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Crystal Structures of Acid Hydrates and Oxonium Salts. XV. The Triclinic Trihydrate and Triclinic Dihydrate of 5-Sulphosalicylic Acid, Their Water Structures and Structural Relationship*

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The structures of two triclinic hydrates of 5-sulphosalicylic acid crystallized from D_2O were determined by single-crystal X-ray diffraction. The trihydrate {exact formulation $(D_7O_3^+)[C_6H_3(COOD)(OD)SO_3^-]$, space group $P\bar{1}$, $a = 6{\cdot}360$ (2), $b = 7{\cdot}886$ (2), $c = 12{\cdot}081$ (3) Å, $\alpha = 103{\cdot}14$ (1), $\beta = 76{\cdot}90$ (1), $\gamma = 101{\cdot}66$ (1)°, $Z = 2$; 3265 independent reflexions, $R = 0{\cdot}041$} has fractional coordinates for the organic molecule nearly identical with those of the dihydrate {$(D_5O_2^+)_{2/2}[C_6H_3(COOD)(OD)SO_3^-]$, space group $P\bar{1}$, $a = 7{\cdot}006$ (3), $b = 6{\cdot}995$ (5), $c = 11{\cdot}689$ (3) Å, $\alpha = 71{\cdot}61$ (4), $\beta = 94{\cdot}09$ (2), $\gamma = 109{\cdot}16$ (2)°, $Z = 2$; 2960 independent reflexions, $R = 0{\cdot}038$}, in spite of the differing number and arrangement of water molecules, which in turn lead to different conformations of the sulpho groups. A central water molecule in the trihydrate is tightly bonded to two outer ones by strong hydrogen bonds [O–O: 2·470 (2) and 2·506 (2) Å]. The two independent water molecules in the dihydrate are hydrogen bonded (not to each other, but to symmetry-related molecules), forming two $D_5O_2^+$ ions across centres of symmetry [O–O: 2·421 (2) and 2·434 (2) Å]. In both structures, the same intramolecular [hydroxyl–carboxyl groups, O–O: 2·673 (2) and 2·645 (2) Å] and intermolecular [carboxyl–sulphonyl groups, O–O: 2·665 (2) and 2·632 (2) Å] hydrogen bonds exist, resulting in dimers around centres of symmetry. These dimers are linked together by hydrogen bonds of the water structure to form a two-dimensional network, and by an interlocking packing mode also in the third dimension.

Introduction

Crystalline hydrates of aromatic sulphonic acids have been intensively studied by X-ray and neutron diffraction because they present a variety of interesting cationic water structures. After an early report of the aggregate $H_7O_3^+$ in an orthorhombic trihydrate of 5-sulphosalicylic acid (SSA) by Mootz & Fayos (1970), two triclinic hydrates of this acid were found containing three and two water molecules per formula unit. Although the aggregate $H_7O_3^+$ is observed in the *triclinic* trihydrate of SSA too, this phase has a much closer relationship to the triclinic *dihydrate*. Therefore, in this paper the structures of the triclinic tri- and dihydrates are described and compared [the dihydrate has already been reported briefly (Attig, 1976) and was further investigated in a neutron diffraction study (Attig & Williams, 1977)].

Experimental

Crystals of the dihydrate of SSA are obtained when a hot saturated solution of SSA in H_2O or D_2O is allowed to cool. Very slow evaporation of the solvent at room temperature yields crystals of the orthorhombic trihydrate when H_2O is used and of the triclinic trihydrate with D_2O. All these crystals lose their water when exposed to air; for this reason and to prevent H/D exchange they had to be protected in sealed glass capillaries for the X-ray work.

