and the co-ordinates listed in Table 1, values of F(*h*0*l*) were calculated, and they are compared with the observed amplitudes in Table 2. To economise space, unobserved reflexions are omitted; the calculated values for these were almost always insignificant. (The only noteworthy exceptions were 204, 10,0,10, and $\bar{5}$,0,10, for each of which $|F_o|$ was $<3·5$, and for which F_c was respectively +8·8, −7·3, and −7·6.) The 366 observed terms represent 71% of those accessible. If 004, 202, and 20$\bar{2}$, which are apparently affected by extinction errors, are omitted, the discrepancy, *R*, is 16·9%.

The determination of the *y*-co-ordinates from F(0*kl*) and F(*hk*0) data had to be made by trial-and-error methods, since the atoms would be insufficiently resolved in the *a*- and *c*-axis projections to permit of a useful application of the Fourier series method. Some guidance as to the position of the ammonium ion was, however, obtained from a " difference Patterson " synthesis, the terms for which were the absolute-scale values of $(F^2_{Rb} - F^2_{NH_4})$ for the 0*kl*-zone. This synthesis indicated that the cations were not far from the positions, $y = 0$ and $\frac{1}{4}b$. The unit cell contains centres of symmetry and 2_1-axes, which cannot be distinguished in a *b*-axis projection. Packing considerations led to the conclusion that a centre must lie between 0(5) and 0(5′), and this point was taken for origin as implied in Fig. 2(*a*). The details of the structure in the *y*-dimension were elucidated by empirical methods, the salicylate residues being assumed planar and the distances between the ammonium ion and the surrounding oxygen atoms not less than 2·8 Å. The *y*-co-ordinates finally adopted are included in Table 1. Observed structure amplitudes for (0*kl*) and (*hk*0) are compared in Table 3 with structure factors calculated with the atom-scattering functions already given. Reflexions not observed are again omitted. In nearly all such cases F_0 was very small, the principal exceptions being 028, 0,2,13, and 820. The values of *R* for these zones are respectively 22·9% and 21·0%.

TABLE 3. *Observed structure amplitudes and calculated structure factors for* 0kl *and* hk0. (See Table 2 for arrangement of data.)

	01*l*		20	10·4	−3·3	10	16·4	+3·1	8	12·4	+22·1		*h*20	
1	12·4	+10·9	21	5·2	+9·2	11	10·4	−12·2	12	11·9	−10·4	1	22·4	+23·6
2	94·2	+99·7	24	5·2	+5·4	12	13·4	+9·0	14	11·8	+5·8	2	29·9	+48·7
3	30·3	−19·8	25	7·3	+6·7	14	4·2	+2·1				3	40·7	+45·0
4	15·2	+27·1	27	6·7	+5·0	15	8·5	+15·2				4	68·1	−76·1
5	23·1	+24·1				16	15·0	−12·1		*h*10		9	15·4	+3·4
8	21·3	+26·3		02*l*		17	10·0	−11·3	1	39·4	+50·2	10	17·3	+22·8
9	19·2	−14·5	0	6·4	−7·7	18	11·0	−12·1	2	45·4	+36·9	11	26·7	+15·5
10	8·3	−8·4	2	25·6	+37·2	19	6·0	−9·4	3	67·1	+75·4	12	19·6	−7·1
11	8·3	−8·0	3	22·5	−15·2				4	13·1	+5·2			
12	8·3	+2·5	4	15·6	+17·5				5	19·6	+9·9		*h*30	
13	15·0	+13·6	5	16·4	−14·1		03*l*		6	29·8	−31·8	1	13·1	+16·4
14	5·8	−2·3	6	14·3	−14·3	4	8·5	+9·8	7	48·6	+48·3	2	11·2	+21·4
15	17·8	−16·3	7	19·2	+13·8	5	13·4	−2·1	9	19·6	−20·4	4	9·8	+14·3
17	21·6	−17·0	9	22·5	+21·4	6	9·8	+8·3	10	21·0	−18·5	5	7·9	+11·7

It is considered that the *x*- and *z*-co-ordinates are unlikely to be in error by more than 0·02 Å. The *y*-co-ordinates are less certain, but—in an asymmetric unit containing 22 atoms—the above measure of agreement seems to be adequate evidence of the essential correctness of the structure found. Bond-lengths, which are given in Table 4, are relatively little affected by small errors in the *y*-co-ordinates; they should generally be correct to within 0·05 Å. Intermolecular distances between non-bonded atoms are not abnormal. The salicylate residues, *L* and *M*, of Fig. 2(*a*), are inclined to (010) at about 25° and 11° respectively.

