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Hydrogen-Bond Studies. XXXVI.[1] The Crystal Structure of the 1:1 Addition Compound of Acetic Acid with Fluorosulfuric Acid

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The crystal structure of $CH_3COOH \cdot HSO_3F$ has been determined from three-dimensional single-crystal X-ray data obtained at −57°. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a cell of dimensions $a = 7.732$ (9) Å, $b = 8.093$ (5) Å, $c = 9.982$ (2) Å, and $\beta = 108.06$ (9)°. The acetic acid exists in the form of $CH_3C(OH)_2^+$ ions (acetate acidium ions), in which one proton is attached to each of the two oxygen atoms. The $CH_3C(OH)_2^+$ and SO_3F^- ions are hydrogen bonded to each other forming infinite chains parallel to the *b* axis. The $O\text{–}H \cdots O$ bond lengths are 2.568 (6) and 2.583 (6) Å. The S–O distances within the fluorosulfate group are 1.418 (5), 1.429 (4), and 1.432 (4) Å; the S–F distance is 1.561 (4) Å. In the $CH_3C(OH)_2^+$ ion the C–C distance is 1.469 (8) Å; the two C–O distances are 1.261 (7) and 1.273 (7) Å. The above distances are not corrected for thermal motion.

Introduction

Acetic acid forms addition compounds with several strong acids. The present investigation forms part of a series of structure determinations of these addition compounds. The structure of $CH_3COOH \cdot H_2SO_4$ has been reported in an earlier paper.[2]

The 1:1 addition compound of acetic acid and fluorosulfuric acid has been isolated by Paul and coworkers.[3] The melting point is 52.5°.

In this paper the crystal structure of $CH_3COOH \cdot HSO_3F$ as determined from three-dimensional X-ray data will be presented. It will be shown below that the compound can be formulated as acetate acidium fluorosulfate ($CH_3C(OH)_2^+SO_3F^-$).

Experimental Section

Fluorosulfuric acid was purified by distilling technical grade fluorosulfuric acid. Water-free acetic acid was prepared from acetic acid, *pro analysi*, by distillation followed by repeated recrystallization. Equimolar quantities of acetic acid and fluorosulfuric acid were mixed; the solid reaction product was recrystallized from nitromethane and dried under vacuum. Single crystals were grown in glass capillaries (wall thickness about 0.02 mm) by a zone-melting technique.

A cylindrical crystal with a diameter of 0.20 mm and a length of about 0.6 mm was used when the intensity data were collected. The crystal was rotated about the *a* axis, which was closely parallel to the glass capillary.

The intensity data were recorded in a low-temperature camera.[4] Equiinclination Weissenberg photographs, layers $0 \leq h \leq 7$, were taken at −57 ± 2° with Cu Kα radiation using the multiple-film method (five films). The relative intensities were measured visually by comparison with an intensity scale. The intensity range was 1–5000. The data were corrected for Lorentz and polarization effects and for absorption (cylindrical specimen, $\mu = 46.9$ cm^{-1}), using a local modification of the program ERLPA.[5] The number of independent reflections recorded was 1236, of which 194 were too weak to be measured. About 80% of the reflections within the copper reflection sphere were recorded.

The *b* and *c* dimensions of the unit cell were obtained from zero-layer oscillation photographs and the *a* dimension was obtained from a rotation photograph. Each of these photographs was taken at −57° and calibrated with a quartz single crystal at +24°. All exposures were recorded on the same film without removing the film from the cassette (λ(Cu Kα_1) 1.54051 Å, λ(Cu Kα_2) 1.54433 Å, λ(Cu Kβ) 1.39217 Å; $a = 4.913$ Å and $c = 5.405$ Å for α-quartz at +24°). The β angle was calculated by the method of angular lag.[6]

The diffraction symmetry and systematic absences as observed from the Weissenberg photographs suggested the space group $P2_1/c$ (no. 14[7]). The crystal data are as follows: acetate acidium fluorosulfatefor mula weight 160.12; $CH_3C(OH)_2^+SO_3F^-$; monoclinic; $a = 7.732$ (9) Å, $b = 8.093$ (5) Å, $c = 9.982$ (2) Å, $\beta = 108.06$ (9)°; $V = 593.8$ Å^3; $D_x = 1.791$ g cm^{-3}; $Z = 4$.