For both hydrates, crystals grown in 99% D_2O were used. The triclinic Laue group for both SSA.3D_2O

Table 1. *Crystallographic data*

	SSA.3D_2O	SSA.2D_2O
Crystal system	Triclinic	Triclinic
Systematic extinctions	None	None
Space group	$P\bar{1}$	$P\bar{1}$
Cell constants*		
a	6·360 (2) Å	7·006 (3) Å
b	7·886 (2)	6·995 (5)
c	12·081 (3)	11·698 (3)
α	103·14 (1)°	71·61 (4)°
β	76·90 (1)	94·09 (2)
γ	101·66 (1)	109·16 (2)
Volume	567·5 Å^3	513·1 Å^3
d_o	1·635 g cm^{-3}	1·695 g cm^{-3}
Z	2 (1·99)	2 (1·99)

* Reduced cells as adopted in *Crystal Data* (Donnay & Ondik, 1972) may be obtained from these cell settings from the matrices (row by row) 0 −1 0 / 0 0 1 / −1 0 0 for the dihydrate and −1 0 0 / 0 1 −1 / 0 −1 0 for the trihydrate.

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* Part XIV: Attig & Mootz (1977).

and SSA.2D_2O was established by Weissenberg photographs. Accurate setting angles of some 20 high-order reflexions were determined on a diffractometer with Mo $K\alpha$ radiation. A least-squares refinement yielded the lattice parameters summarized with other crystallographic data in Table 1. The cell setting of SSA.3D_2O uses the three shortest non-coplanar lattice vectors in ascending magnitude, whereas the different setting of the SSA.2D_2O unit cell was chosen for optimal comparison of related atomic positions in both structures. The densities were measured by flotation.

Intensities were collected on an automatic single-crystal diffractometer (Siemens AED) with paper-tape control. Within the limit of $\theta_{max} = 30°$ for Mo $K\alpha$ radiation, 3265 independent reflexions were collected for SSA.3D_2O and 2960 for SSA.2D_2O with a θ–2θ scan. Standard reflexions were measured after every 30 reflexions; their intensities remained constant.

Structure determination and refinement

The two structures were solved from sharpened Patterson maps. Water O atoms were found in subsequent structure factor/Fourier summation calculations. Full-matrix least-squares refinement of all non-hydrogen atom parameters was done first with isotropic and then anisotropic temperature factors. Difference syntheses revealed the positions of all H atoms in SSA.3D_2O and in SSA.2D_2O, with the exception of two atoms in special positions; these were situated in very short hydrogen bonds in SSA.2D_2O across centres of symmetry. H atoms were placed at these two sites for chemical reasons only.

The H atom parameters were included in the refinement with isotropic temperature factors. Introduction of an isotropic extinction parameter and, for SSA.2D_2O, application of an absorption correction,

Table 2. *Positional parameters* ($\times 10^4$) *of non-hydrogen atoms*

	SSA.3D_2O			SSA.2D_2O		
	x	*y*	*z*	*x*	*y*	*z*
S	3044 (1)	3737 (1)	6871 (1)	2992 (1)	3765 (1)	6753 (1)
O(51)	4584 (2)	2468 (2)	6484 (1)	3237 (2)	1759 (2)	6806 (1)
O(52)	4201 (2)	5500 (1)	7210 (1)	4852 (2)	5323 (2)	6916 (1)
O(53)	1718 (2)	3659 (2)	6024 (1)	2053 (2)	4617 (2)	5634 (1)
O(2)	−2900 (2)	1256 (2)	10889 (1)	−2893 (2)	1505 (2)	10699 (1)
O(71)	3590 (2)	3629 (2)	11059 (1)	3320 (2)	3473 (2)	11261 (1)
O(72)	470 (2)	2303 (2)	11996 (1)	225 (2)	2468 (2)	12066 (1)
O(*W*1)	7962 (2)	3115 (2)	4601 (1)	5853 (2)	1196 (2)	5576 (1)
O(*W*2)	1899 (2)	1322 (2)	3810 (1)	85 (2)	1805 (2)	4433 (1)
O(*W*3)	5739 (2)	823 (2)	3338 (1)			
C(1)	682 (2)	2684 (2)	10071 (1)	606 (2)	2716 (1)	10021 (1)
C(2)	−1502 (2)	1908 (2)	10013 (1)	−1479 (2)	2051 (2)	9833 (1)
C(3)	−2293 (2)	1785 (2)	9005 (1)	−2160 (2)	1947 (2)	8696 (1)
C(4)	−942 (2)	2383 (2)	8058 (1)	−798 (2)	2507 (2)	7760 (1)
C(5)	1239 (2)	3105 (2)	8102 (1)	1276 (2)	3164 (2)	7944 (1)
C(6)	2037 (2)	3268 (2)	9105 (1)	1971 (2)	3256 (2)	9065 (1)
C(7)	1543 (2)	2849 (2)	11132 (1)	1354 (2)	2868 (2)	11205 (1)

