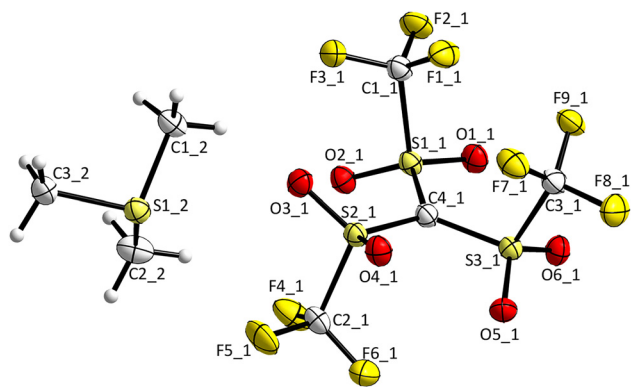


Raphael Wirthensohn and Maik Finze*

The crystal structure of trimethylsulfonium tris(trifluoromethylsulfonyl)methanide, $C_7H_9F_9O_6S_4$

**Table 1:** Data collection and handling.

Crystal:	Colourless block
Size:	0.50 × 0.33 × 0.28 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	6.57 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy,
θ_{\max} , completeness:	77.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	106,974, 3454, 0.052
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3451
$N(\text{param})_{\text{refined}}$:	239
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Diamond [4]

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Abstract

$C_7H_9F_9O_6S_4$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 8.80180(10)$ Å, $b = 10.96580(10)$ Å, $c = 16.91360(10)$ Å, $V = 1632.48(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0222$, $wR_{\text{ref}}(F^2) = 0.0604$, $T = 100$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Trifluoromethylsulfonyl fluoride (0.2 g, 1.3 mmol) was transferred to diethyl ether (5 mL) in vacuum at -196 °C.

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The mixture was warmed to 0 °C and a solution of MeMgCl in THF (1.52 mL, 3 mol L⁻¹, 4.55 mmol) was added. The reaction mixture was allowed to warm to room temperature over the course of 12 h. A few crystals of the title compound were obtained by slow evaporation of the reaction mixture within 14 days.

Experimental details

Hydrogen atoms were located from difference Fourier maps. For the refinement, a riding model was applied and their U_{iso} values were set to 1.5 U_{eq} of the parent atoms. Using a hole-in-one method a Flack parameter of 0.459(16) [3] was calculated. Using Parsons' method [5] using 1456 selected quotients the parameter was very similar [0.461(8)]. The structure was finally refined as a 2-component inversion twin with a refined twin ratio of 0.459(6)/0.541(6).

Comment

Weakly coordinating anions (WCAs) have a low tendency to coordinate because the negative charge is delocalized and they are chemically and electrochemically robust [6–11]. Thus, WCAs have been applied for the stabilization of highly reactive cations and they serve as important

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C1_1	0.3067 (3)	0.3541 (2)	0.42660 (14)	0.0249 (5)
S1_1	0.35961 (6)	0.49696 (5)	0.37304 (3)	0.02142 (13)
F1_1	0.42950 (19)	0.29494 (15)	0.45107 (11)	0.0359 (4)
O1_1	0.3952 (2)	0.57813 (18)	0.43680 (11)	0.0280 (4)
C2_1	0.4757 (3)	0.4897 (2)	0.15300 (14)	0.0279 (5)
S2_1	0.50395 (6)	0.38004 (5)	0.23488 (3)	0.02170 (13)
F2_1	0.22620 (19)	0.38664 (16)	0.48996 (9)	0.0346 (4)
O2_1	0.2323 (2)	0.52015 (17)	0.32299 (10)	0.0259 (4)
C3_1	0.7838 (3)	0.3973 (2)	0.40938 (15)	0.0270 (5)
S3_1	0.69775 (7)	0.51786 (5)	0.34747 (3)	0.02185 (13)
F3_1	0.22247 (19)	0.27995 (15)	0.38364 (9)	0.0309 (3)
O3_1	0.3649 (2)	0.31357 (17)	0.23848 (11)	0.0281 (4)
C4_1	0.5214 (3)	0.4663 (2)	0.31936 (14)	0.0214 (4)
O4_1	0.6429 (2)	0.31989 (17)	0.21490 (11)	0.0285 (4)
F4_1	0.3499 (2)	0.55323 (18)	0.16235 (10)	0.0430 (4)
O5_1	0.7951 (2)	0.52201 (17)	0.27979 (10)	0.0268 (4)
F5_1	0.4628 (3)	0.42691 (18)	0.08633 (10)	0.0449 (5)
O6_1	0.6911 (2)	0.61938 (17)	0.39992 (11)	0.0283 (4)
F6_1	0.5911(2)	0.56497 (18)	0.14605 (11)	0.0454 (5)
F7_1	0.7794 (2)	0.28927 (14)	0.37505 (10)	0.0351 (4)
F8_1	0.92796 (19)	0.42713 (18)	0.42247 (11)	0.0399 (4)
F9_1	0.71355 (18)	0.38993 (16)	0.47885 (9)	0.0321 (3)
C1_2	0.0209 (3)	0.2908 (3)	0.22124 (15)	0.0297 (5)
H1A_2	-0.089631	0.289526	0.228302	0.044*
H1AB_2	0.066205	0.347712	0.259168	0.044*
H1AC_2	0.061834	0.208845	0.230161	0.044*
S1_2	0.06499 (7)	0.33877 (5)	0.12289 (4)	0.02495 (13)
C2_2	-0.0184 (4)	0.4872 (2)	0.12157 (17)	0.0349 (6)
H2A_2	-0.013737	0.520471	0.067837	0.052*
H2AB_2	0.037455	0.540894	0.157657	0.052*
H2AC_2	-0.124672	0.481822	0.138490	0.052*
C3_2	-0.0694 (4)	0.2522 (3)	0.06682 (16)	0.0345(6)
H3A_2	-0.067806	0.279482	0.011649	0.052*
H3AB_2	-0.171373	0.264242	0.088786	0.052*
H3AC_2	-0.042768	0.165545	0.069320	0.052*

building blocks for many applications in materials science. For example, they are used as components of the electrolytes applied in electrochemical devices such as batteries, supercapacitors, and dye-sensitized solar cells (DSSCs). The tris(trifluoromethylsulfonyl)methanide anion ([Tf₃C]⁻) is a WCA that is accessible from trifluoromethylsulfonyl fluoride and methylmagnesium bromide [12]. So far, only few crystallographic studies on salts of the [Tf₃C]⁻ anion with different types of counterions have been described [12–15].

In the course of our studies on reactions of trifluoromethylsulfonyl fluoride with methylmagnesium bromide single crystals of the title compound trimethylsulfonium tris(trifluoromethylsulfonyl)methanide ([SMe₃][Tf₃C]) have

been obtained. The [SMe₃]⁺ cation formed during storage of a reaction mixture for 14 days.

The asymmetric unit of the title compound contains one [Tf₃C]⁻ anion and one [SMe₃]⁺ cation. The C–S₃ unit of the anion is planar. The SO₂CF₃ groups have different orientations with respect to the central C–S₃ core with two groups facing up and one facing down with regard to the CS₃ plane. The bond lengths and angles are similar to those reported earlier for the [Tf₃C]⁻ anion [12–15].

The [SMe₃]⁺ cation reveals the typical pyramidal structure and the bond parameters are close to values reported for other trimethylsulfonium salts, e.g. [SMe₃][1-H₂N-6-F-*closo*-1-CB₁₁I₁₀] [16].

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