Determination of the Atomic Coordinates

The position of the sulfur atom was determined from the Harker vectors and the rest of the atoms in the fluorosulfate group from the general vectors in a three-dimensional Patterson synthesis. The remaining carbon and oxygen atoms were located from a three-dimensional F_o synthesis. All atoms are in general fourfold positions of the space group $P2_1/c$. The preliminary atomic coordinates were improved in a series of three-dimensional electron density calculations.

The atomic coordinates, individual isotropic thermal parameters, and interlayer scale factors were further refined by the method of least squares using the full-matrix program LALS. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, and the weighting scheme used was $w = 1/(a + |F_o| + c|F_o|)^2$ with $a = 4.0$ and $c = 0.03$ (these values were based on the results of the weight analysis). Several cycles of refinement reduced the discrepancy index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, to 0.125. Unobserved reflections were given zero weight in all calculations. Twenty reflections which were inaccurately measured because of large intensity on the last film or spot deformation were excluded in the final refinements. These reflections are not included in the calculation of the *R* values.

A few cycles of anisotropic refinement reduced the *R* value to 0.097. The parameters varied were atomic

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(4) I. Olovsson, *Arkiv Kemi*, **16**, 437 (1960).

(5) J. H. van den Hende, Report CBRL-27M-62 Esso Research and Engineering Co., 1962.

(6) M. J. Buerger, "X-Ray Crystallography," John Wiley & Sons, Inc., New York, N. Y., 1962.

(7) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 99.

coordinates, anisotropic thermal parameters, and an over-all scale factor making a total number of 82 parameters as compared to 44 in the isotropic case. The interlayer scale factors were fixed to the values obtained in the last cycle of isotropic refinement. The final shifts of the atomic parameters were all smaller than 0.02σ.

A difference Fourier synthesis based on reflections with $(\sin\theta)/\lambda$ less than 0.5 Å^{-1} was calculated in order to locate the hydrogen atoms. Positions for all five hydrogen atoms could be determined from the difference maps. The peak heights in e^- Å^{-3} for the hydrogens were: H(1), 0.57; H(2), 0.32; H(3), 0.73; H(4), 0.73; H(5), 0.83. Some other spurious peaks of height less than 0.73 e^- Å^{-3} could be definitely excluded as possible hydrogen positions.

Some cycles of anisotropic least-squares calculations were performed with the five hydrogen atoms included with fixed parameters. The isotropic thermal parameter used for the hydrogen atoms was 4.0 Å^2. The R value decreased to 0.090. Refinement of the positional parameters for the hydrogen atoms did not significantly improve the result. Tables I–IV show the atomic parameters and their estimated standard deviations. The refined hydrogen positions obtained are listed in Table IV. The root-mean-square components of thermal displacement along the principal axes of the ellipsoids are given in Table III. The observed and calculated structure factors are compared in Table V. Bond distances and angles are listed in Table VI. Distances corrected for thermal riding motion are also listed in Table VI. As no experimental scaling of the individual films has been done, the thermal parameters may be inaccurate and the distances corrected for thermal motion have therefore not been used in the discussion.

TABLE I

ATOMIC COORDINATES[a] (×10^4)

Atom	x	y	z
S	2224 (2)	2702 (2)	4590 (1)
O(1)	1472 (6)	1107 (5)	4126 (5)
O(2)	990 (6)	4012 (5)	3985 (5)
O(3)	4052 (6)	2953 (6)	4622 (5)
F	2293 (6)	2730 (5)	6170 (4)
O(4)	2978 (6)	8972 (5)	2917 (5)
O(5)	1709 (6)	7098 (5)	3876 (5)
C(1)	2601 (8)	7462 (6)	3052 (5)
C(2)	3229 (8)	6235 (7)	2222 (6)

[a] Standard deviations are given in parentheses.