Table 3. *Positional* ($\times 10^3$) *and thermal* ($\times 10^3$) *parameters of the hydrogen atoms*

Here, and elsewhere for this X-ray study, hydrogen atoms are symbolized as H regardless of a possible H/D distinction.

	SSA.3D_2O				SSA.2D_2O			
	x	*y*	*z*	*U* (Å^2)	*x*	*y*	*z*	*U* (Å^2)
H(1)	411 (4)	367 (3)	1166 (2)	54 (6)	374 (4)	376 (4)	1189 (2)	69 (7)
H(2)	−240 (4)	137 (4)	1145 (2)	72 (8)	−225 (4)	153 (4)	1138 (2)	67 (7)
H(3)	−376 (4)	131 (3)	901 (2)	51 (6)	−360 (3)	146 (3)	863 (2)	48 (5)
H(4)	−144 (3)	231 (3)	735 (2)	51 (6)	−115 (3)	244 (3)	697 (2)	46 (5)
H(6)	351 (3)	372 (3)	916 (2)	41 (5)	336 (3)	368 (3)	919 (2)	37 (5)
H(11)	813 (5)	410 (4)	448 (3)	82 (9)	500 (3)	143 (3)	597 (2)	58 (6)
H(12)	744 (4)	322 (4)	526 (3)	73 (8)	649 (4)	246 (4)	517 (2)	66 (7)
H(13)					500	0	500	101 (13)
H(21)	143 (5)	177 (4)	433 (3)	76 (9)	−84 (4)	266 (4)	476 (2)	76 (8)
H(22)	149 (4)	163 (3)	310 (2)	67 (7)	−38 (4)	214 (4)	360 (2)	74 (7)
H(23)					0	0	500	96 (12)
H(31)	658 (5)	172 (4)	385 (3)	82 (9)				
H(32)	421 (5)	91 (3)	350 (2)	68 (7)				
H(33)	561 (6)	−15 (6)	353 (3)	96 (14)				

led to final R values of 0·041 for SSA.3D_2O and 0·038 for SSA.2D_2O, including all reflexions. The atomic form factors used for S, O and C were the values of Cromer & Mann (1968), and for H of Stewart, Davidson & Simpson (1965). Anomalous-dispersion effects for S were accounted for. The resulting atomic parameters are summarized in Tables 2 and 3.*

Discussion

The sulphosalicylic acid ions in both unit cells of fairly different dimensions display many strikingly similar fractional atomic coordinates (Table 3). Both are deprotonated at the sulpho group, thus formally transferring H^+ into the water structures. This results in an aggregate $H_7O_3^+$ for the SSA.3D_2O, similar to that of the orthorhombic trihydrate (Mootz & Fayos, 1970), and, unexpectedly, in two $H_5O_2^+$ species residing at centres of symmetry for SSA.2D_2O, where a single, unrestricted group was expected. So a more sophisticated formulation of these hydrates (including H/D assignment) would be $(D_7O_3^+)[C_6H_3(COOD)(OD)SO_3^-]$ and $(D_5O_2^+)_{2/2}[C_6H_3(COOD)(OD)SO_3^-]$ respectively. Hydrogen bonds of the crystal structures are listed in Table 4.

