Discussion. The final positional and equivalent isotropic thermal parameters are in Table 1,* and bond lengths and interbond angles in Table 2. The numbering of the atoms and packing arrangement of the molecules showing the H-bond system are in Fig. 1. The phenyl rings of the molecules are effectively planar, r.m.s. displacements of the atoms being 0·011 (4) Å for molecule '*A*' and 0·012 (4) Å for molecule '*B*'. The carboxyl groups are rotated by +5·38 (5) and +1·71 (5)° respectively from the planes of their rings. The two phenyl rings make an angle of +138·85 (5)°.

Comparison of the neutron and X-ray results shows some quite appreciable differences, which may be due to the lower accuracy of the X-ray intensity data. However, the properties being measured are not the same by the two methods, the centre of gravity of the diffracting electrons by X-rays, and the position of the atomic nucleus by neutrons. Nevertheless, variations of up to 0·07 Å in bond lengths are more than might be expected, and difficult to account for convincingly. A re-determination of the X-ray structure might clarify the discrepancies.

* Lists of structure factors, anisotropic thermal parameters and mean-planes' details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39884 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1970). *NRC* crystallographic programs for the IBM/360 system. National Research Council, Ottawa, Canada.

BROWN, C. J. (1968). *Proc. R. Soc. London Ser. A*, **302**, 185–199.

International Tables for X-ray Crystallography (1962). Vol. III, p. 229. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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Refinement of 4-Methyl-5-sulfosalicylic Acid Tetrahydrate, $C_8H_8O_6S.4H_2O$*

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Abstract. $M_r = 304·27$, monoclinic, $P2_1/c$, $a = 7·425$ (1), $b = 25·353$ (3), $c = 8·291$ (2) Å, $\beta = 118·09$ (1)°, $V = 1377$ (1) Å^3, $Z = 4$, $D_x = 1·467$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·255$ mm^{-1}, $F(000) = 640$, $T = 295$ K. Refinement based on 2860 reflexions gave a final $wR(F^2)$ value of 0·074. The molecular structure can best be formulated as the diaquaoxonium salt $H_7O_3^+.CH_3C_6H_2$-$COOH(OH)SO_3^-.H_2O$. The salicylic acid molecules are linked by hydrogen bonds *via* the H_2O molecule and the disordered $H_7O_3^+$ complex.

Introduction. A large number of papers dealing with the geometry of water–proton complexes have been published. The different types of complexes occurring in such systems were identified by Lundgren (1974) and Lundgren & Olovsson (1976). Taesler (1981) showed that the type of complex formed in one specific compound is governed mainly by the water/proton ratio and the type of anion.

The structure of 4-methyl-5-sulfosalicylic acid (4,5-MSSA) (Vyas, Sakore & Biswas, 1978) showed some unexpected features in the water–proton system, both regarding the nature and the geometry of the complex. They described the molecular structure as $H_7O_3^+$.-$H_3O^+.CH_3C_6H_2COO^-.(OH)SO_3^-$. One of the internal hydrogen bonds in the $H_7O_3^+$ ion was 2·40 (3) Å which is 0·1 Å shorter than expected. This could have been caused by an unresolved disorder in the $H_7O_3^+$ ion. The oxygen–oxygen distances from the H_3O^+ ion are 2·55, 2·81 and 3·00 (σ ~0·03) Å. The expected mean value is 2·57 Å. The structure has been redetermined to clarify these points.

Experimental. Crystals obtained by treating 4-methylsalicylic acid with conc. sulfuric acid, followed by recrystallization from aqueous solution; crystal 0·4 × 0·3 × 0·1 mm, in glass capillary. CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Cell parameters (significantly different from values of Vyas *et al.*) from 20 reflexions ($16 < \theta < 19°$). 2900 reflexions collected for $\sin\theta/\lambda \leq 0·62$ Å^{-1}, $0 \leq h \leq 9$, $-31 \leq k \leq 0$, $-9 \leq l \leq 9$, 40 excluded due to overlap. Profiles corrected for background (Lehmann & Larsen, 1974). Variations in five test reflexions were not significant, $\sigma^2(I_o) = [\sigma_c^2 +$

* Hydrogen Bond Studies. 150.

