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Crystal and Structural Data on Two Alkali Salts of Bis(trifluoromethanesulfonyl)methane

KJELL T. DÅVØY, THOR GRAMSTAD and STEINAR HUSEBYE

Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway

Bis(trifluoromethanesulfonyl)methane has been prepared by reaction between trifluoromethanesulfonic anhydride and methylmagnesium bromide. Its rubidium and cesium salts were prepared by addition of the respective carbonates. Crystals of the rubidium salt, $Rb(CF_3SO_2)_2CH$ are monoclinic, space group $C2/c$. The cell dimensions are $a = 22.845(6)$ Å, $b = 5.284(1)$ Å, $c = 16.850(3)$ Å, $\beta = 99.63(2)°$ and $Z = 8$. The structure has been determined and refined by full-matrix least-squares analysis of three-dimensional counter data. The structure is built up of layers of cations alternating with double layers of anions, parallel to (100). There is extensive delocalization of charge in the anion, which has the *cis* configuration. The central C – S bonds have an average length of only 1.65 Å and the S – C – S angle is 126.3(1.3)°. The unit cell dimensions of the cesium salt have also been determined, and the crystals are found to be isomorphous with those of the rubidium salt.

Trifluoromethanesulfonyl is a very strong electron withdrawing group with a Hammett σ-parameter of 0.79.[1,2] It is therefore not unexpected that bis(trifluoromethanesulfonyl)methane, $(CF_3SO_2)_2CH_2$, is a remarkably strong acid with a pK_a-value of -1.[3] It is characteristic that when the trifluoromethyl groups are replaced by methyl groups, the pK_a-value increases to 12.55.[4] From a structural point of view, both bis(trifluoromethanesulfonyl)methane, H_2A, and its salts, MHA, should be interesting. The high acidity is probably due to a strong delocalization of negative charge in the anion. The X-ray crystallographic study of the rubidium salt, RbHA, was carried out to establish the structural changes caused by such a delocalization. The electron withdrawing group CF_3 in addition to oxygen will induce a high degree of polarization in the sulfur atom which will therefore contract its 3*d* orbitals so that they are made more suitable for bonding.[5,6] This strong π-bonding is expected to take place not only between sulfur and oxygen, but also between sulfur and the central carbon atom which has two electrons in a *p*-orbital of appropriate symmetry.

EXPERIMENTAL

Bis(trifluoromethanesulfonyl)methane, H_2A. The acid was prepared by a novel route, using the easier accessible anhydride instead of trifluoromethanesulfonyl fluoride which has been used earlier.[1,3] The reaction will be described in more detail elsewhere.

Preparation of salts. The rubidium and cesium salts of bis(trifluoromethanesulfonyl)methane, H_2A, were prepared by a method described by Gramstad and Hazeldine.[1] The yields were well above 90 %. The uncorrected m.p.'s are RbHA, 259 °C and CsHA, 241 °C. The salts are readily soluble in polar solvents. The IR spectra of the compounds correspond well to those of the acid and its sodium salt published earlier.[1]

Crystal data for the rubidium and cesium salts of bis(trifluoromethanesulfonyl)methane. Both salts were recrystallized from ethyl ether/acetone mixtures and gave similar crystals. The crystals are colourless prisms, elongated along *b*, and have a strong tendency to split into flakes parallel to the *bc*-plane. Unit cell data are for RbHA: $a = 22.845(6)$ Å, $b = 5.284(1)$ Å, $c = 16.850(3)$ Å, $\beta = 99.63(2)°$, $Z = 8$, $D_m = 2.41$ g/cm^3, $D_x = 2.42$ g/cm^3. For CsHA, the following values are found: $a = 22.98$ Å, $b = 5.36$ Å, $c = 17.52$ Å, $\beta = 99.0°$, $Z = 8$, $D_m = 2.56$ g/cm^3, $D_x = 2.57$ g/cm^3. The cell dimensions for RbHA are based on accurate measurements of high order diffractometer reflections and calculated using a

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least-squares procedure. In the case of CsHA the cell dimensions were calculated from Weissenberg and oscillation photographs and are estimated to be accurate within 0.5 %.

