

formation does not occur. Bell, Christoph, Fronczek & Marsh (1975) have found  $\text{H}_{13}\text{O}_6^+$  to exist, however, as a discrete complex in  $[(\text{C}_9\text{H}_{18})_3(\text{NH})_2\text{Cl}]^+\text{Cl}^-\text{H}_{13}\text{O}_6^+\text{Cl}^-$ . This can presumably be explained by the presence of the large cation.

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#### References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.  
 ALMLÖF, J. (1973). *Chem. Scr.* **3**, 73–79.  
 ALMLÖF, J., LUNDGREN, J.-O. & OLOVSSON, I. (1971). *Acta Cryst.* **B27**, 898–904.  
 BELL, R. A., CHRISTOPH, G. G., FRONCZEK, F. R. & MARSH, R. E. (1975). *Science*, **190**, 151–152.  
 COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.  
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.  
 HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

- International Tables for X-ray Crystallography* (1969). Vol. 1, 3rd ed. Birmingham: Kynoch Press.  
 LOEHLIN, J. H. & KVICK, Å. (1978). *Acta Cryst.* **B34**. To be published.  
 LUNDGREN, J.-O. (1974). *Abstr. Uppsala Diss. Sci.* No. 271, 1–63.  
 LUNDGREN, J.-O. (1976). *Crystallographic Computer Programs*. Report UUIC-B13-4-03. Institute of Chemistry, Univ. of Uppsala.  
 LUNDGREN, J.-O. & OLOVSSON, I. (1967). *Acta Cryst.* **23**, 966–976.  
 LUNDGREN, J.-O. & OLOVSSON, I. (1968). *J. Chem. Phys.* **49**, 1068–1074.  
 LUNDGREN, J.-O. & OLOVSSON, I. (1976). In *The Hydrogen Bond. Recent Developments in Theory and Experiments*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY. Amsterdam: North-Holland.  
 PICKERING, S. U. (1893). *Ber. Dtsch. Chem. Ges.* **26**, 277–284.  
 RUPERT, F. F. (1909). *J. Am. Chem. Soc.* **31**, 851–866.  
 SASVÁRI, K. & JEFFREY, G. A. (1966). *Acta Cryst.* **20**, 875–881.  
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.  
 VUILLARD, G. (1955). *C. R. Acad. Sci.* **241**, 1308–1311.  
 YOON, Y. K. & CARPENTER, G. B. (1959). *Acta Cryst.* **12**, 17–20.

*Acta Cryst.* (1978). **B34**, 2428–2431

### Hydrogen Bond Studies.

## CXXX. The Crystal Structure of Trifluoromethanesulphonic Acid Tetrahydrate, $\text{H}_9\text{O}_4^+\text{CF}_3\text{SO}_3^-$

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The structure of  $\text{CF}_3\text{SO}_3\text{H} \cdot 4\text{H}_2\text{O}$  has been determined by X-ray diffraction at 95 K. The crystals are monoclinic, space group  $P2_1/c$ , with  $a = 7.6200$  (4),  $b = 8.6804$  (3),  $c = 12.8297$  (2) Å,  $\beta = 91.940$  (2)°,  $Z = 4$ . The structure contains triaquaonium ions,  $\text{H}_9\text{O}_4^+$ , hydrogen-bonded to  $\text{CF}_3\text{SO}_3^-$  ions. O—H...O hydrogen bonds within the  $\text{H}_9\text{O}_4^+$  complex are 2.502 (2), 2.532 (2) and 2.572 (2) Å.  $\text{H}_9\text{O}_4^+$  ions are linked together by weak hydrogen bonds, 2.967 (2) Å, to form chains.

#### Introduction

This report is a continuation of a systematic investigation of the structures of the hydrates of trifluoromethanesulphonic acid. Earlier papers in this series report the crystal structures of the hemi-, mono- and dihydrates (Spencer & Lundgren, 1973; Delaplane,

Lundgren & Olovsson, 1975*a,b*). The composition of the present compound presents the possibility of the formation of the triaquaonium ion,  $\text{H}_9\text{O}_4^+$ . Hydrated oxonium ions have, in a few earlier cases, been described in terms of  $\text{H}_9\text{O}_4^+$  ions:  $\text{HBr} \cdot 4\text{H}_2\text{O}$  (Lundgren & Olovsson, 1968),  $\text{HClO}_4 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  (Almlöf, Lundgren & Olovsson, 1971),  $\text{HClO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$  (Almlöf,

1973), and  $\text{HCl} \cdot 6\text{H}_2\text{O}$  (Taesler & Lundgren, 1978). The present investigation is based on single-crystal X-ray diffractometer data recorded at 95 K.