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Table 1. *Fractional atomic coordinates* ($\times 10^5$) *and equivalent isotropic temperature factors* ($Å^2$)

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S	16100 (8)	34237 (2)	53986 (8)	4·09
O(1)	37998 (20)	58442 (5)	58135 (18)	4·31
O(2)	50742 (23)	52350 (6)	80030 (21)	4·70
O(3)	10556 (24)	55853 (6)	26059 (20)	4·79
O(4)	−2731 (22)	33120 (5)	54514 (20)	5·16
O(5)	18753 (22)	30616 (5)	41637 (22)	5·65
O(6)	33724 (22)	34278 (5)	72104 (20)	5·22
O(*W*1*A*)	−4324 (117)	28550 (25)	83450 (127)	5·56
O(*W*1*B*)	−11537 (1240)	26560 (360)	74128 (1709)	6·02
O(*W*2)	27150 (40)	40062 (8)	99977 (27)	6·37
O(*W*3*A*)	46690 (91)	31473 (14)	28204 (134)	6·11
O(*W*3*B*)	53491 (281)	30791 (43)	41167 (474)	6·54
O(*W*4*A*)	64104 (53)	27348 (12)	85999 (114)	5·27
O(*W*4*B*)	40169 (259)	73411 (57)	25987 (458)	6·23
C(1)	25953 (27)	49698 (7)	50871 (26)	2·98
C(2)	12105 (29)	50940 (7)	32852 (25)	3·46
C(3)	−612 (33)	47051 (8)	21272 (29)	3·82
C(4)	−12 (29)	41919 (7)	26926 (26)	3·55
C(5)	14246 (28)	40681 (7)	45115 (26)	3·26
C(6)	26842 (29)	44504 (7)	56716 (26)	3·23
C(7)	38796 (29)	53852 (7)	63320 (27)	3·32
G(8)	−14370 (48)	37947 (12)	13574 (39)	5·19

($1{\cdot}05 \times 10^{-2} \times I)^2$] (McCandlish, Stout & Andrews, 1975). Absorption correction, transmission factor 0·94–0·97, Lp factors applied. f, f' and f'' from *International Tables for X-ray Crystallography* (1974). All programs described by Lundgren (1982). Refinement based on F^2, $w = \sigma(F^2)^{-2}$, starting values from Vyas *et al.* Disorder in the diaquaoxonium ion detected and included in the model. All H atoms from $\Delta\rho$ maps. In the last cycle of refinement one scale factor, one isotropic-extinction factor, 111 positional parameters, 16 isotropic temperature parameters and two occupancy factors were refined. 2860 reflexions included gave $R = 0{\cdot}073$, $wR(F^2) = 0{\cdot}074$, $S = 1{\cdot}79$, $\Delta/\sigma < 0{\cdot}1$ for ordered non-hydrogen atoms, $\Delta/\sigma < 1$ for others, $|\Delta\rho| < 0{\cdot}15$ e $Å^{-3}$ [$F^2 \geq 3\sigma(F^2)$]. The final positional parameters are given in Table 1.*

