Acta Cryst. (1990). C**46**, 1478–1481

Structure of 5-Sulfosalicylic Acid Pentahydrate*

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(*Received* 11 *August* 1989; *accepted* 27 *November* 1989)

Abstract. 5-Sulfosalicylic acid pentahydrate, $C_7H_6O_6S.5H_2O$, $M_r = 308{\cdot}26$, monoclinic, Im, $a = 6{\cdot}856\,(1)$, $b = 28{\cdot}294\,(5)$, $c = 7{\cdot}210\,(1)$ Å, $\beta = 99{\cdot}78\,(2)^\circ$, $V = 1378{\cdot}3\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}49$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}29$ mm^{-1}, $F(000) = 648$, $T = 160$ K, $R = 0{\cdot}026$ for 2012 unique observed reflections. The crystal structure of this hydrate, melting incongruently at 285 K, corresponds to the oxonium-salt formula $(H_9O_4)_{2/2}$-$[C_6H_3(COOH)(OH)SO_3].H_2O$. The two independent $H_9O_4^+$ ions on the mirror planes of the space group are manifested by the strong internal hydrogen bonds and, conforming to their positive charge, by acting as proton donors only, not acceptors, of longer hydrogen bonds to acid anions and neutral H_2O molecules.

Introduction. Over the years, three hydrates of 5-sulfosalicylic acid (SSA) have been subjected to crystal structure analysis because of an interest in their cationic water structures: an orthorhombic trihydrate with $H_7O_3^+$ ions (Mootz & Fayos, 1970; Williams, Peterson & Levy, 1972) and both a triclinic O-deuterated dihydrate and a trihydrate (Attig & Mootz, 1977; Attig & Williams, 1977) with $D_5O_2^+$ and $D_7O_3^+$ ions, respectively. A systematic study of the formation and stability ranges of these and other hydrate phases in their non-deuterated form in the system SSA–H_2O, using difference thermal analysis and temperature-dependent X-ray powder diffraction, led to the selective preparation of single crystals of a pentahydrate, SSA.5H_2O. The structure determination of this new hydrate and its results are reported in the following.

Experimental. A single crystal was grown at 257 K from a solution with 90 mol% H_2O, sealed in a thin-walled capillary of 0·3 mm inner diameter. A miniature zone-melting technique using focused heat radiation (Brodalla, Mootz, Boese & Osswald, 1985) was applied on a Syntex $P2_1$ diffractometer, equipped with a modified LT-1 low-temperature device. For the X-ray measurements, the crystal was cooled to 160 K. Lattice parameters from setting angles of 15 reflections with $40 < 2\theta < 48^\circ$. Intensities by ω scan, maximum $(\sin\theta)/\lambda$ 0·704 Å^{-1}; $h = 0$–9, $k = 0$–± 39, $l = 0$–± 10; three standard reflections ($29\bar{5}$, $2,18,2$, $2,18,\bar{2}$) after every 50 reflections with no significant variations; 4315 reflections measured, 2050 unique reflections, 38 unobserved reflections, Friedel pairs averaged.

Patterson function, heavy-atom method, full-matrix least-squares refinement based on F magnitudes, H atoms from difference map of electron density. In final refinement variation of one scale factor and 242 positional and thermal parameters. The occupancy factors of those O atoms which were treated as twofold disordered were fixed at 80 and 20% in their respective split-atom sites, based on initial refinement. The H atoms at the 20% sites were not located, those at the 80% sites could be located but were not refined. $R = 0{\cdot}026$, $wR = 0{\cdot}034$, $w = 1/(\sigma^2_F + 0{\cdot}0004|F_o|^2)$, $S = 1{\cdot}534$, $(\Delta/\sigma)_{\max} = 0{\cdot}00$ in last cycle, $(\Delta\rho)_{\min,\max} = (-0{\cdot}3, +0{\cdot}4)$ e Å^{-3}. Atomic