The group $H_7O_3^+$

The cationic water structure of SSA.3D_2O is illustrated in Fig. 1(*a*). O(*W*3) as the central atom of the group is linked *via* short hydrogen bonds to a sulphonyl O atom and to O(*W*1) and O(*W*2). The O···O distances of the latter two hydrogen bonds at 2·506 (2) and 2·470 (2) Å are more similar to each other than the 2·516 (3) and 2·442 (3) Å in the analogous $H_7O_3^+$ cation of the orthorhombic trihydrate. O(*W*2), which should share some more positive charge with O(*W*3) than does O(*W*1), is still engaged in longer hydrogen bonds to one sulphonyl and one carbonyl O atom (mean O···O 2·868 Å) than O(*W*1), with two hydrogen bonds to sulphonyl O atoms at an average distance of 2·792 Å. In the orthorhombic modification the two terminal O(*W*) atoms of the $H_7O_3^+$ cation bond to two sulphonyl O atoms, each at average distances of 2·719 at the more positive and 2·826 Å at the less positive end of the cation.

The mean value of all five external hydrogen bonds of the cation is 2·79 Å in the triclinic form and is thus somewhat larger than the 2·75 Å in the orthorhombic form and the 2·74 Å in the trihydrate of 2,5-dibromobenzoic acid, which also contains a discrete $H_7O_3^+$ cation (Lundgren, 1972). The observed lengthening in SSA.3D_2O may at least partly be due to an H/D isotope effect.

The central O(*W*3) displays another contact less than 3·0 Å to the hydroxyl O(2), which at 2·967 (2) Å could be a weak hydrogen bond. The distance 2·41 (3) Å to the refined position of H(2) is somewhat large for such an interaction, which is also not very favourable in

Table 4. *Geometry of the hydrogen bonds of the triclinic trihydrate and dihydrate of* 5-*sulphosalicylic acid*

Numbers in parentheses are the values determined in a neutron diffraction study of the dihydrate (Attig & Williams, 1977). Standard deviations for the X-ray results are 0·002 Å for $D\cdots A$, 0·03 Å for D–H and $H\cdots A$, 2–3° for all angles; for the neutron results: 0·003 Å and 0·3°. Roman superscripts refer to the following symmetry operations: (i) $1-x, 1-y, 2-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y, -1+z$; (iv) $1-x, -y, 1-z$; (v) $-x, -y, 1-z$.

	SSA.3D_2O				SSA.2D_2O			
	$D\cdots A$	D–H	$H\cdots A$	DHA	$D\cdots A$	D–H	$H\cdots A$	DHA
O(71)–H(1)···O(52^{i})	2·665 Å	0·86 Å	1·85 Å	158°	2·632 Å (2·630	0·81 Å 0·989	1·89 Å 1·667	151° 163·6)
O(2)–H(2)···O(72)	2·673	0·79	2·03	139	2·645 (2·642	0·89 0·970	1·86 1·803	146 143·0)
O(*W*1)–H(11)···O(51)	2·814	0·79	2·14	144	2·605 (2·603	0·86 0·977	1·74 1·626	177 179·1)
O(*W*1)–H(12)···O(53^{ii})	2·772	0·81	1·97	172	2·756 (2·755	0·84 0·980	1·91 1·789	175 168·1)
O(*W*2)–H(21)···O(53)	2·875	0·68	2·26	151	2·726 (2·724	0·83 0·979	1·91 1·758	168 168·2)
O(*W*2)–H(22)···O(72^{iii})	2·861	1·04	1·82	172	2·661 (2·658	0·95 0·979	1·73 1·699	165 165·2)
O(*W*3)–H(31)···O(*W*1)	2·506	0·98	1·53	177				
O(*W*3)–H(32)···O(*W*2)	2·470	0·96	1·51	172				
O(*W*3)–H(33)···O(51^{iv})	2·616	0·83	1·81	165				
O(*W*1)–H(13)–O(*W*1^{iv})					2·434 (2·442	1·22 1·221	1·22 1·221	180 180)
O(*W*2)–H(23)–O(*W*2^{v})					2·421 (2·435	1·21 1·218	1·21 1·218	180 180)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32483 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