Discussion. The molecular structure is best described in terms of the diaquaoxonium salt $H_7O_3^+.CH_3C_6H_2$-$COOH(OH)SO_3^-.H_2O$. The internal geometry of the 4-methyl-5-sulfosalicylic acid anion is shown in Fig. 1. Bond distances and angles agree with earlier results within 3σ (Vyas *et al.*, 1978). The similarity in the three S—O bond distances shows that the sulfo group is deprotonated as stated by Vyas *et al.* The difference between the C(7)—O(1) and C(7)—O(2) bonds indicates that the proton of the carboxylic group is bonded to O(2) in contradiction to earlier results, and the refined O—H distance is 0·89 (3) Å. As usual the apparent bond distances involving H atoms quoted here are 0·1–0·2 Å shorter than the true internuclear distances. All H atoms in the acid anion refined to 'reasonable' positions and temperature factors. The acid anions are hydrogen bonded to three water molecules O(*W*2) and to the $H_7O_3^+$ complex. O(*W*2) accepts one hydrogen bond from O(2) in one molecule and donates two to O(3) and O(6) in two other molecules (Fig. 1). The distance to the carboxylic group [2·565 (3) Å] agrees well with earlier results (Takusagawa, Hirotsu & Shimada, 1971; Mo & Adman, 1975). The bond angle around O(*W*2) formed with O(2),O(3) is 108·9 (1), with O(2),O(6), 126·8 (1) and with O(3),O(6) 93·1 (1)°. The H—O—H angle of the O(*W*2) molecule is 110 (3)° and the H—O distances are 0·85 (4) and 0·74 (3) Å, respectively.

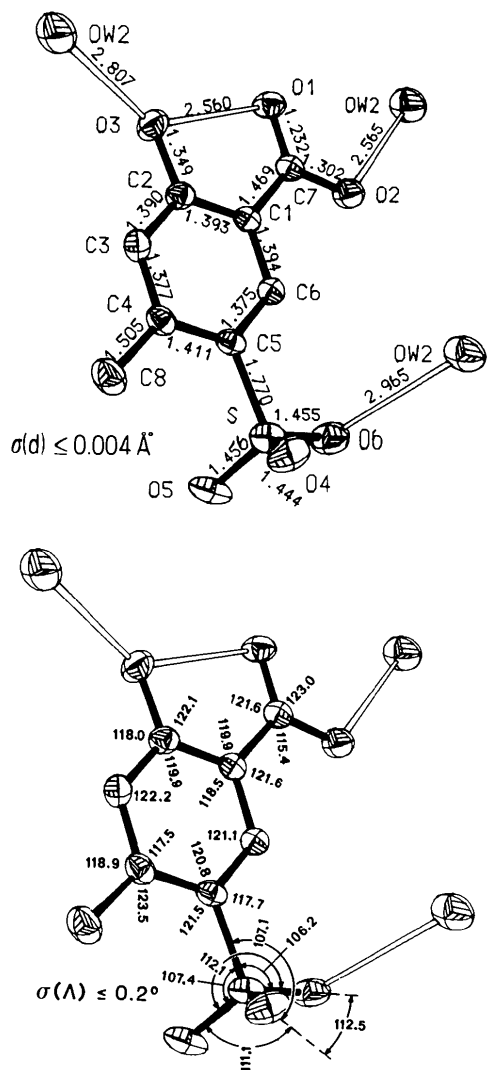
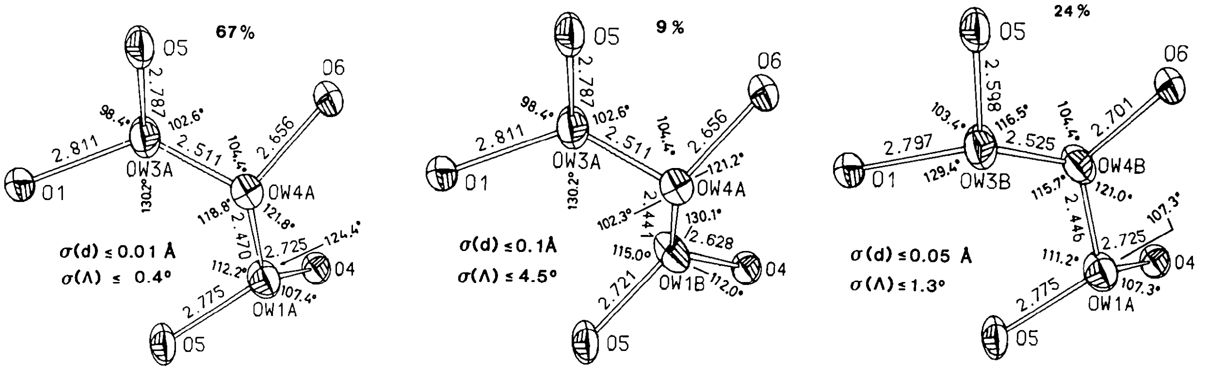