TABLE II

ANISOTROPIC THERMAL PARAMETERS IN THE FORM $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ (×10^4)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	95 (3)	68 (2)	71 (2)	7 (3)	27 (3)	2 (2)
O(1)	126 (9)	80 (6)	122 (6)	−27 (10)	45 (11)	−10 (9)
O(2)	105 (8)	86 (6)	124 (6)	22 (10)	26 (10)	28 (9)
O(3)	90 (9)	142 (8)	119 (6)	−7 (11)	31 (10)	14 (10)
F	185 (10)	178 (8)	95 (5)	−7 (12)	84 (10)	−10 (9)
O(4)	154 (9)	70 (6)	109 (6)	−9 (10)	69 (11)	27 (8)
O(5)	124 (9)	84 (6)	98 (5)	−9 (10)	71 (10)	−4 (8)
C(1)	113 (12)	86 (8)	61 (5)	11 (12)	−12 (12)	9 (10)
C(2)	129 (12)	105 (9)	83 (7)	4 (15)	56 (13)	−11 (12)

[a] Standard deviations are given in parentheses.

TABLE III

ROOT-MEAN-SQUARE COMPONENTS R_i (Å) OF THERMAL VIBRATION ALONG PRINCIPAL AXES OF THE ELLIPSOIDS OF VIBRATION (×10^3)[a]

Atoms	R_1	R_2	R_3
S	149 (3)	159 (4)	191 (3)
O(1)	157 (9)	190 (9)	245 (7)
O(2)	156 (11)	179 (10)	253 (8)
O(3)	156 (8)	215 (7)	245 (8)
F	207 (6)	225 (6)	244 (6)
O(4)	149 (8)	205 (7)	229 (8)
O(5)	166 (7)	184 (8)	211 (5)
C(1)	142 (14)	171 (9)	214 (14)
C(2)	184 (12)	187 (10)	201 (14)
H(1)–H(5)	225	225	225

[a] Standard deviations are given in parentheses.

TABLE IV

ATOMIC COORDINATES (×10^3) AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS

Atoms	x	y	z	B, Å^2
C(2)–H(1)	387	542	293	4.0
C(2)–H(2)	449	691	194	4.0
C(2)–H(3)	208	564	149	4.0
O(4)–H(4)	239	972	360	4.0
O(5)–H(5)	161	586	389	4.0

The atomic scattering factors used for neutral S, O, F, and C were those given in ref 8. The spherical scattering factor proposed by Stewart, Davidson, and Simpson[9] was used for the hydrogen atoms.

Computer Programs.—The calculations were all done on the CD 3600 computer in Uppsala. The following programs were used: CELSIUS, DRF, LALS, DISTAN, ORFFE, PLANE, ERLPA, and ORTEP. References to these programs except ERLPA and PLANE have been given elsewhere.[10,11]

Discussion of the Structure

General Data.—A stereoscopic illustration of the structure is found in Figure 1. The covalent bond lengths and the hydrogen positions clearly show that the structure consists of SO_3F^- and $CH_3C(OH)_2^+$ (acetate acidium) ions. These ions are linked to each other by hydrogen bonds (2.568 and 2.583 Å) forming chains parallel to the b axis. These O–H···O hydrogen-bond lengths (Table VI) are not significantly different (2σ). The acceptor atoms are O(1) and O(2) in the fluorosulfate ion whereas O(3) and F are not engaged in hydrogen bonding.

The Fluorosulfate Ion.—The fluorosulfate group forms a distorted tetrahedron (Table VI) with the three S–O distances (1.429, 1.432, and 1.418 Å) slightly shorter than those found in the HSO_4^- ion.[2,12] The

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TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS. THE THREE COLUMNS ARE IN THE ORDER: l, $|F_o|$, $|F_c|$[a]