### Crystal data

Trifluoromethanesulphonic acid tetrahydrate,  $\text{CF}_3\text{SO}_3 \cdot \text{H} \cdot 4\text{H}_2\text{O}$ , FW 222.12, monoclinic,  $a = 7.6200$  (4),\*  $b = 8.6804$  (3),  $c = 12.8297$  (2) Å,  $\beta = 91.940$  (2)°,  $V = 848.13$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.739$  g cm<sup>-3</sup> at 95 K,  $\mu(\text{Cu } K\alpha) = 40.46$  cm<sup>-1</sup>, space group  $P2_1/c$ .

### Experimental

Trifluoromethanesulphonic acid tetrahydrate melts congruently at  $-48^\circ\text{C}$  (Karlsson, 1978; Delaplane *et al.*, 1975a). Crystals were grown by cooling aqueous solutions of commercial trifluoromethanesulphonic acid (molar ratio 4:1) sealed in glass capillaries. Crystallization could be induced in the capillaries only when seed crystals of the tetrahydrate were put into them. The seed crystals were taken from a larger batch where crystallization was more readily attainable.

The cell dimensions and intensities were measured at 95 K on a Stoe-Philips semi-automatic two-circle diffractometer which had been modified for low-temperature work [Cu  $K\alpha$  radiation monochromatized with a graphite crystal,  $\lambda(\text{Cu } K\alpha_1) = 1.54051$ ,  $\lambda(\text{Cu } K\alpha_2) = 1.54433$  Å]. The cell parameters were determined by least-squares refinement from the measured  $2\theta$  values of 43 reflexions from two different crystals mounted around [100] and [010].

Intensities for layers  $h0l$  to  $h7l$  were recorded from a crystal mounted around [010]. The crystal was cylindrical with a diameter of 0.22 mm and a length of 0.26 mm. The measurements were made in the equi-inclination  $\omega$ -scan mode with a variable scan range (Freeman, Guss, Nockolds, Page & Webster, 1970). 1799 independent reflexions were measured. Four test reflexions were monitored at regular intervals within each layer. A linear decrease in the intensities of the test reflexions of the  $h0l$  layer with respect to elapsed time was found for which a correction was later applied to all  $h0l$  reflexions. For the  $h1l$  reflexions an increase in intensity was observed. The other layers showed no systematic variations. Later in the least-squares refinement unusually large and systematic  $F_o^2 - F_c^2$  discrepancies were found for the  $h1l$  reflexions. Furthermore, the scale factor for the layer appeared to be underestimated. All  $h1l$  reflexions were therefore removed from the data set, leaving 1315 reflexions. Owing to the experimental difficulties in growing a new crystal the  $h1l$  layer was not remeasured.

A complementary set of 661 independent reflexions (layers  $hk0$  to  $hk3$ ) was similarly measured at 95 K

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

from a crystal mounted around [001]. This set was used only to determine the relative scale factors between layers in the previous data set.

The raw intensities for each data set were corrected for background effects, and standard deviations  $\sigma_c(I)$  were assigned on the basis of counting statistics. The values of  $I$  and  $\sigma_c(I)$  were corrected for Lorentz, polarization and absorption effects with the program *DATAPW*. A  $\delta m$  plot was obtained after the interlayer scaling procedure by plotting  $(F_1^2 - F_2^2)/[\sigma^2(F_1^2) + \sigma^2(F_2^2)]^{1/2}$  for pairs  $F_1^2$  and  $F_2^2$  of the same reflexion measured with the two crystals *vs* the corresponding values expected for a normal distribution (0,1) (Abrahams & Keve, 1971). This plot indicated that the e.s.d.'s were underestimated by a factor of 1.8 and they were thus changed accordingly.