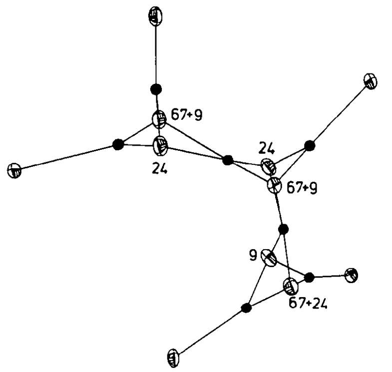
Fig. 1. The geometry of the anion. Covalent bonds are filled, hydrogen bonds are open. Thermal ellipsoids are scaled to include 30% probability.

* Lists of structure factors, anisotropic thermal parameters, details of crystal geometry and orientation and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39818 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(a) (b) (c)

Fig. 2. (a), (b), (c) The geometry of the three probable conformations of the water proton complexes. Thermal ellipsoids are scaled to include 50% probability.



(d)

Fig. 2 (cont.) (d) A superposition of the probable $H_7O_3^+$ conformations. The occupancy (%) is indicated at each water oxygen position.

The $H_7O_3^+$ complex formed by the water molecules O(*W*1), O(*W*3) and O(*W*4) and the proton is disordered. Each O atom in an $H_7O_3^+$ complex is bonded to three H atoms. The configuration around an O atom is pyramidal. The distance from the O atom to the plane of the three corresponding H atoms is usually less than 0·5 Å. A displacement of the O atom less than 1 Å through the H-atom plane will turn the coordination pyramid inside out. This type of disorder of the O atoms was detected during the refinement. Two positions were refined for each of O(*W*1), O(*W*3) and O(*W*4). O(*W*1*A*) has an occupancy of 91 (3)%. O(*W*3*A*) and O(*W*4*A*) have occupancies of 76 (2)%. The distances between the water oxygens are given in Table 2. Only three of the eight possible conformations of the complex are reasonable since all other conformations give O—O distances less than 2·40 Å. On this reasoning O(*W*3*A*) and O(*W*4*A*) must have the same occupancy. The probable conformations are O(*W*1*A*)—O(*W*4*A*)—O(*W*3*A*), O(*W*1*B*)—O(*W*4*A*)—O(*W*3*A*) and

Table 2. *Oxygen–oxygen distances* (Å) *in the eight possible* $H_7O_3^+$ *complexes*

O(*W*1*A*)—O(*W*1*B*)	0·86 (11)	O(*W*3*A*)—O(*W*3*B*)	0·96 (4)
O(*W*4*A*)	2·47 (1)	O(*W*4*A*)	2·51 (1)
O(*W*4*B*)	2·45 (2)	O(*W*4*B*)	2·36 (2)
O(*W*1*B*)—O(*W*4*A*)	2·44 (10)	O(*W*3*B*)—O(*W*4*A*)	2·32 (2)
O(*W*4*B*)	2·12 (9)	O(*W*4*B*)	2·53 (3)
O(*W*4*A*)—O(*W*4*B*)	0·91 (5)	O(*W*4*B*)	2·75 (5)

Table 3. *Geometries of the three probable* $H_7O_3^+$ *conformations*

$H_3O^+\cdots H_2O$ is the average internal H-bond distance, $X\cdots H_3O^+\cdots X$ is the average of all three angles around H_3O^+. $H_2O\cdots O$ is the average outer H-bond distance of the water molecules.