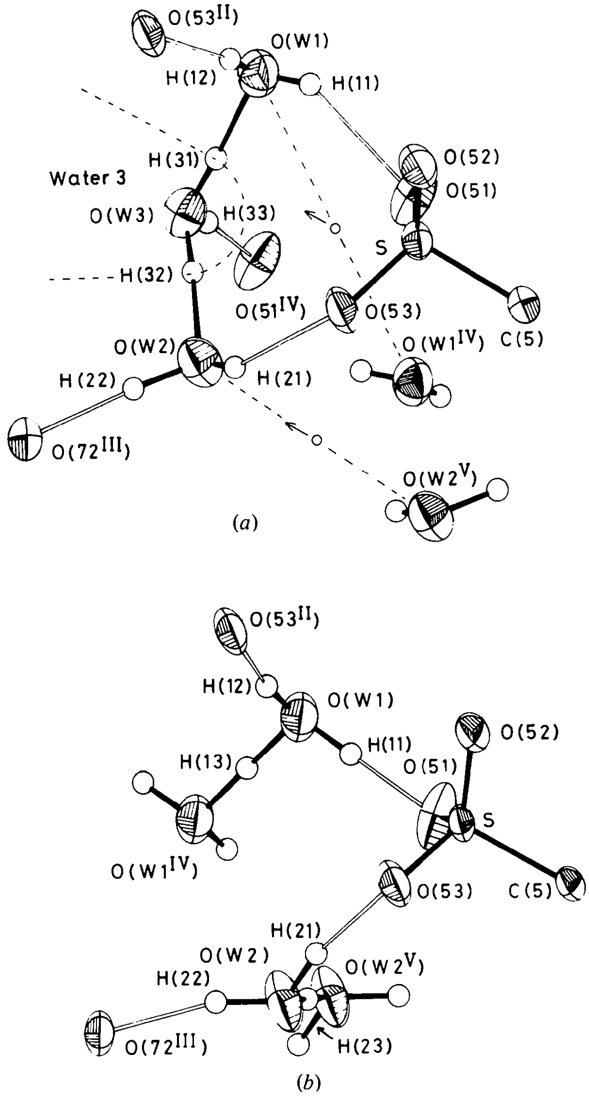


Fig. 1. The arrangement of water molecules in (*a*) the triclinic trihydrate and (*b*) the triclinic dihydrate of 5-sulphosalicylic acid, each with hydrogen-bond partners of the water molecules of the asymmetric unit. A model transition for trihydrate to dihydrate requires only the removal of water molecule 3 and $H_5O_2^+$ formation by O(W1) and O($W1^{iv}$), and O(W2) and O($W2^{v}$). Roman superscripts are explained in Table 4. Arrows indicate directions of shift of symmetry centres relative to atomic positions as a result of general unit-cell deformation. The direction of view in both cases is normal to the benzene-ring plane.

view of the positive charge accumulated at O(W3) and the involvement of H(2) in the strong intramolecular hydrogen bond to O(72).

The two $H_5O_2^+$ *cations*

The two water molecules in SSA.$2D_2O$ both reside near centres of symmetry, across which they form two hydrogen bonds of lengths 2·434 (2) and 2·421 (2) Å. The resulting $H_5O_2^+$ groups in the *trans* conformation are illustrated in Fig. 1(*b*). They are well described in the neutron diffraction work (Attig & Williams, 1977), where the location and vibrational behaviour of the H atoms are discussed. For easy comparison the neutron results pertinent to the hydrogen-bonding geometry are incorporated in Table 4.

Relationship of the water arrangements

With very similar packing of the organic anions the cationic water structures in the two triclinic hydrates at first sight appear to be quite different. But according to Table 4 and Fig. 1, the same types of hydrogen bonds are present originating from the two terminal H_2O of the $H_7O_3^+$ and the two independent H_2O of the centrosymmetric $H_5O_2^+$ ions. Therefore, a very simple model transition from the tri- to the dihydrate structure is possible. The first step is the formal removal of one H_2O from the centre of the $H_7O_3^+$ group, thus eliminating three hydrogen bonds and leaving half an excess proton at each of the two remaining H_2O. In the second and final step certain displacements and reorientations of these H_2O towards two crystallographic centres of symmetry reduce the O···O distances across these