The crystals are isomorphous and from systematic extinctions, the space group is $C2/c$ or Cc.

Intensity data. Intensity data for RbHA were collected on a Siemens automatic, off-line, single crystal diffractometer (AED-1). The diffractometer was operated as a three-circle instrument, using Mo$K\alpha$ radiation and the θ-2θ scan technique. A crystal with dimensions $0.45 \times 0.15 \times 0.01$ mm^3 was mounted with its b axis along the ψ-axis of the instrument, and all reflections with $2\theta \leq 50°$ were collected. Out of 2026 independent reflections, only 1120 had $I \geq 2\sigma$ and were considered observed. It was very difficult to find suitable crystals for X-ray crystallography among the two salts prepared. The crystal mounted had a slight tendency to split and was very thin. Therefore the quality of the intensity data was only fair, but they seemed to be the best obtainable. The data were corrected for Lorentz and polarization effects, as well as for absorption ($\mu = 57.4$ cm^{-1}).

Structure determination. The space group $C2/c$ was chosen, and the solution and refinement of the structure justified the choice. A refinement using the alternative, *non*-centric space group Cc was not successfull.

Conventional heavy atom techniques were used to solve the structure. Full-matrix, least squares refinement with anisotropic temperature factors for all atoms gave a final R-value of 0.106, corresponding to a weighted R of 0.133. The computer programs used are those of the X-ray system, version of 1972.[8] The weight for a reflection in the least-squares refinement was $w = 1/(52 + F_o + 0.0052F_o^2)$.

The single hydrogen atom could not be located from the difference map and was not included in the refinement. The scattering factors for rubidium and fluorine were taken from the International Tables,[9] while scattering factors for the other atoms were generated by the computer program. Those for

Table 1. Atomic coordinates for atoms in the asymmetric unit in fractions of cell edges. Standard deviations in parentheses.

Atom	x	y	z
Rb	0.4668(1)	0.0361(4)	0.1090(1)
S1	0.0945(2)	0.0337(10)	0.0720(3)
S2	0.0931(2)	0.1027(9)	0.2453(3)
C1	0.0968(10)	−0.0708(40)	0.1663(12)
C2	0.1699(15)	0.0817(73)	0.0481(14)
C3	0.1677(11)	0.2109(55)	0.2961(14)
O1	0.0716(9)	−0.1603(33)	0.0172(11)
O2	0.0699(8)	0.2817(31)	0.0598(9)
O3	0.0730(8)	−0.0489(32)	0.3060(9)
O4	0.0646(7)	0.3417(30)	0.2264(8)
F1	0.1987(11)	−0.1479(57)	0.0562(16)
F2	0.1673(8)	0.1614(42)	−0.0241(10)
F3	0.1986(8)	0.2342(59)	0.0987(12)
F4	0.2011(8)	−0.0004(47)	0.3133(12)
F5	0.1921(7)	0.3579(39)	0.2501(9)
F6	0.1620(7)	0.3191(38)	0.3634(9)

Table 2. Components of atomic vibration tensors, $U \times 10^2$ in Å^2, with standard deviations referred to crystallographic axes. The expression is $\exp[-2\pi^2(h^2a^{-2}U_{11} + \cdots + 2hka^{-1}b^{-1}U_{12} + \cdots)]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	5.48(13)	3.23(11)	3.48(11)	0.85(10)	−0.03(8)	0.03(8)
S1	4.21(28)	3.28(27)	3.81(27)	0.03(23)	−0.36(21)	0.00(22)
S2	3.85(29)	3.46(28)	3.46(26)	0.17(21)	−0.21(21)	0.86(21)
C1	4.8(13)	3.2(11)	4.4(12)	−0.4(10)	−0.2(9)	−0.1(9)
C2	8.7(21)	12.6(29)	3.0(13)	−1.4(22)	0.7(13)	−1.3(16)
C3	5.8(16)	8.0(20)	3.5(13)	0.5(15)	0.0(11)	−1.1(12)
O1	9.4(14)	4.8(10)	5.8(10)	−2.0(10)	−2.3(10)	−2.3(8)
O2	8.5(13)	4.9(10)	3.7(9)	3.4(9)	0.4(8)	1.7(7)
O3	7.7(12)	5.8(10)	5.0(9)	−0.3(10)	1.0(8)	2.5(8)
O4	5.8(9)	4.7(9)	3.7(8)	2.0(8)	0.0(7)	0.5(7)
F1	11.9(18)	17.3(25)	16.5(23)	9.1(19)	4.5(16)	3.0(20)
F2	11.2(15)	13.2(17)	5.6(10)	−1.6(13)	2.8(10)	−0.4(11)
F3	7.4(12)	26.2(33)	9.0(14)	−9.9(17)	2.3(10)	−5.4(17)
F4	6.4(11)	16.2(21)	10.6(14)	4.0(13)	−2.7(10)	−0.8(14)
F5	7.7(10)	15.3(17)	5.2(9)	−8.2(12)	1.5(8)	−1.7(10)
F6	7.7(11)	12.0(15)	5.5(9)	0.1(11)	−1.3(8)	−2.1(10)