Complex	*a*	*b*	*c*	Average of six other compounds (extracted from Taesler, 1981)
O—H[H_3O^+] (Å)	1·09	1·09	1·14	
$H_3O^+\cdots H_2O$ (Å)	2·49	2·48	2·49	2·50
H—O—H[H_3O^+] (°)	107	107	101	
$H_2O\cdots H_3O^+\cdots H_2O$ (°)	118·8	102·3	115·7	111·0
$H_3O^+\cdots O$ (Å)	2·66	2·66	2·70	2·67
$X\cdots H_3O^+\cdots X$ (°)	115·0	109·3	113·7	112·7
O—H [H_2O] (Å)	0·90	0·94	1·00	
H—O—H [H_2O] (°)	103	97	90	
$H_2O\cdots O$ (Å)	2·77	2·74	2·72	2·79

O(*W*1*A*)—O(*W*4*B*)—O(*W*3*B*) (Fig. 2*a*–*c*). The parameters for O(*W*1*B*) have large standard deviations due to its barely significant occupancy. The geometries of the three conformations are summarized in Table 3. No corresponding disorder is resolved for the H-atom positions. This is not surprising since the displacement is expected to be much smaller for the H atoms than for the O atoms. A similar situation is described by Lundgren (1979).

All three conformations are of the $H_3O^+(H_2O)_2$ type and not of the $H_5O_2^+(H_2O)$ type since the two internal hydrogen bonds do not differ significantly in any of the conformations. The geometries agree well with the mean values given by Taesler (1981). It is not evident from the internal geometry why conformation (*a*) is the most favorable. However, both (*b*) and (*c*) give rise to non-bonded O–O distances which are less than 3·0 Å. These contacts which are close to van der Waals contacts, can give an energy difference favoring conformation (*a*).

When the water to proton ratio in a crystal is three or more the hydrated proton complex can appear either isolated or as part of an infinite water structure (Taesler, 1981). A high water to proton ratio together with a high overall water content favors the non-isolated situation. The present compound is the only one so far reported with four water molecules per proton which contains an isolated water-proton complex. The occurrence of the isolated $H_7O_3^+$ complex is probably due to the large anion with favorable hydrogen-bond-accepting properties.

I wish to thank Dr I. Taesler who inspired me to do this work, Mr H. Karlsson who grew the crystals, Professor I. Olovsson who placed all the necessary facilities at my disposal, and Dr J.-O. Lundgren who has contributed with many valuable suggestions and ideas during this work.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.
LUNDGREN, J.-O. (1974). *Acta Univ. Ups.* No. 271.
LUNDGREN, J.-O. (1979). *Acta Cryst.* B**35**, 780–783.
LUNDGREN, J.-O. (1982). *Crystallographic Computer Programs.* Report UUIC-B13-4-04. Institute of Chemistry, Univ. of Uppsala, Sweden.
LUNDGREN, J.-O. & OLOVSSON, I. (1976). *The Hydrogen Bond, Recent Developments in Theory and Experiments,* edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 471–526. Amsterdam: North Holland.
MCCANDLISH, L. E., STOUT, G. H. & ANDREWS, L. C. (1975). *Acta Cryst.* A**31**, 245–249.
MO, F. & ADMAN, E. (1975). *Acta Cryst.* B**31**, 192–198.
TAESLER, I. (1981). *Hydrated Proton Complexes in the Solid State. Acta Univ. Ups.* No. 591.
TAKUSAGAWA, F., HIROTSU, K. & SHIMADA, A. (1971). *Bull. Chem. Soc. Jpn,* **44**, 1274–1278.
VYAS, N. K., SAKORE, T. D. & BISWAS, A. B. (1978). *Acta Cryst.* B**34**, 3486–3488.