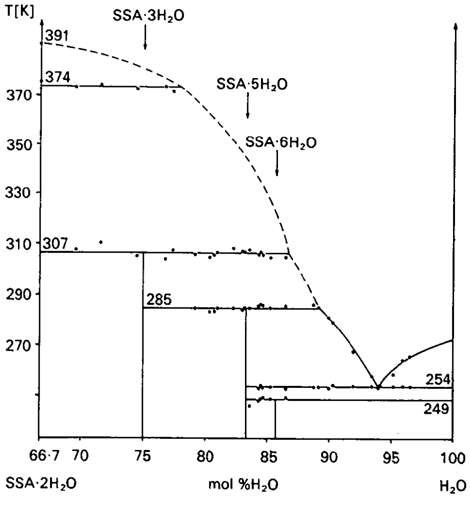

Fig. 1. The melting diagram of the system 5-sulfosalicylic acid (SAA)–water between 66·7 (composition of the dihydrate) and 100 mol% H_2O. The DTA measuring points are given; the dashed part of the liquidus is derived from visual observation.

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* Crystal structures of Acid Hydrates and Oxonium Salts. 32. Part 31: Poll, Lohmeyer & Mootz (1989).

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Table 1. *Fractional atomic coordinates and (equivalent) isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}/B_{iso}*
S	0·2000	0·11385 (1)	0·2000	1·49 (1)
O(2)	0·2064 (3)	0·28966 (5)	0·6381 (2)	2·42 (3)
O(51)	0·3702 (2)	0·08523 (4)	0·2840 (2)	2·05 (3)
O(52)	0·0144 (2)	0·09070 (4)	0·2211 (2)	2·41 (3)
O(53)	0·2059 (2)	0·12667 (5)	0·0048 (2)	2·29 (3)
O(71)	0·2116 (2)	0·29475 (4)	0·0606 (2)	1·99 (3)
O(72)	0·2120 (2)	0·33588 (4)	0·3267 (2)	2·27 (3)
O(*W*1)	0·1240 (3)	0·0	−0·2745 (3)	2·40 (4)
O(*W*2)	−0·0809 (3)	0·07292 (5)	−0·2507 (2)	2·6 1 (3)
O(*W*3)	0·3249 (5)	0·0	−0·5322 (4)	4·28 (8)
O(*W*4)	−0·2648 (2)	0·11878 (4)	−0·5727 (2)	1·92 (3)
O(*W*5)	0·4729 (3)	0·07861 (5)	−0·1786 (2)	2·66 (3)
O(*W*61)†	0·5442 (5)	0·0	−0·0012 (6)	4·21 (9)
O(*W*62)‡	0·640 (1)	0·0	−0·143 (2)	2·9 (3)
O(*W*71)†	0·8586 (4)	0·0	0·2232 (8)	4·25 (10)
O(*W*72)‡	0·923 (2)	0·0	0·100 (2)	3·0 (3)
C(1)	0·2107 (2)	0·25202 (5)	0·3386 (2)	1·39 (3)
C(2)	0·2092 (3)	0·25052 (5)	0·5337 (2)	1·59 (3)
C(3)	0·2107 (3)	0·20652 (6)	0·6244 (2)	1·85 (3)
C(4)	0·2107 (3)	0·16536 (5)	0·5240 (2)	1·69 (3)
C(5)	0·2099 (2)	0·16697 (5)	0·3286 (2)	1·41 (3)
C(6)	0·2108 (2)	0·20981 (5)	0·2374 (2)	1·37 (3)
C(7)	0·2113 (2)	0·29793 (5)	0·2423 (2)	1·55 (3)
H(2)	0·197 (7)	0·3089 (16)	0·562 (7)	5·7 (9)
H(3)	0·214 (5)	0·2058 (11)	0·761 (5)	3·2 (6)
H(4)	0·199 (5)	0·1375 (12)	0·589 (5)	3·4 (6)
H(6)	0·209 (4)	0·2130 (9)	0·110 (4)	2·3 (5)
H(7)	0·209 (5)	0·3218 (12)	0·015 (5)	3·3 (6)
H(11)	0·218 (9)	0·0	−0·370 (9)	5·4 (13)
H(12)	0·041 (7)	0·0263 (15)	−0·268 (7)	6·0 (10)
H(21)	−0·136 (5)	0·0865 (11)	−0·330 (5)	3·1 (6)
H(22)	−0·007 (6)	0·0937 (13)	−0·183 (5)	3·9 (7)
H(31)	0·342 (5)	0·0218 (13)	−0·602 (6)	5·1 (8)
H(41)	−0·379 (4)	0·1083 (9)	−0·623 (4)	2·1 (5)
H(42)	−0·194 (6)	0·1121 (11)	−0·638 (6)	4·0 (8)
H(51)	0·391 (5)	0·0949 (12)	−0·108 (5)	3·4 (6)
H(52)	0·567 (6)	0·0949 (13)	−0·187 (5)	3·8 (7)
H(61)†	0·676	0·0	0·051	5·0
H(62)†	0·523	0·0223	−0·077	5·0
H(71)	0·943	0·0223	0·216	5·0