### Structure determination and refinement

Direct methods were used to solve the structure. Phases were determined for 212 reflexions with  $|E| \geq 1.50$  by the iterative application of Sayre's equation with the program *REL*. A trial solution was chosen for an  $E$  map which exhibited features similar to the geometry of a  $\text{CF}_3\text{SO}_3$  group. The model was refined by full-matrix least-squares techniques with the program *UPALS*. The function minimized was  $\sum w(F_o^2 - F_c^2)^2$ , where  $w^{-1} = \sigma^2(F^2) + (0.01F^2)^2$ . After refinement with anisotropic temperature factors, the H atoms were located from a difference synthesis calculated from data with  $\sin \theta/\lambda < 0.45$  Å<sup>-1</sup>.

In the final cycles, 146 parameters were allowed to vary; these included one overall scale factor, an isotropic extinction parameter, coordinates for all atoms, anisotropic thermal parameters for the non-hydrogen atoms and isotropic temperature factors for the H atoms. All parameter shifts were  $< 0.1\sigma$  in the last cycle. The final  $R(F^2) = \sum |F_o^2 - F_c^2|/\sum F_o^2 = 0.039$ ,  $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2} = 0.052$ , and  $R(F) = 0.026$ . The refined value of the isotropic extinction parameter  $g$  (Coppens & Hamilton, 1970)

Table 1. Atomic coordinates for non-hydrogen atoms ( $\times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>
S	38625 (4)	33610 (4)	19536 (2)
O(1)	49195 (14)	24993 (13)	12413 (8)
O(2)	48611 (14)	39915 (13)	28364 (8)
O(3)	22277 (15)	26570 (13)	22087 (9)
C	31914 (23)	50689 (20)	12137 (11)
F(1)	45758 (17)	58784 (12)	9422 (8)
F(2)	21871 (16)	59646 (12)	17847 (9)
F(3)	22767 (17)	46610 (12)	3533 (8)
O( <i>w</i> 1)	1851 (15)	31359 (15)	43974 (8)
O( <i>w</i> 2)	31760 (14)	42642 (14)	47168 (9)
O( <i>w</i> 3)	84876 (16)	44120 (18)	28602 (9)
O( <i>w</i> 4)	86821 (15)	21841 (15)	11141 (9)

was  $3.4(2) \times 10^3$ . The e.s.d. of an observation of unit weight was  $s = [\sum w(F_o^2 - F_c^2)^2 / (m - n)]^{1/2} = 1.23$ , where  $m$  is the number of observations and  $n$  the number of parameters varied.

Scattering factors for S, F, C and  $O^{0.33-}$  (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.\*

### Description of the structure

A stereoscopic view of the structure is shown in Fig. 1. The hydrogen-bond distances are included in Fig. 2 and are listed with angles in Table 2. The structure is composed of  $H_3O_4^+$  and  $CF_3SO_3^-$  ions linked together by hydrogen bonds. This ionic formulation is based on the positions of the H atoms and the hydrogen-bond distances.

Eight of the nine different hydrogen bonds within the structure are used to connect water molecules and sulphonate groups to form layers parallel to the *ac* plane. The  $-CF_3$  groups point in the positive and negative *b* directions out from these layers. The ninth hydrogen bond links the layers in the *b* direction to

\* 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 33521 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

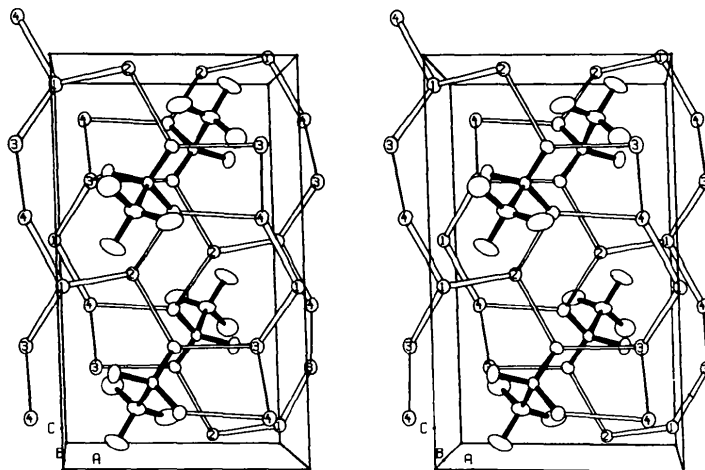


Fig. 1. Stereoscopic *ORTEP* (Johnson, 1965) illustration of the crystal structure of  $H_3O_4^+CF_3SO_3^-$ . The O atoms of the oxonium ion (1) and the water molecules (2–4) are numbered. H atoms have been omitted. Covalent bonds are filled and hydrogen bonds are open. The weak hydrogen bond (2.97 Å) linking the  $H_3O_4^+$  ions is drawn as a single line. The thermal ellipsoids are scaled to enclose 60% probability.

