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Hydrogen Bond Studies.
CXXXI. The Crystal Structure of Trifluoromethanesulphonic Acid Pentahydrate, $H_3O^+CF_3SO_3^-.4H_2O$

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The structure of $CF_3SO_3H.5H_2O$ has been determined by X-ray diffraction at 90 K. The crystals are triclinic, space group $P\bar{1}$, with a = 7·8248 (1), b = 8·2392 (1), c = 8·0495 (1) Å, α = 79·124 (2), β = 111·168 (2), γ = 84·812 (2)°, Z = 2. The structure contains oxonium ions (H_3O^+) and water molecules bonded to each other and to $CF_3SO_3^-$ ions to form a three-dimensional network. The H_3O^+ ion is hydrogen-bonded to three water molecules with different lengths [2·482 (2), 2·579 (1) and 2·639 (2) Å]. Other O—H···O bonds between water molecules are in the range 2·74–2·81 Å.

Introduction

The present paper reports the structure of trifluoromethanesulphonic acid pentahydrate determined from X-ray data recorded at 90 K. This crystal structure is of particular interest since the number of water molecules per proton provides the possibility of the formation of higher hydrates, such as $H_9O_4^+$ or $H_{11}O_5^+$. For references to crystal structure determinations of other hydrates of CF_3SO_3H see Lundgren (1978).

Crystal data

Trifluoromethanesulphonic acid pentahydrate, $CF_3SO_3H.5H_2O$, FW 240·13, triclinic, a = 7·8248 (1),* b = 8·2392 (1), c = 8·0495 (1) Å, α = 79·124 (2), β = 111·168 (2), γ = 84·812 (2)°, V = 468·07 Å^3, Z = 2, D_x = 1·704 g cm^{-3} at 90 K, μ(Cu $K\alpha$) = 37·91 cm^{-1}, space group $P\bar{1}$.

Experimental

Trifluoromethanesulphonic acid pentahydrate melts congruently at −46 °C (Karlsson, 1978; Delaplane, Lundgren & Olovsson, 1975). For experimental details of crystal preparation, data collection and data reduction see Lundgren (1978).

The cell dimensions were determined by least-squares refinement from the measured 2θ values of 92 reflexions from three different crystals mounted around [100], [010] and [001] respectively.

Intensities for layers $h0l$ to $h7l$ were recorded from a crystal mounted around [010]. The crystal was cylindrical with a diameter of 0·29 mm and a length of 0·26 mm. 1727 independent reflexions were measured. The intensities of the test reflexions monitored in each layer showed no systematic variations.

A complementary set of 1070 independent reflexions (layers $0kl$ to $4kl$) was similarly measured from a second cylindrical crystal mounted around [100]. This set was used only to determine the relative scale factors between the layers in the previous data set. A δm comparison of the two sets (Abrahams & Keve, 1971; Lundgren, 1978) made after the interlayer scaling procedure indicated that the e.s.d.'s based on counting statistics were underestimated by a factor of 1·8 and they were thus changed accordingly.

Structure determination and refinement

The structure was solved by Patterson methods, and refined with the full-matrix least-squares program *UPALS*. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, where $w^{-1} = \sigma^2(F^2)$. After refinement of the non-hydrogen atoms, the H atoms were located from difference maps based on reflexions with $\sin\theta/\lambda < 0{\cdot}45$ Å^{-1}. A final refinement of 163 variables included a scale factor, an isotropic extinction parameter, positional parameters for all atoms, individual anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for H. The final $R(F^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2 = 0{\cdot}049$, $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2} = 0{\cdot}073$, and $R(F) = 0{\cdot}028$. The refined value of the isotropic extinction parameter g (Coppens & Hamilton, 1970) was 7·0 (2) × 10^3. The e.s.d. of an observation of unit weight was $s = [\sum w(F_o^2 - F_c^2)^2/(m$

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* E.s.d.'s in the least significant digits are given in parentheses.

$- n)]^{1/2} = 1{\cdot}87$, where m is the number of observations and n the number of parameters varied.

Scattering factors for S, F, C and $O^{0\cdot33-}$ (obtained by interpolating O^0 and O^{1-} tables) were from Hanson, Herman, Lea & Skillman (1964). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for H. An anomalous-dispersion correction was included for the non-hydrogen atoms (Cromer & Liberman, 1970). The programs used for all computations with IBM 370/155 and 1800 computers have been described by Lundgren (1976). The final positional parameters for the non-hydrogen atoms are given in Table 1.*