* For the non-H atoms calculated with $B = \frac{1}{3}(B_{11}a^{*2}a^2 + \cdots + B_{23}b^*c^* \times bc\cos\alpha)$.

† Occupancy factor 0·8, owing to disorder.

‡ Occupancy factor 0·2, owing to disorder.

scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations with the program system *XTL* (Syntex) on an Eclipse *S*/200 minicomputer (Data General) and *ORTEP*II (Johnson, 1976) on a TR 445 computer (Telefunken).

Discussion. The melting diagram obtained (Fig. 1) shows the existence of four stable hydrates SSA.nH$_2$O with $n = 2$, 3, 5 and 6. The dihydrate, found to melt incongruently at 374 K yielding the anhydrous acid and liquid phase, is isotypic to the O-deuterated dihydrate of known crystal structure. The trihydrate, melting incongruently at 307 K, is the orthorhombic phase, of which the structure is also known. A second trihydrate was found as a metastable phase isotypic to the O-deuterated triclinic trihydrate of known structure.

Table 2. *Interatomic distances* (Å) *and angles* (°) *not given in Fig.* 2.

O(*W*62)···O(*W*5)	2·496 (5)	O(*W*62)···O(*W*72)	2·38 (2)	O(*W*72)···O(52^d)	2·750 (5)

H(41)—O(*W*4)—H(42)	107 (3)	C(1)—C(7)—O(72)	122·4 (2)
H(41)—O(*W*4)···H(21)	116 (2)	O(71)—C(7)—O(72)	123·4 (2)
H(41)—O(*W*4)···H(7^b)	109 (2)	C(7)—O(72)···H(52^j)	142 (1)
H(42)—O(*W*4)···H(21)	101 (3)	C(7)—O(72)···H(2)	95 (1)
H(42)—O(*W*4)···H(7^b)	124 (3)	C(2)—C(1)—C(7)	119·9 (1)
H(21)···O(*W*4)···H(7^b)	100 (1)	C(6)—C(1)—C(7)	120·4 (1)
H(31^g)···O(51)···H(41^h)	109 (1)	C(6)—C(1)—C(2)	119·7 (1)
H(42^g)···O(52)···H(71^i)	96	C(1)—C(2)—C(3)	119·4 (2)
H(22)···O(53)···H(51)	87 (2)	C(2)—C(3)—C(4)	120·5 (2)
H(2)···O(72)···H(52^j)	108 (2)	C(3)—C(4)—C(5)	120·0 (2)
O(71)—H(7)···O(*W*4^k)	173 (3)	C(4)—C(5)—C(6)	120·4 (1)
O(*W*4)—H(41)···O(51^c)	176 (3)	C(5)—C(6)—C(1)	120·1 (1)
O(*W*4)—H(42)···O(52^a)	172 (4)	C(6)—C(5)—S	120·1 (1)
O(2)—H(2)···O(72)	158 (5)	C(4)—C(5)—S	119·5 (1)
O(*W*5)···O(*W*62)···O(*W*5^f)	126·1 (4)	O(51)—S—C(5)	107·3 (1)
O(*W*5)···O(*W*62)···O(*W*72)	112·3 (5)	O(52)—S—C(5)	106·5 (1)
C(2)—C(3)—H(3)	119 (2)	O(53)—S—C(5)	106·9 (1)
C(4)—C(3)—H(3)	121 (2)	S—O(51)···H(31^g)	123 (1)
C(3)—C(4)—H(4)	117 (2)	S—O(51)···H(41^k)	125 (1)
C(5)—C(4)—H(4)	123 (2)	S—O(52)···H(42^g)	129 (1)
C(5)—C(6)—H(6)	124 (2)	S—O(52)···H(71^i)	130
C(1)—C(6)—H(6)	116 (2)	S—O(53)···H(22)	113 (1)
C(2)—O(2)—H(2)	101 (4)	S—O(53)···H(51)	116(1)
C(7)—O(71)—H(7)	109 (2)	O(51)—S—O(52)	110·8 (1)
C(1)—C(2)—O(2)	122·6 (2)	O(51)—S—O(53)	112·7 (1)
C(3)—C(2)—O(2)	118·0 (2)	O(52)—S—O(53)	112·2 (1)
C(1)—C(7)—O(71)	114·2 (1)		