form a three-dimensional hydrogen-bonded network. The overall structure has close similarities to the lower hydrates of  $CF_3SO_3H$  as far as their layer structures are concerned, but in these structures there is no hydrogen-bond connexion between the different layers, and the hydrogen-bonded single or double layers are separated by normal van der Waals distances between the  $-CF_3$  groups of different layers.

### The $H_3O_4^+$ ion

The  $H_3O_4^+$  complex consists of an oxonium ion,  $H_3O^+$ , hydrogen-bonded to three water molecules at distances of 2.502 (2), 2.532 (2) and 2.572 (2) Å in a pyramidal arrangement (Fig. 2). The average  $O \cdots O(w1) \cdots O$  angle is  $114^\circ$ . The water molecules of the  $H_3O_4^+$  complex each donate two hydrogen bonds to sulphonate O atoms, with the exception of  $H_2O(w4)$ , where one of these two hydrogen bonds is donated to a

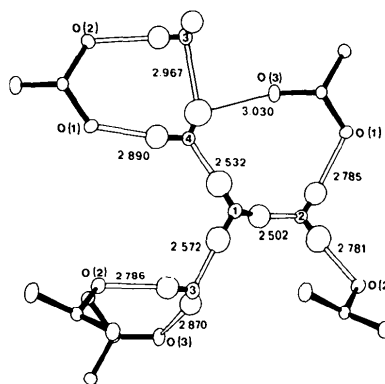


Fig. 2. Hydrogen-bond distances (Å). H atom positions and thermal parameters are as obtained from the refinement. The distances refer to non-hydrogen atoms. Thermal ellipsoids enclose 50% probability. The contact  $O(w4) \cdots O(3)$  which is not considered a hydrogen bond is also indicated.

Table 2. *Interatomic distances (Å) and angles (°) involving non-hydrogen atoms*

(a) Covalent bonds			
S—O(1)	1.447 (1)	C—F(1)	1.324 (2)
S—O(2)	1.450 (1)	C—F(2)	1.328 (2)
S—O(3)	1.435 (1)	C—F(3)	1.333 (2)
S—C	1.824 (2)		
O(1)—S—O(2)	113.57 (6)	S—C—F(1)	110.88 (12)
O(1)—S—O(3)	115.47 (7)	S—C—F(2)	110.20 (10)
O(2)—S—O(3)	114.78 (7)	S—C—F(3)	110.15 (12)
C—S—O(1)	104.11 (7)	F(1)—C—F(2)	108.27 (14)
C—S—O(2)	103.31 (7)	F(1)—C—F(3)	108.79 (12)
C—S—O(3)	103.56 (7)	F(2)—C—F(3)	108.49 (14)
(b) Hydrogen bonds			
O(w1)···O(w2)	2.502 (2)	O(w3)···O(2)	2.786 (2)
O(w1)···O(w3)	2.572 (2)	O(w3)···O(3)	2.870 (2)
O(w1)···O(w4)	2.532 (2)	O(w3)···O(w4)	2.967 (2)
O(w2)···O(1)	2.785 (2)	O(w4)···O(1)	2.890 (2)
O(w2)···O(2)	2.781 (2)		
S—O(1)···O(w2)	117.72 (6)	S—O(2)···O(w2)	117.66 (6)
S—O(1)···O(w4)	131.23 (6)	S—O(2)···O(w3)	123.50 (6)
O(w2)···O(1)···O(w4)	111.03 (5)	O(w2)···O(2)···O(w3)	117.78 (5)
O(w2)···O(w1)···O(w3)	112.87 (6)		
O(w2)···O(w1)···O(w4)	109.69 (6)		
O(w3)···O(w1)···O(w4)	118.93 (6)		
O(1)···O(w2)···O(2)	109.82 (5)		
O(1)···O(w2)···O(w1)	108.06 (5)		
O(2)···O(w2)···O(w1)	105.63 (5)		
O(2)···O(w3)···O(3)	86.61 (5)		
O(2)···O(w3)···O(w1)	115.13 (6)		
O(3)···O(w3)···O(w1)	122.43 (6)		
O(3)···O(w3)···O(w4)	129.11 (6)		
O(2)···O(w3)···O(w4)	88.93 (5)		
O(w1)···O(w3)···O(w4)	105.16 (6)		
O(1)···O(w4)···O(w1)	122.57 (5)		
O(1)···O(w4)···O(w3)	79.67 (4)		
O(w1)···O(w4)···O(w3)	139.81 (6)		