Table 3. Bond lengths (Å) in the anion, with standard deviations.

C1 – S1 = 1.673(21)	S2 – O4 = 1.431(16)
C1 – S2 = 1.631(22)	C2 – F1 = 1.38(5)
S1 – C2 = 1.851(35)	C2 – F2 = 1.28(3)
S1 – O1 = 1.420(19)	C2 – F3 = 1.27(4)
S1 – O2 = 1.427(20)	C3 – F4 = 1.36(4)
S2 – C3 = 1.864(30)	C3 – F5 = 1.29(3)
S2 – O3 = 1.434(19)	C3 – F6 = 1.30(3)

rubidium and sulfur were corrected for anomalous dispersion. A list of final observed and calculated structure factors can be obtained from the author S.H. upon request. Atomic coordinates and temperature parameters are shown in Tables 1 and 2. The final bond lengths and angles are listed in Tables 3 and 4, respectively.

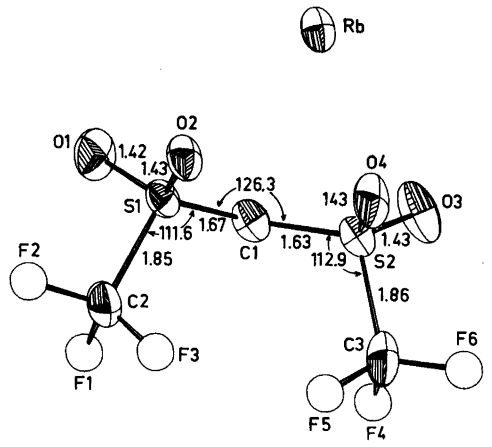


Fig. 1. Rubidium bis(trifluoromethanesulfonyl)-methane as seen along *b*. Bond lengths in Å, angles in degrees.

RESULTS AND DISCUSSION

The structure of the anion. From Fig. 1 it can be seen that the bis(trifluoromethanesulfonyl)methane anion, HA^-, has the *cis* configuration. The anion contains an approximate mirror plane which is perpendicular to the S – C – S plane and passes through the central carbon atom. The related dibenzenesulfonamide anion, also has the *cis* configuration, while the parent acid occurs in the *trans* configuration.[10] The *cis* configuration allows a closer approach of the negatively charged oxygen and central carbon atoms to the cation, and should thus be the preferred configuration in anions of this type. In the parent acid, bis(trifluoromethanesulfonyl)methane, H_2A, the preferred configuration will probably be the one that best minimizes steric repulsions in the neutral molecule. This may indicate a *trans* configuration of the trifluoromethyl groups in H_2A. However, the related sulfone, $(Br-ArSO_2)CH_2$ occurs in the *cis* configuration.[11]

The coordination about the central carbon atom (including the hydrogen atom) is probably planar. Both central carbon to sulfur bonds are strong. The average value, 1.65 Å is much less than 1.78 Å, the sum of covalent radii for sulfur and sp^2 hybridized carbon. This shows that there is appreciable double bond character in those bonds. According to the VSEPR theory[12] the corresponding inter-bond angle, S – C – S, should then be larger than the

Table 4. Bond angles in the anion (°) with standard deviations.