Symmetry codes (also for Fig. 2): (*a*) $x, y, -1 + z$; (*b*) $-0·5 + x, 0·5 - y, -0·5 + z$; (*c*) $-1 + x, y, -1 + z$; (*d*) $1 + x, y, z$; (*e*) $0·5 + x, 0·5 - y, -0·5 + z$; (*f*) $x, -y, z$; (*g*) $x, y, 1 + z$; (*h*) $1 + x, y, 1 + z$; (*i*) $-1 + x, y, z$; (*j*) $-0·5 + x, 0·5 - y, 0·5 + z$; (*k*) $0·5 + x, 0·5 - y, 0·5 + z$.

The new pentahydrate of the present structure determination melts incongruently at 285 K. Its crystal growth as described was a process in equilibrium, whereas at the temperature of measurement chosen, the sample on the whole was in a frozen-in metastable state. A second, presumably metastable form of the pentahydrate could be observed in X-ray powder photographs.

Finally, the new hexahydrate was found to decompose at 249 K, forming the pentahydrate and ice. A check of its exact composition is needed, but it could not be obtained in the form of single crystals suitable for structure analysis.

The atomic parameters of the crystal structure of the pentahydrate of 5-sulfosalicylic acid are listed in Table 1, interatomic distances and angles in Table 2.* Complementary dimensions are given in Fig. 2, which shows the constituent building units according to the relevant oxonium-salt formula $(H_9O_4)_{2/2}$-$[C_6H_3(COOH)(OH)SO_3].H_2O$. Fig. 3 is a stereoscopic view of a larger part of the crystal structure.

The structure contains $H_9O_4^+$ ions of pyramidal shape which lie on the mirror planes of the space group. Thus they are present as two independent ions. One of them features a twofold 80:20% disorder of the central and one terminal O atom. With O···O distances between 2·465 (2·38 in the 20%-occupancy ion) and 2·571 Å, the internal hydrogen bonds of the $H_9O_4^+$ ions are in every instance more than 0·20 Å shorter than the adjacent external bonds

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52807 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