water molecule, H<sub>2</sub>O(w3), of an adjacent H<sub>3</sub>O<sub>4</sub><sup>+</sup> ion. This O(w4)—H···O(w3) bond is rather long (2.967 Å) and bent [150 (3)°]. A sulphonate O(3) is at a distance of 3.030 Å from O(w4) (Fig. 2), but the H···O distance [2.56 (3) Å] and O(w4)—H···O(3) angle [118 (2)°] do not satisfy the generally accepted geometrical requirements for hydrogen bonding (H···O ≤ 2.4 Å, ∠O—H···O ≥ 130°). H<sub>2</sub>O(w3) is the only water molecule of the H<sub>3</sub>O<sub>4</sub><sup>+</sup> ion to accept a hydrogen bond other than from the central H<sub>3</sub>O<sup>+</sup> ion. The different H<sub>3</sub>O<sub>4</sub><sup>+</sup> complexes are thus bonded together by very weak hydrogen bonds to form chains running in the c direction.

#### 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<sub>3</sub>O<sup>+</sup> ion are 0.90, 0.92 and 0.96 (3) Å and 107, 109 and 115 (2)° respectively. The O—H distances in the water molecules are 0.79–0.94 (3) Å, and all H—O—H angles are 106 (3)°. The hydrogen bonds seem to be almost linear in most cases. The O—H···O angles are all >170° except for O(w4)—H···O(w3) (150°) and O(w3)—H···O(3) (158°) where the

O···O···O angles are also far from the H—O—H angle of a water molecule. The isotropic temperature factors for the H atoms all refined to values within the range 3.3–5.2 (6) Å<sup>2</sup>.

#### The trifluoromethanesulphonate ion

The CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ion has a staggered conformation with pseudo C<sub>3v</sub> symmetry. The sulphonate group has an average S—O distance of 1.444 Å, an average O—S—O angle of 114.6°, an average C—S—O angle of 103.7° and a C—S distance of 1.824 Å. In the present structure, the S—O bond involving O(3) is shorter than the other two; O(3) is the acceptor for only one hydrogen bond, while O(1) and O(2) each accept two. The —CF<sub>3</sub> group has an approximately regular tetrahedral conformation with an average C—F distance of 1.328 Å. The average S—C—F and F—C—F angles are 110.4 and 108.5° respectively. The F—C—S—O torsion angles for F and O in the *trans* position are 178.24, 178.71 and 179.50° respectively.

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#### References

- ABRAHAM, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- ALMLÖF, J. (1973). *Chem. Scr.* **3**, 73–79.
- ALMLÖF, J., LUNDGREN, J.-O. & OLOVSSON, I. (1971). *Acta Cryst.* **B27**, 898–904.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- DELAFLANE, R. G., LUNDGREN, J.-O. & OLOVSSON, I. (1975a). *Acta Cryst.* **B31**, 2202–2207.
- DELAFLANE, R. G., LUNDGREN, J.-O. & OLOVSSON, I. (1975b). *Acta Cryst.* **B31**, 2208–2213.
- FREEMAN, H. C., GUSS, J. M., NOCKOLDS, C. E., PAGE, R. & WEBSTER, A. (1970). *Acta Cryst.* **A26**, 149–152.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KARLSSON, H. (1978). To be published.
- LUNDGREN, J.-O. (1976). *Crystallographic Computer Programs*. Report UUIC-B13-4-03. Institute of Chemistry, Univ. of Uppsala.
- LUNDGREN, J.-O. & OLOVSSON, I. (1968). *J. Chem. Phys.* **49**, 1068–1074.
- SPENCER, J. B. & LUNDGREN, J.-O. (1973). *Acta Cryst.* **B29**, 1923–1928.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- TAESLER, I. & LUNDGREN, J.-O. (1978). *Acta Cryst.* **B34**, 2424–2428.