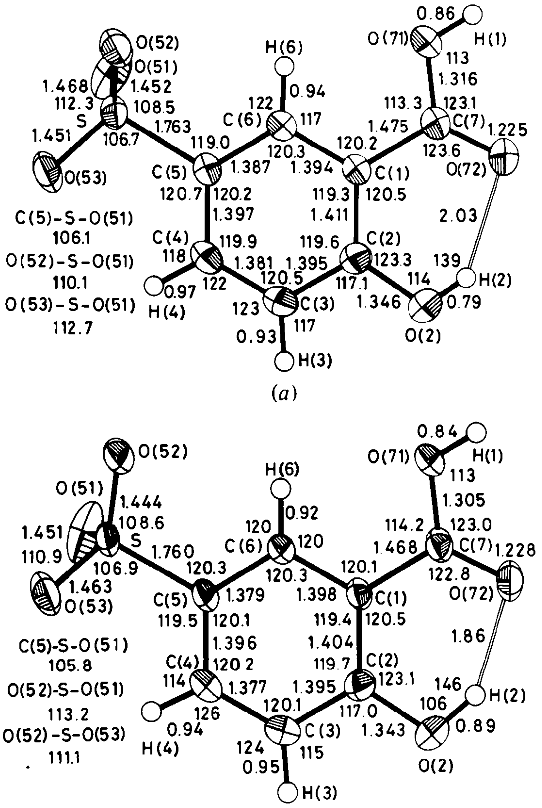
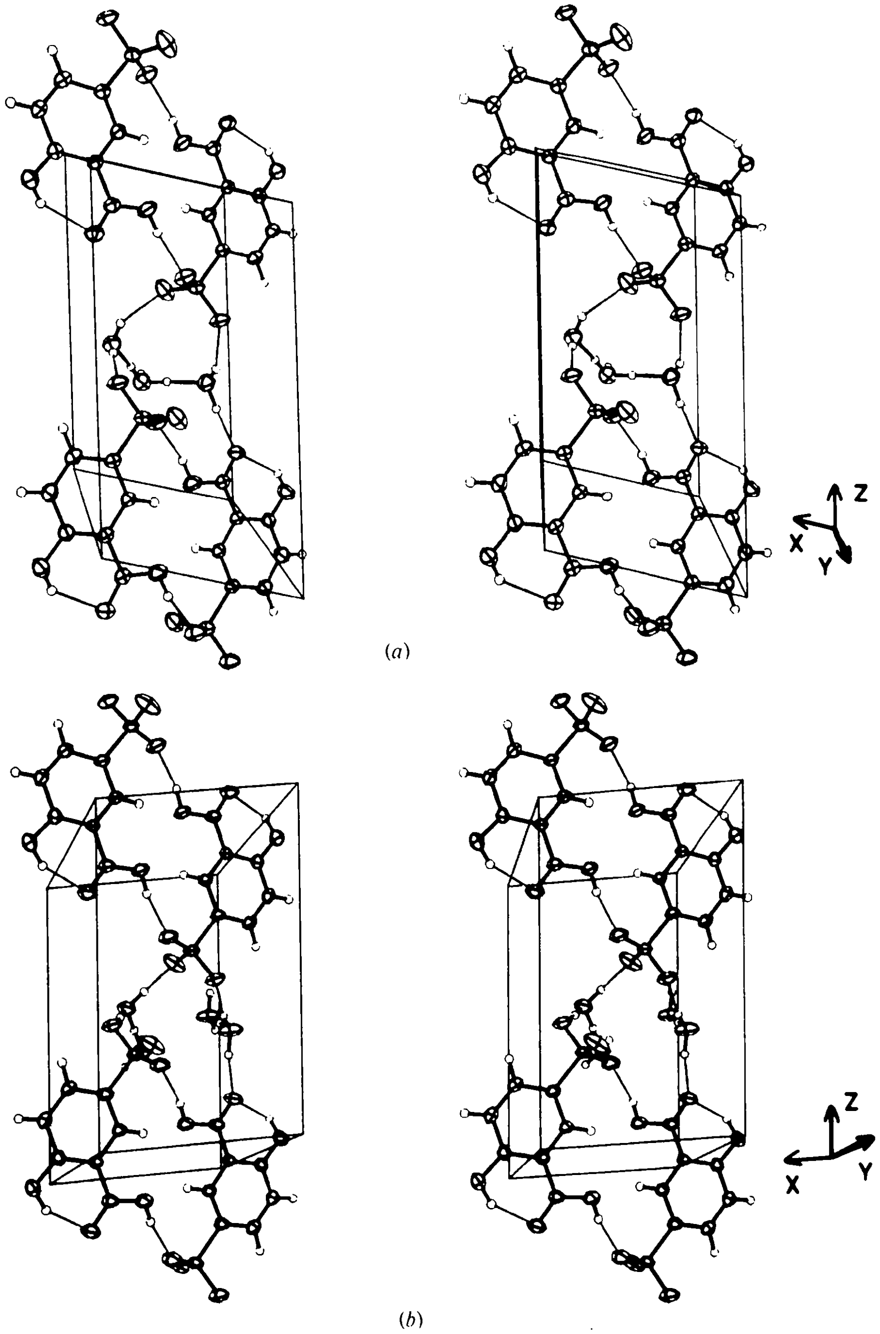