TABLE 4. *Principal interatomic distances* (Å) *and certain bond-angles.*

C(1)–C(2)	1·42	C (8)–C(9)	1·48	O(1) . . . O(2)	2·22	O(4) . . . O(5)	2·27
C(2)–C(3)	1·40	C (9)–C(10)	1·38	O(2) . . . O(3)	2·63	O(5) . . . O(6)	2·45
C(3)–C(4)	1·39	C(10)–C(11)	1·38				
C(4)–C(5)	1·37	C(11)–C(12)	1·35	O(1) . . . H_2O	2·76 (3·34)	NH_4^+ . . . O(2)	2·87 (3·81)
C(5)–C(6)	1·38	C(12)–C(13)	1·39	NH_4^+ . . . H_2O	2·91 (3·48)	NH_4^+ . . . O(6)	2·95 (3·10)
C(6)–C(7)	1·40	C(13)–C(14)	1·38	H_2O . . . O(4′)	2·65 (3·87)	NH_4^+ . . . O(5′)	2·84 (2·84)
C(7)–C(2)	1·37	C(14)–C(9)	1·41	H_2O . . . O(4″)	2·65 (3·90)		
C(1)–O(1)	1·34	C (8)–O(4)	1·29				
C(1)–O(2)	1·29	C (8)–O(5)	1·27				
C(7)–O(3)	1·33	C(10)–O(6)	1·37				

<O(1)–C(1)–O(2)	115°	<O (4)–C (8)–O (5)	124°	<O(4′) . . . H_2O . . . O(4″)	99°
O(1)–C(1)–C(2)	122	O (4)–C (8)–C (9)	120	O(1) . . . H_2O . . . O(4″)	105
C(2)–C(1)–O(2)	124	C (9)–C (8)–O (5)	116	O(1) . . . H_2O . . . NH_4^+	108
C(1)–C(2)–C(7)	120	C (8)–C (9)–C(10)	127	O(4′) . . . H_2O . . . NH_4^+	92
C(2)–C(7)–O(3)	125	C (9)–C(10)–O (6)	112		
C(6)–C(7)–O(3)	116	C(11)–C(10)–O (6)	123		

DISCUSSION

In the structures of the acid salts described in Parts I—III (*locc. cit.*), the metallic cations and acidic hydrogen atoms are in special positions. The hydrogen bond is effectively symmetrical, and the two acid residues are crystallographically equivalent, so that free acid, HA, and anion, A^-, cannot be distinguished by *X*-ray methods. The salicylate structure, on the other hand, has all atoms in general positions, and the acid residues are crystallographically distinct. Indeed, there appear to be reasons for regarding residue *L* as corresponding to HA, and *M* to A^-. The difference between the bond lengths C(1)–C(2) and C(8)–C(9) is almost certainly real, and it is in the sense required by the distinction; and in so far as they are collectively significant, the same applies to the C–O lengths, to the valency-angles round C(1) and C(8), and to the distances O(2) . . . O(3) and O(5) . . . O(6). (It is presumed that there will be considerable co-ordination between the C=O bond and the benzene ring in HA, but that this co-ordination will be diminished in A^- on account of the cross-co-ordination between the carboxylic oxygen atoms.)

In a few ammonium compounds (*e.g.*, the fluoride) the ammonium ion has a tetrahedral environment of electronegative atoms, and its four hydrogens will certainly be engaged in forming hydrogen bonds with its four neighbours. Far oftener there are more than four nearest neighbours co-ordinated round the ammonium ion (*e.g.*, in the sulphate), and this will be the situation when there is strict isomorphism with a potassium compound (*e.g.*, potassium sulphate). This point has been discussed by Wells (" Structural Inorganic Chemistry," Univ. Press, Oxford, 1950, pp. 245, 246; see also van Niekerk and Schoening, *Acta Cryst.*, 1952, **5**, 475). In the acid salicylates, each cation is surrounded by six approximately equidistant (see Table 4) oxygen atoms, whose situations at the corners of a somewhat irregular trigonal prism are suggested in Fig. 2(*b*). The N . . . O distances are consistent with the ionic radius, 1·48 Å, for ammonium suggested by Pauling (" Nature of the Chemical Bond," Univ. Press, Cornell, 1940, p. 350). The four nearest neighbours of each water molecule are in a tetrahedral arrangement, and the angles at H_2O quoted in Table 4 refer to this environment.

Since the ammonium and potassium (or rubidium) salts are so closely isomorphous, it seems that only such hydrogen bonds should be postulated in the ammonium compound as could also occur in the potassium compound. It is, therefore, inferred that the acidic hydrogen atom from one of the salicylate residues has been taken over by the ammonium ion, and that no significant hydrogen-bonding can exist between that ion and its surroundings. The structure would then involve five hydrogen bonds per stoicheiometric molecule, NH_4A,HA,H_2O. This is equal to the number of protons available, *viz.*, one from the remaining acid hydrogen atom, two from the phenolic groups, and two from the water molecule. Although hydrogen atoms were not detected in this work, it seems reasonable to suggest (cf. Donohue, *J. Phys. Chem.*, 1952, **56**, 502) that they may be disposed as indicated in Fig. 2(*a*), with residue *L* in the rôle of neutral acid, HA, and *M* in that of anion, A^-. The chief difference in unit-cell dimensions in going from the ammonium to the potassium salt lies in the *a*-parameter. The radius of K^+ being less than that of NH_4^+, the reduction observed is to be expected, since the shortest contact, that between cation and O(5), would be most affected, and this lies nearly in the direction of the *a*-axis.

Cochran (*Acta Cryst.*, 1953, **6**, 260) has recently published an account of a very precise determination of the structure of salicylic acid. The present work is necessarily much less exact; but the bond-lengths shown in Table 4 are not inconsistent with Cochran's values.

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