Table 1. *Coordinates for non-hydrogen atoms* ($\times 10^5$)

	x	y	z
S	28367 (4)	34914 (4)	35260 (4)
O(1)	16531 (14)	41097 (15)	43500 (14)
O(2)	46618 (13)	26000 (15)	48057 (13)
O(3)	28761 (16)	46530 (15)	19469 (13)
C	17322 (20)	18568 (21)	25106 (19)
F(1)	27283 (14)	11480 (13)	17232 (13)
F(2)	434 (12)	25017 (13)	12367 (12)
F(3)	15592 (14)	6773 (13)	37873 (12)
O(*w*1)	97012 (15)	77471 (17)	27565 (14)
O(*w*2)	72073 (15)	1740 (15)	20096 (14)
O(*w*3)	77933 (14)	26804 (14)	39887 (13)
O(*w*4)	74276 (14)	56715 (14)	15491 (13)
O(*w*5)	42685 (15)	76228 (16)	13588 (14)

Description of the structure

A stereoscopic illustration of the structure is shown in Fig. 1. The hydrogen-bond distances are included in Fig. 2 and also listed with angles in Table 2.

The hydrogen-bond distances and the positions of the H atoms indicate an ionic formulation of the compound. The oxonium ion and three of the crystallographically non-equivalent water molecules are hydrogen-bonded to one another to form centro-

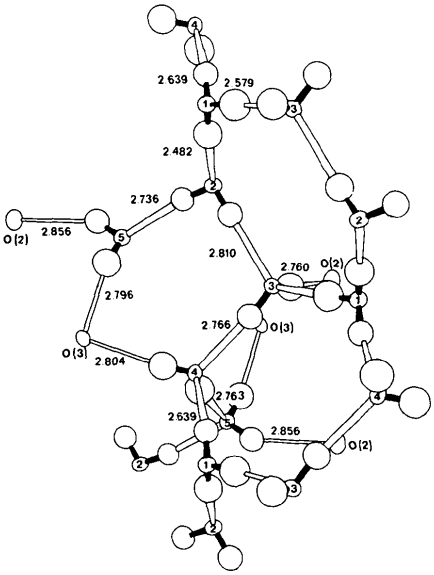

Fig. 2. Hydrogen-bond distances (Å). H atom positions and thermal parameters are as obtained from least-squares refinement. The distances refer to non-hydrogen atoms. Thermal ellipsoids enclose 50% probability.

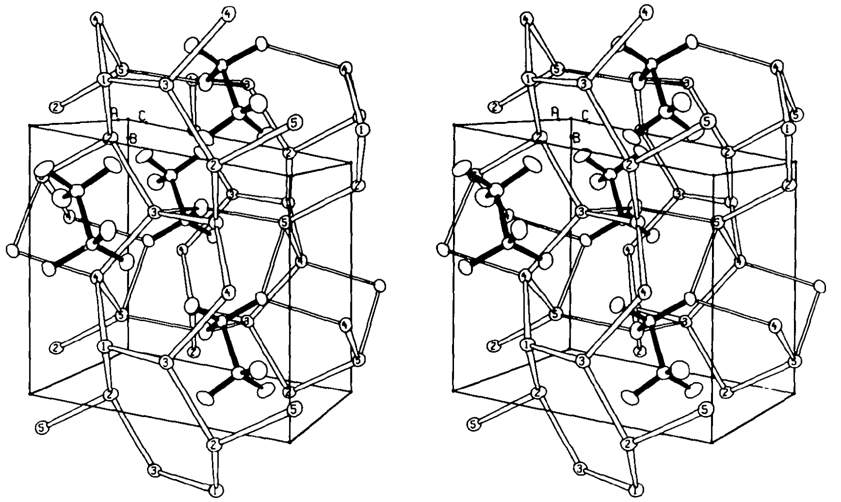

Fig. 1. Stereoscopic *ORTEP* (Johnson, 1965) illustration of the crystal structure of $H_3O^+CF_3SO_3^-.4H_2O$. The O atoms of the oxonium ion (1) and the water molecules (2–5) are numbered. The H atoms have been omitted. Covalent bonds are filled and hydrogen bonds open. The thermal ellipsoids are scaled to enclose 60% probability.

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* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33522 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°)

(*a*) Covalent bonds

S–O(1)	1·429 (1)	C–F(1)	1·328 (2)	O(1)–S–O(2)	115·02 (6)	F(1)–C–F(2)	108·05 (11)
S–O(2)	1·450 (1)	C–F(2)	1·330 (2)	O(1)–S–O(3)	115·64 (7)	F(1)–C–F(3)	108·77 (13)
S–O(3)	1·452 (1)	C–F(3)	1·329 (2)	O(2)–S–O(3)	113·54 (5)	F(2)–C–F(3)	108·14 (12)
S–C	1·829 (2)			C–S–O(1)	104·81 (7)	S–C–F(1)	110·86 (10)
				C–S–O(2)	103·28 (7)	S–C–F(2)	110·52 (11)
				C–S–O(3)	102·34 (6)	S–C–F(3)	110·41 (9)