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Structures of Five α-Cyclohexylacetophenones, $XC_6H_4COCH_2C_6H_{11}$*

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Abstract. $T = 295$ K, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å. (1) $X = CH_3$, $C_{15}H_{20}O$, $M_r = 216{\cdot}32$, monoclinic, $P2_1/c$, $a = 8{\cdot}065$ (2), $b = 11{\cdot}977$ (1), $c = 13{\cdot}281$ (3) Å, $\beta = 92{\cdot}84$ (1)°, $V = 1281{\cdot}3$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}121$ g cm^{-3}, $\mu = 0{\cdot}68$ cm^{-1}, $F(000) = 472$, final $R = 0{\cdot}085$ for 810 observed reflections. (2) $X = Cl$, $C_{14}H_{17}ClO$, $M_r = 236{\cdot}73$, monoclinic, $P2_1/a$, $a = 7{\cdot}944$ (1), $b = 10{\cdot}789$ (1), $c = 14{\cdot}898$ (2) Å, $\beta = 95{\cdot}81$ (1)°, $V = 1270{\cdot}3$ (3) Å^3, $Z = 4$, $D_x = 1{\cdot}238$ g cm^{-3}, $\mu = 2{\cdot}79$ cm^{-1}, $F(000) = 504$, final $R = 0{\cdot}053$ for 1749 observed reflections. (3) $X = CH_3O$, $C_{15}H_{20}O_2$, $M_r = 232{\cdot}31$, triclinic, $P\bar{1}$, $a = 6{\cdot}377$ (2), $b = 10{\cdot}613$ (4), $c = 10{\cdot}735$ (5) Å, $\alpha = 111{\cdot}13$ (2), $\beta = 100{\cdot}62$ (2), $\gamma = 97{\cdot}02$ (2)°, $V = 651{\cdot}8$ (5) Å^3, $Z = 2$, $D_x = 1{\cdot}184$ g cm^{-3}, $\mu = 0{\cdot}73$ cm^{-1}, $F(000) = 252$, final $R = 0{\cdot}070$ for 959 observed reflections. (4) $X = CO_2H$, $C_{15}H_{18}O_3$, $M_r = 246{\cdot}31$, monoclinic, $P2_1/n$, $a = 13{\cdot}450$ (5), $b = 5{\cdot}470$ (1), $c = 17{\cdot}800$ (5) Å, $\beta = 93{\cdot}42$ (1)°, $V = 1307{\cdot}3$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}251$ g cm^{-3}, $\mu = 0{\cdot}80$ cm^{-1}, $F(000) = 528$, final $R = 0{\cdot}053$ for 1351 observed reflections. (5) $X = CN$, $C_{15}H_{17}NO$, $M_r = 227{\cdot}31$, triclinic, $P\bar{1}$, $a = 7{\cdot}161$ (4), $b = 7{\cdot}945$ (3), $c = 11{\cdot}927$ (5) Å, $\alpha = 89{\cdot}21$ (3), $\beta = 79{\cdot}34$ (3), $\gamma = 80{\cdot}77$ (3)°, $V = 658{\cdot}1$ (5) Å^3, $Z = 2$, $D_x = 1{\cdot}147$ g cm^{-3}, $\mu = 0{\cdot}73$ cm^{-1}, $F(000) = 244$, final $R = 0{\cdot}059$ for 1131 observed reflections. All five compounds crystallize in a common conformation in which the carbonyl-containing side chain is equatorial with respect to the chair-shaped cyclohexane ring. An equatorial γ-H atom is suitably oriented for abstraction

* (1) 2-Cyclohexyl-1-(*p*-tolyl)ethanone. (2) 1-(4-Chlorophenyl)-2-cyclohexylethanone. (3) 2-Cyclohexyl-1-(4-methoxyphenyl)-ethanone. (4) 1-(4-Carboxyphenyl)-2-cyclohexylethanone (alternative name 4-cyclohexylmethylcarbonylbenzoic acid). (5) 1-(4-Cyanophenyl)-2-cyclohexylethanone (alternative name 4-cyclohexylmethylcarbonylbenzonitrile).

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