

Sodium trichloromethanesulfonate
monohydrate

Emiliana Damian,* Lars Eriksson and Magnus Sandström

Department of Physical, Inorganic and Structural Chemistry, Arrhenius Laboratory,
Stockholm University, SE-10691 Stockholm, Sweden

Correspondence e-mail: emiliana@struc.su.se

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Sodium trichloromethanesulfonate monohydrate, $\text{Na}^+\cdot\text{CCl}_3\text{SO}_3^-\cdot\text{H}_2\text{O}$, crystallizes in $P2_1/a$ with all the atoms located in general positions. The trichloromethanesulfonate (trichlate) anion consists of pyramidal SO_3 and CCl_3 groups connected via an S—C bond in a staggered conformation with approximate C_{3v} symmetry. The water molecule is hydrogen bonded to the sulfonate O atoms, with one water H atom forming weak bifurcated O—H \cdots O hydrogen bonds to two different trichlate ions. Two water O atoms and three O atoms from different SO_3 groups form a square-pyramidal arrangement around the sodium ion.

Comment

Trichloromethanesulfonate (trichlate, $\text{CCl}_3\text{SO}_3^-$) salts were prepared more than 150 years ago (Kolbe, 1845). The trichlate and the related trifluoromethanesulfonate (triflate, CF_3SO_3^-) and mesylate (CH_3SO_3^-) anions have been studied by means of vibrational spectroscopy complemented by normal coordinate analysis (Miles *et al.*, 1969; Bürger *et al.*, 1970). Gejji *et al.* (1994) performed quantum chemical calculations of the structure and vibrational frequencies of trichloromethanesulfonic acid, $\text{CCl}_3\text{SO}_3\text{H}$, and its anion. Edwards & Smith (1991) reported vibrational assignments of the acid and determined its dissociation constant in 2 mol dm^{-3} aqueous solution by Raman measurements. A recent ^{35}Cl nuclear quadrupole resonance study concluded that the trichlate anion has weaker coordination ability than several chloroacetate anions (Wulfsberg *et al.*, 2004). The present study of sodium trichloromethanesulfonate monohydrate ($\text{CCl}_3\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$) seems to be the first crystal structure reported containing a trichlate anion.

The crystal structure is described in the space group $P2_1/a$, with all atoms located on general sites ($4e$). The pyramidal SO_3 and CCl_3 groups of the trichlate anion are in a staggered conformation (Fig. 1 and Table 1). One water H atom (H42) is involved in a weak bifurcated hydrogen bond to two O atoms, O1 and O2, of different trichlate ions, while the other H atom (H41) forms a shorter hydrogen bond (Fig. 1 and Table 2). The

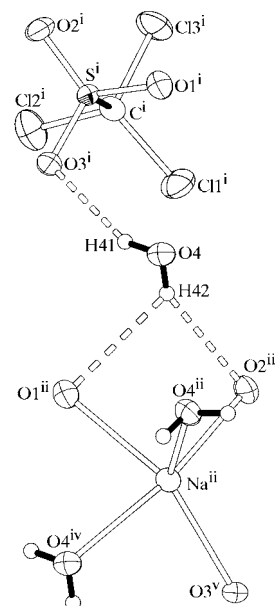


Figure 1

The trichlate ion and the environment of the sodium ion and the water molecule (40% probability displacement ellipsoids). Broken lines indicate hydrogen bonds (see Table 2 for geometric details). [Symmetry codes: (i) $-x - \frac{1}{2}, y + \frac{1}{2}, -z$; (ii) $-x - \frac{1}{2}, y - \frac{1}{2}, -z$; (iii) $-x, -y, -z$; (iv) $x, y - 1, z$; (v) $-x, -y - 1, -z$.]

Na^+ ion has an almost square-pyramidal environment of O atoms from two water molecules and three different SO_3 groups, with a mean $\text{Na}^+\cdots\text{O}$ distance of 2.38 Å.

As shown in Table 3, the mean S—O bond distance is not significantly influenced by hydrogen bonding or by replacing the $-\text{CCl}_3$ group with $-\text{CH}_3$ or $-\text{CF}_3$. The C—S bond increases considerably from the mesylate ($\text{H}_3\text{C}-\text{SO}_3^-$) to the triflate ($\text{F}_3\text{C}-\text{SO}_3^-$) ion, with an even longer C—S bond for the trichlate ($\text{Cl}_3\text{C}-\text{SO}_3^-$), as predicted by theoretical studies. The electron-withdrawing effect of the electronegative Cl and F atoms evidently weakens the C—S bond and makes the O—S—O angles about 2° larger than in the mesylate ion. The mean C—Cl bond length and Cl—C—Cl angle determined in this work agree well with the values found for trichloromethane (Sutton, 1965).