Fig. 2. The anions of 5-sulphosalicylic acid (*a*) trihydrate and (*b*) dihydrate, as seen on the benzene-ring plane. Bond lengths in Å, σ = 0·002 Å, 0·03 Å to H atoms; bond angles in degrees, σ = 0·1° and 2° when H is involved.



(a)

(b)

Fig. 3. Stereoscopic drawings of the unit cells with four anions each, forming two dimers around centres of symmetry for (a) the trihydrate, (b) the dihydrate. Only one set of cations is given for optimal comparison.

centres from 5·682 (3) Å for O(*W*1)···O(*W*1^{iv}) and 3·999 (3) Å for O(*W*2)···O(*W*2^{v}) to those of the short hydrogen bonds observed in the two $H_5O_2^+$ species of SSA . $2D_2O$.

The remaining hydrogen-bonding network of the trihydrate is maintained during this process by a general deformation of the unit cell and a moderate rotation of the sulpho group relative to the benzene ring.

The SSA anions

The anion in SSA . $3D_2O$ and SSA . $2D_2O$ is shown in Fig. 2 with bond lengths and angles. The distribution of bond lengths in the benzene ring is very similar in both these hydrates, and also in the orthorhombic trihydrate. The conformation of C(5)–S is nearly identical in the orthorhombic trihydrate and in SSA . $2D_2O$, with two sulphonyl O atoms almost equidistant from the ring plane. In $SSA.3D_2O$, on the other hand, one sulphonyl O atom lies approximately in this plane.

The equation of the best plane through the six benzene C atoms is

$$-2\cdot4983x + 7\cdot2254y + 0\cdot9385z - 2\cdot7048 = 0$$

for $SSA.3D_2O$ and

$$-2\cdot2136x + 6\cdot7656y + 0\cdot7518z - 2\cdot4532 = 0$$

for $SSA.2D_2O$, with the crystal coordinates. Except for the sulphonyl O atoms, all the atoms of the anions are very close to these planes, even H(1) and H(2). The S atom in $SSA.3D_2O$ is 0·120 Å out of plane, compared with 0·061 Å in $SSA.2D_2O$. All other displacements are less than the 0·074 Å of O(72) in $SSA.2D_2O$, indicating a slight tilt of the carboxy group in this molecule.

Packing of the anions

The packing of the anions is illustrated in the two stereo plots of Fig. 3. In each case two hydrogen-bonded dimers are shown with part of the water structure. The $H_7O_3^+$ cations link anions translated along **b** and inverted ones translated along **c** into corrugated double layers normal to **a***. Adjacent double layers are interlocked into a three-dimensional array by zigzag stacking with successive inversion of the anions with their exposed hydrophobic ends. With angles between the normals of the benzene-ring planes and the stacking direction **b** of 23·6 and 14·7° respectively, alternating distances between planes in the stacks are 3·53 and 3·69 Å for $SSA.3D_2O$ and 3·36 and 3·40 Å for $SSA.2D_2O$.

For data collection and reduction the programs *ELSA* and *RECA* (Albrand, 1972) were used; for all other calculations the XRAY system (1972) and for the plots the program *ORTEP* II (Johnson, 1971) were used.

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