(*b*) Hydrogen bonds

O(*w*1)···O(*w*2)	2·482 (2)	O(*w*2)···O(*w*1)···O(*w*3)	111·91 (6)	O(*w*3)···O(*w*4)···O(*w*5)	104·72 (5)
O(*w*3)	2·579 (1)	O(*w*2)···O(*w*1)···O(*w*4)	95·49 (5)	O(*w*3)···O(*w*4)···O(3)	114·54 (5)
O(*w*4)	2·639 (2)	O(*w*3)···O(*w*1)···O(*w*4)	126·93 (6)	O(*w*5)···O(*w*4)···O(3)	110·85 (5)
		O(*w*1)···O(*w*2)···O(*w*3)	120·92 (5)	O(*w*2)···O(*w*5)···O(*w*4)	107·36 (5)
O(*w*2)···O(*w*3)	2·810 (2)	O(*w*1)···O(*w*2)···O(*w*5)	121·96 (5)	O(*w*2)···O(*w*5)···O(2)	143·20 (6)
O(*w*5)	2·736 (2)	O(*w*3)···O(*w*2)···O(*w*5)	94·77 (5)	O(*w*2)···O(*w*5)···O(3)	120·19 (5)
		O(*w*1)···O(*w*3)···O(*w*2)	123·98 (6)	O(*w*4)···O(*w*5)···O(2)	97·79 (4)
O(*w*3)···O(*w*4)	2·766 (2)	O(*w*1)···O(*w*3)···O(*w*4)	115·93 (5)	O(*w*4)···O(*w*5)···O(3)	87·42 (5)
O(2)	2·760 (1)	O(*w*1)···O(*w*3)···O(2)	99·83 (4)	O(2)···O(*w*5)···O(3)	86·69 (4)
		O(*w*2)···O(*w*3)···O(*w*4)	107·54 (5)	S–O(2)···O(*w*3)	122·50 (6)
O(*w*4)···O(*w*5)	2·763 (2)	O(*w*2)···O(*w*3)···O(2)	96·40 (5)	S–O(2)···O(*w*5)	119·90 (6)
O(3)	2·804 (1)	O(*w*4)···O(*w*3)···O(2)	110·21 (5)	O(*w*3)···O(2)···O(*w*5)	108·48 (4)
		O(*w*1)···O(*w*4)···O(*w*3)	117·13 (5)	S–O(3)···O(*w*4)	132·91 (7)
O(*w*5)···O(2)	2·856 (1)	O(*w*1)···O(*w*4)···O(*w*5)	95·59 (5)	S–O(3)···O(*w*5)	135·84 (6)
O(3)	2·796 (2)	O(*w*1)···O(*w*4)···O(3)	111·91 (5)	O(*w*4)···O(3)···O(*w*5)	89·04 (4)

symmetric hexagons. These hexagons form zigzag chains along **b**, in a plane parallel to (010). Different chains of hexagons are bonded together *via* the fourth water molecule to form irregular layers parallel to $(10\bar{1})$. $CF_3SO_3^-$ ions are interspersed in the cavities formed between these layers. Two of the sulphonate O atoms are hydrogen-bonded to water molecules. A three-dimensional network of hydrogen bonds is thus formed.

The role of the $CF_3SO_3^-$ ion as a link between hydrogen-bonded layers in the present structure differs from that found in the hemi-, mono- and dihydrates, where water molecules and sulphonate groups form infinite hydrogen-bonded layers with no hydrogen-bond interactions between layers. The $-CF_3$ groups point out at right-angles to the layers. In the tetrahydrate, the $-CF_3$ groups also point out in both directions from the hydrogen-bonded layers, but one of the nine different hydrogen bonds in this structure is used to connect the different layers. Finally, in the present structure the $CF_3SO_3^-$ ions are parallel to the hydrogen-bonded layers of water molecules, and the sulphonate groups are used entirely for interconnecting adjacent layers.

The oxonium ion and the water molecules

The oxonium ion, H_3O^+, is hydrogen-bonded to three water molecules by rather short bonds in a pyramidal arrangement (Fig. 2). The O(*w*1)···O distances are 2·482 (2), 2·579 (1) and 2·639 (2) Å. $H_2O(w2)$, which participates in the short 2·48 Å bond, also has a pyramidal bonding arrangement. All other water molecules have a tetrahedral environment. The complex formed by H_3O^+ and its three nearest water molecules can be regarded as an $H_9O_4^+$ complex. The average $H_3O^+\cdots O(w)$ distance is 2·57 Å, which is comparable to distances found in $H_9O_4^+Cl^-.2H_2O$ (2·52 Å) (Taesler & Lundgren, 1978) and $H_9O_4^+$-$CF_3SO_3^-$ (2·54 Å) (Lundgren, 1978). The layers of water molecules in the structure could then be described as consisting of chains of $H_9O_4^+$ ions linked *via* the remaining water molecules. The hydrogen bonds formed by the other water molecules are only slightly longer than the O(*w*1)···O(*w*4) bond within the complex, however. The difference between the bonds O(*w*4)···O(*w*1) and O(*w*4)···O(*w*5) is only 0·12 Å, which is less than the difference between the bonds O(*w*1)···O(*w*4) and O(*w*1)···O(*w*2) within the complex (0·16 Å). The formulation $H_9O_4^+$ could, of course, be used for *any* complex consisting of an oxonium ion hydrogen-bonded to three water molecules but, for this formulation to be useful as a concept in describing a structure, it should be a requirement that the complex be well separated from other water molecules. The formulation $H_9O_4^+$ would therefore seem less natural in the present case.