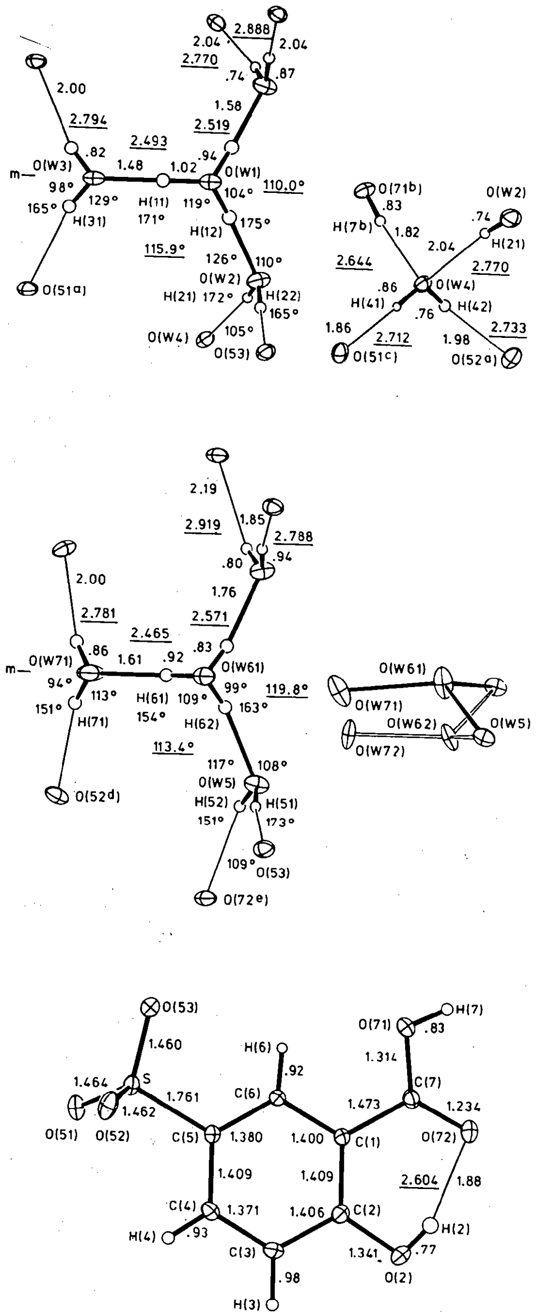

Fig. 2. The units of structure with selected interatomic distances in Å and angles, underlined for O···O and O···O···O of hydrogen bonds. The two $H_9O_4^+$ ions and the neutral H_2O molecule are shown with their complete hydrogen-bonding environment (for the symmetry code see Table 2), the anion only as an isolated unit. The strong hydrogen bonds within the cations are drawn with bond lines like the covalent bonds. E.s.d.'s 0·002–0·006 Å for O···O and 0·1–0·2° for O···O···O, 0·001–0·002 Å for distances between non-H atoms in the anion, otherwise 0·03–0·06 Å and 3–5°. Ellipsoids at the 30% probability level, H-atom isotropic B values reduced to 20%. Of the disordered cation an additional side view shows also the 20%-occupancy positions O(W62) and O(W72), with separations from the related 80% ones of 1·30 (1) and 1·06 (1) Å, respectively.

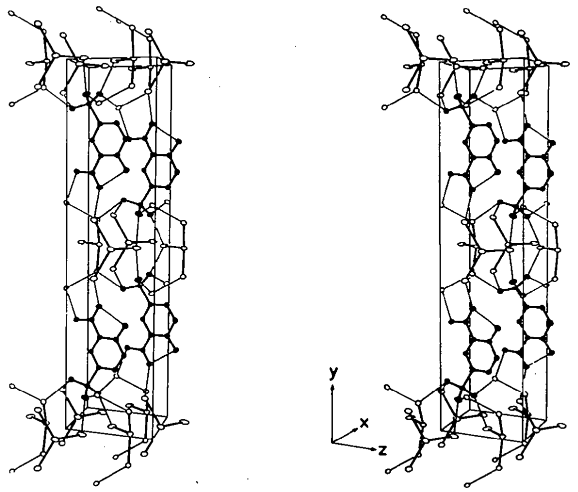

Fig. 3. Stereoscopic drawing of the crystal structure. Atoms of $H_9O_4^+$ ions and H_2O molecules in white, of anions in black. O atoms with 20% occupancy and H atoms not shown.

of this kind, which in addition are only donated to – nowhere accepted from – sulfonate, carboxylate and neutral water O atoms. So by geometry *and* function the $H_9O_4^+$ ions are very well defined entities in this crystal structure. A similarly well defined case is given by the $H_9O_4^+$ ion in the structure of HCl.6H_2O (Taesler & Lundgren, 1978), whereas in further hydrated-proton species reported as $H_9O_4^+$ ions (Taesler, 1981; Henke, 1982; Gustafsson, 1987; Hanson, 1987) one or more outer water molecules are four-coordinated.

The bond lengths and angles in the 5-sulfosalicylate anion (deprotonation at the sulfo group) agree well with those of the SSA hydrates studied previously (for references see the *Introduction*). The cations, anions and four-coordinated neutral water molecules are linked by hydrogen bonds into a three-dimensional network.

This work was supported by the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Fonds der Chemischen Industrie and Dr Jost Henkel-Stiftung.

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