∠S1 – C1 – S2 = 126.3(1.3)	∠S1 – C2 – F1 = 110.8(2.1)
∠C1 – S1 – C2 = 111.6(1.1)	∠S1 – C2 – F2 = 109.3(2.7)
∠C1 – S1 – O1 = 109.2(1.1)	∠S1 – C2 – F3 = 109.6(2.2)
∠C1 – S1 – O2 = 112.9(1.0)	∠F1 – C2 – F2 = 109.3(2.7)
∠C2 – S1 – O1 = 102.6(1.3)	∠F1 – C2 – F3 = 107.9(2.6)
∠C2 – S1 – O2 = 101.6(1.4)	∠F2 – C2 – F3 = 111.5(3.1)
∠O1 – S1 – O2 = 118.4(1.0)	∠S2 – C3 – F4 = 106.6(1.9)
∠C1 – S2 – C3 = 112.9(1.0)	∠S2 – C3 – F5 = 111.4(1.6)
∠C1 – S2 – O3 = 109.6(1.1)	∠S2 – D3 – F6 = 108.7(1.8)
∠C1 – S2 – O4 = 113.4(0.9)	∠F4 – C3 – F5 = 109.8(2.3)
∠C3 – S2 – O3 = 102.6(1.1)	∠F4 – C3 – F5 = 108.1(2.0)
∠C3 – S2 – O4 = 100.2(1.1)	∠F5 – C3 – F6 = 112.1(2.4)
∠O3 – S2 – O4 = 117.7(1.0)	

normal sp^2 angle of 120°. The experimental value of 126.3(1.3)° is in good agreement with this. Also intramolecular S–S and F–F repulsion may contribute to the widening of the angle. For example, the S···S nonbonded distance across this angle is only 2.894(7) Å while the F3···F5 distance is 2.66(3) Å, as compared to van der Waals contacts of 3.7 and 2.7 Å, respectively.

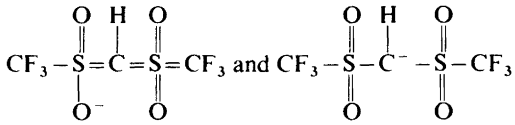
In the anion $(CH_3SO_2)_3C^-$, the average $C_{sp^2}-S$ bond length is 1.70 Å,[13] which is greater than that found in the present investigation. In the sulfones $(RSO_2)_2C=C-NR$,[14-16] the average central carbon to sulfur bond length is 1.73 Å. This demonstrates the influence of the electron withdrawing group CF_3 on the degree of double bonding to sulfur.

The coordination about the sulfur atoms is approximately tetrahedral, with an average S–O bond length of 1.428 Å. This is a value which is normal for sulfones and corresponds to a double bond order of *ca.* 0.7.[17] In tris(methanesulfonyl)-methane and its anion, the average S–O bond lengths are 1.435 and 1.43 Å, respectively.[13] The average central carbon to sulfur bond length of 1.65 Å corresponds to a double bond order of 0.55. Thus the total double bond order around each sulfur atom is approximately two in good agreement with Cruickshanks assumption that the outer d_{z^2} and $d_{x^2-y^2}$ orbitals on sulfur will overlap with *p*-orbitals on coordinated atoms to give π-bonds.[17] The bond angles centered on sulfur vary between 102 and 118°, the O–S–O angles being significantly larger than the others. This is probably chiefly due to nonbonded repulsion between the coordinated atoms and to the double bond character of the S–O bonds.[12]

Between trifluoromethyl carbon and sulfur, the average bond length is 1.86 Å. This is longer than the covalent single bond of 1.81 Å and the corresponding distance of 1.827(5) Å found in trifluoromethylsulfonic acid hydrate, $CF_3SO_2H.H_2O$,[19] but the differences are not significant. The strong electron withdrawing substituents (fluorine atoms bonded to carbon, oxygen atoms bonded to sulfur) may lead to partial positive charges on the neighbour carbon and sulfur atoms. The resulting repulsion would then tend to lengthen the F_3C-S bond, and thus the apparent bond lengthening found in the present investigation may be real.

The C–F bond lengths have an average value of 1.31 Å. This is a normal value, but the spread in C–F bond lengths is large and reflects the low quality of the intensity data.