Hydrogen atoms

Distances and angles involving H atoms, though inaccurately determined, are all near their expected values. The O–H distances and H–O–H angles within the H_3O^+ ion are 0·84, 0·86 and 0·86 (3) Å and 106, 111 and 116 (2)° respectively. The O–H distances in the water molecules are 0·79–0·89 (3) Å; the H–O–H angles are 98–107 (2)°. The O–H···O angles are in the range 165–176 (2)°, except for the angle O(w5)—H···O(2) (147°) (Fig. 2), where the O(w2)···O(w5)···O(2) angle is also very large (143·2°). The isotropic temperature factors for the H atoms all refined to values within the range 2·5–4·1 (5) Å^2.

The trifluoromethanesulphonate ion

The $CF_3SO_3^-$ ion has a staggered conformation with pseudo C_{3v} symmetry. The F—C—S—O torsion angles for F and O in the *trans* position are 177·69, 178·70 and 179·16° respectively. The —CF_3 group has an approximately regular tetrahedral conformation with an average C—F distance of 1·329 Å. The average S—C—F and F—C—F angles are 110·6 and 108·9° respectively.

The sulphonate group accepts four hydrogen bonds. O(2) and O(3) each accept two hydrogen bonds, whereas O(1) does not participate in hydrogen bonding. This is also reflected in the S—O bond distances: S—O(1) is 0·02 Å shorter than the other two S—O distances. The sulphonate group has an average S—O distance of 1·444 Å, an average O—S—O angle of 114·7°, an average C—S—O angle of 103·5° and a C—S distance of 1·829 Å. These values compare well with the corresponding values obtained in the hemi-, mono-, di- and tetrahydrates of CF_3SO_3H. The average distances and angles for the five independently determined $CF_3SO_3^-$ ions are: S—O 1·445 (9), C—S 1·827 (5), C—F 1·326 (6) Å, O—S—O 114·6 (16), C—S—O 103·9 (7) and S—C—F 110·2 (6)°. (The e.s.d.'s express the deviations of the individual values from the mean.) The large difference (10·7°) between the O—S—O and C—S—O bond angles is typical for substituted sulphonate groups (Greenberg & Okaya, 1969).

The largest spread is found for values involving O atoms which participate in different hydrogen-bonding interactions, especially the S—O distances and O—S—O angles. In the fifteen independent S—O bonds, one O atom is not hydrogen-bonded at all, eight accept one hydrogen bond, and six accept two hydrogen bonds. In Fig. 3, the S—O lengths are plotted *versus* the number of hydrogen bonds accepted by the O atoms. The average S—O distances are 1·429, 1·442 and 1·451 Å for zero, one and two accepted hydrogen bonds.

The three longest S—O distances for O atoms accepting one hydrogen bond are found for the monohydrate (Spencer & Lundgren, 1973). These values may well be affected by an additional source of systematic error: the data-collection procedure used for this particular study was not optimized for a diffractometer with Weissenberg geometry. Neither, in this case, could positional and thermal parameters for the H atoms be refined successfully. This can also be taken as a measure of the quality of the data. If the three monohydrate S—O distances are removed, the corresponding average is 1·438 Å.

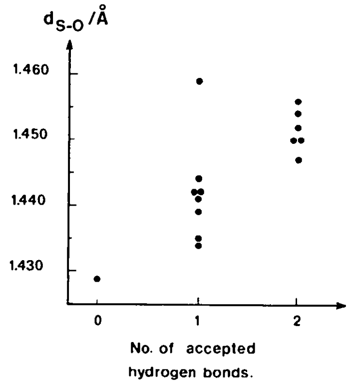

Fig. 3. Plot of S—O bond length *versus* number of hydrogen bonds accepted by the O atoms of the $CF_3SO_3^-$ ion in CF_3SO_3H hydrates.

If S—O distances corrected for thermal riding motion are used, the mean S—O distances are 1·435, 1·446 and 1·457 Å respectively.

The general conclusion to be drawn from Fig. 3 is that the S—O length increases by 0·01 Å for each hydrogen bond the O atom accepts.

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