Experimental

$\text{CCl}_3\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$ was obtained from a solution prepared by stirring and heating [323 (2) K] wax-like crystals of trichloromethanesulfonyl chloride ($\text{CCl}_3\text{SO}_2\text{Cl}$, 2.547 g, Aldrich) in an excess (36 ml) of 1 mol dm^{-3} sodium hydroxide solution (Edwards & Smith, 1991). After evaporating the solvent, first in a rotary evaporator at 355 (2) K and then at reduced pressure in a vacuum desiccator, colourless crystals were obtained, which were recrystallized from water.

Crystal data

$\text{Na}^+\cdot\text{CCl}_3\text{O}_3\text{S}^-\cdot\text{H}_2\text{O}$
 $M_r = 239.43$
 Monoclinic, $P2_1/a$
 $a = 10.727$ (7) Å
 $b = 5.828$ (3) Å
 $c = 12.613$ (9) Å
 $\beta = 103.24$ (8) $^\circ$
 $V = 767.6$ (9) Å 3

$Z = 4$
 $D_x = 2.072\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.47\text{ mm}^{-1}$
 $T = 291$ (2) K
 Pentagonal prism, colourless
 $0.5 \times 0.3 \times 0.1\text{ mm}$

Data collection

Stoe IPDS diffractometer	6794 measured reflections
φ scans	1805 independent reflections
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1997)	1312 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.579$, $T_{\max} = 0.953$	$R_{\text{int}} = 0.100$
	$\theta_{\max} = 27.8^\circ$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0767P)^2]$
$wR(F^2) = 0.127$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{\max} < 0.001$
1805 reflections	$\Delta\rho_{\max} = 0.86 \text{ e } \text{\AA}^{-3}$
99 parameters	$\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

S—O1	1.444 (3)	C—Cl2	1.757 (4)
S—O2	1.446 (2)	C—Cl3	1.764 (3)
S—O3	1.455 (2)	C—Cl1	1.777 (3)
S—C	1.847 (4)		
O1—S—O2	115.05 (15)	O3—S—C	103.84 (14)
O1—S—O3	113.80 (14)	Cl2—C—Cl3	110.18 (19)
O2—S—O3	113.77 (13)	Cl2—C—Cl1	110.11 (19)
O1—S—C	104.58 (17)	Cl3—C—Cl1	109.25 (17)
O2—S—C	104.09 (16)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H41 \cdots O3 ⁱ	0.85 (5)	2.09 (5)	2.871 (4)	153 (4)
O4—H42 \cdots O1 ⁱⁱ	0.74 (5)	2.54 (5)	3.016 (4)	123 (5)
O4—H42 \cdots O2 ⁱⁱⁱ	0.74 (5)	2.25 (5)	2.915 (4)	148 (5)

Symmetry codes: (i) $-x - \frac{1}{2}, y + \frac{1}{2}, -z$; (ii) $-x - \frac{1}{2}, y - \frac{1}{2}, -z$; (iii) $-x, -y, -z$.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1997); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Table 3

S—C and mean S—O and C—X bond distances (\AA) and O—S—O, C—S—O and X—C—X angles ($^\circ$) for several related compounds (X = F or Cl).

Compound	S—C	S—O	C—X	O—S—O	C—S—O	X—C—X
1	1.754 (2)	1.45	—	111.9	106.9	—
2	1.746 (5)	1.45	—	112.8	105.9	—
3	1.747 (6)	1.44	—	112.5	106.2	—
4	1.811 (4)	1.43	1.31	114.3	104.1	108.5
5	1.809 (4)	1.43	1.31	113.8	104.3	108.7
6	1.833 (6)	1.44	1.31	114.4	103.9	109.3
7	1.878	1.438	1.777	—	102.3	—
8	1.907	1.476	1.778	—	101.7	—
9	1.847 (4)	1.45	1.77	114.2	104.2	109.8
10	—	—	1.76	—	—	110.9

Notes: (1) $\text{CH}_3\text{SO}_3\text{Na}$ (Wei & Hingerty, 1981); (2) $\text{C}_{20}\text{H}_{23}\text{ClN}_3\text{O}_5^+\cdot\text{CH}_3\text{SO}_3^-$ (Wei, 1981); (3) $\text{C}_{21}\text{H}_{26}\text{NO}^+\cdot\text{CH}_3\text{SO}_3^-\cdot\text{H}_2\text{O}$ (Jones *et al.*, 1978); (4) $\text{CF}_3\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$ at 225 K (Delaplane *et al.*, 1975); (5) $\text{CF}_3\text{SO}_3\text{Na}$ (Sofina *et al.*, 2003); (6) $\text{Tb}(\text{H}_2\text{O})_9(\text{CF}_3\text{SO}_3)_3$ (Abbasi *et al.*, 2005); (7) $\text{CCl}_3\text{SO}_3^-$ at HF6-31G* (Gejji *et al.*, 1994); (8) $\text{CCl}_3\text{SO}_3^-$ at MP26-31G* (Gejji *et al.*, 1994); (9) $\text{CCl}_3\text{SO}_3\text{Na}\cdot\text{H}_2\text{O}$ (this work); (10) CHCl_3 (Sutton, 1965).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3009). Services for accessing these data are described at the back of the journal.

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