The ionic charge is delocalized over the entire $O_2S-C-SO_2$ part of the ion as illustrated by resonance forms of the types



This is also in agreement with the observed bond lengths and angles discussed earlier and explains the strong acidity of the parent acid. A similar result is found for the related anion in the sodium salt of dibenzenesulfonamide.[10]

In the parent acid, H_2A, the central carbon atom is sp^3-hybridized, and there are no orbitals on this atom available for π-overlap with *d*-orbitals on sulfur. Therefore the central carbon to sulfur bonds should be normal, single bonds.

Coordination about the Rb^+ ion. Each cation is surrounded by seven oxygen atoms and one carbon atom coming from six different anions, *cf.* Fig. 2. The coordination geometry is highly irregular. Table 5 shows the relevant distances.

Molecular packing. The packing of ions, Rb^+ and $(CH_3SO_2)_2CH^-$ in the unit cell is shown in Fig. 3. The cations and the anions are arranged in separate layers parallel to (100). The sequence is –cation–anion–anion–cation–layers. Within a double layer of anions, the CF_3 groups from one of the two layers point towards the CF_3 groups from the other layer. This arrangement makes it possible for the oxygen atoms to point towards the cation

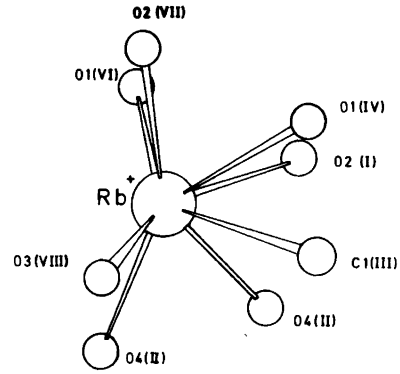


Fig. 2. The rubidium ion and its nearest neighbours. For notations, see Table 5.

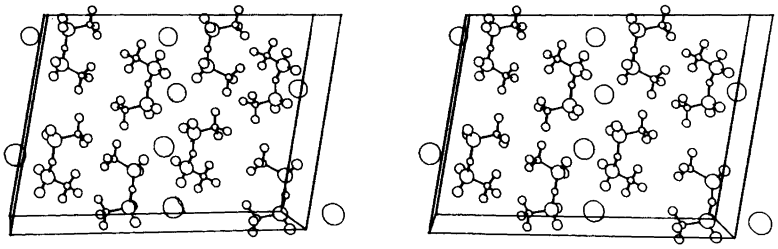


Fig. 3. The packing of the ions in the unit cell, as seen along *b*.

Table 5. Distances from the rubidium ion to its nearest neighbours (Å) with standard deviations. The symmetry operation that generates the second atom is given in the right column.

Rb–O2 (I)	=2.95(2)	$\frac{1}{2}+x, -\frac{1}{2}+y, z$
Rb–O4 (II)	=2.91(3)	$\frac{1}{2}+x, -\frac{1}{2}+y, z$
Rb–C1 (III)	=3.62(3)	$\frac{1}{2}+x, \frac{1}{2}+y, z$
Rb–O1 (IV)	=3.45(3)	$\frac{1}{2}+x, \frac{1}{2}+y, z$
Rb–O4 (V)	=3.15(2)	$\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$
Rb–O1 (VI)	=2.93(2)	$\frac{1}{2}-x, -\frac{1}{2}-y, -z$
Rb–O2 (VII)	=2.99(2)	$\frac{1}{2}-x, \frac{1}{2}-y, -z$
Rb–O3 (VIII)	=2.85(2)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$

layers. Thus each cation layer is electrostatically attracted to two anion layers, chiefly through oxygen. Between neighbour anion layers, there are strong repulsive forces operating. This repulsion is due to the partial negative charge on the very electronegative fluorine atoms which form the only nearest neighbour contacts between the anion layers. It is characteristic that all such F···F contacts are greater than van der Waals contacts. This repulsive force operating between anion layers also explains the strong flaking tendency parallel to (100) in the crystals. It may also partly explain the large thermal parameters found for the fluorine atoms.

Distances from the expected hydrogen position to other atoms were calculated, but no short contacts were found.

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