l	$\|F_o\|$	$\|F_c\|$
0, 0, L		
2	31.9	36.7**
4	17.4	17.3
6	24.7	23.1
8	5.7	5.3
10	0	2.0*
12	13.9	15.3
0, 1, L		
1	14.3	14.3
2	3.3	2.8
3	18.0	18.8
4	51.3	64.4**
5	19.7	19.1
6	43.4	45.0
7	11.8	11.1
8	24.3	24.0
9	0	2.5*
10	4.1	4.1
11	0	0.0*
12	4.1	4.0
0, 2, L		
0	49.8	114.9**
1	5.8	5.4
2	45.6	52.4
3	5.6	4.1
4	2.5	1.3
5	12.4	10.9
6	0	1.3*
7	17.3	16.3
8	0	3.9*
9	0	3.4*
10	9.5	6.8
11	0	1.9*
12	8.0	12.8
0, 3, L		
1	34.8	41.5
2	37.0	40.8
3	15.0	14.0
4	12.1	10.5
5	13.3	12.3
6	43.4	46.2
7	9.3	8.2
8	30.0	28.7
9	0	3.2*
10	5.3	4.7
11	4.7	3.5
0, 4, L		
0	17.1	18.8
1	19.0	18.8
2	34.3	35.1
3	4.1	4.0
4	4.4	3.4
5	23.6	24.2
6	14.8	12.8
7	21.8	21.4
8	6.0	4.6
9	10.1	8.2
10	11.1	9.4
11	3.5	2.7
0, 5, L		
1	40.5	46.4
2	11.8	9.9
3	0	1.9*
4	23.4	22.4
5	7.1	6.6
6	18.2	17.0
7	12.6	9.9
8	18.4	16.3
9	0	0.9*
10	0	2.4*
0, 6, L		
0	41.4	50.7
1	5.4	5.6
2	9.8	8.9
3	8.0	7.7
4	0	0.4*
5	26.4	24.8
6	6.0	4.3
7	20.2	17.7
8	7.4	6.6
9	7.6	6.5
10	0	0.3*
0, 7, L		
1	30.8	33.2
2	11.6	10.7
3	8.0	7.2
4	23.6	22.9
5	5.2	3.5
6	0	1.2*
7	0	3.4*
8	0	3.1*
9	0	0.3*
0, 8, L		
0	24.8	21.5
1	5.2	4.4
2	0	0.4*
3	4.2	3.8
4	7.0	4.8
5	18.2	15.5
6	0	2.5*
7	14.8	14.1
0, 9, L		
1	18.8	16.5
2	0	1.4*
3	10.9	9.4
4	0	2.7*
5	0	3.0*
6	3.0	3.0
0,10, L		
0	9.7	7.8
1	4.0	2.1
2	0	0.5*
3	0	4.8*
1, 0, L		
-12	4.6	4.6
-10	0	0.1*
-8	5.0	4.3
-6	44.3	60.6**
-4	52.9	86.4**
-2	37.0	58.6**
2	60.2	97.8**
4	?	3.0*
6	24.7	25.4
8	15.1	14.1
10	7.0	5.7
1, 1, L		
-12	8.3	6.7
-11	0	1.1*
-10	19.8	19.1
-9	0	0.9*
-8	5.2	4.2
-7	0	1.9*
-6	8.7	8.3
-5	5.9	5.0
-4	4.6	2.7
-3	19.8	21.5
-2	59.5	102.7**
-1	0	6.1*
0	35.4	48.1**
1	3.8	3.2
2	63.9	94.7**
3	7.1	6.1
4	3.7	2.9
5	0	1.7*
6	7.5	6.0
7	0	1.0*
8	0	0.6*
9	10.9	8.4
10	14.3	12.0
11	0	0.1*
1, 2, L		
-12	3.7	3.7
-11	8.0	6.6
-10	4.7	5.1
-9	0	3.3*
-8	16.6	17.1
-7	11.8	11.6
-6	34.2	38.9
-5	19.1	20.9
-4	28.8	32.7
-3	19.0	19.0
-2	22.8	26.0
-1	17.8	18.7
0	5.4	4.5
1	18.4	19.5
2	5.7	6.9
3	0	0.3*
4	17.2	17.7
5	23.3	24.3
6	30.3	34.1
7	4.0	4.0
8	19.9	19.4
9	0	2.1*
10	5.3	4.4
11	7.2	5.7
1, 3, L		
-11	2.9	3.0
-10	15.3	13.0
-9	0	2.7*
-8	5.0	4.0
-7	10.6	9.1
-6	13.4	12.6
-5	15.5	14.6
-4	17.2	18.3
-3	23.4	26.2
-2	21.9	20.5
-1	11.1	10.2
0	36.8	45.6
1	5.8	5.0
2	38.3	46.0
3	3.9	3.3
4	34.7	39.1
5	11.1	10.3
6	2.3	1.8
7	8.9	7.5
8	10.7	9.1
9	11.1	9.1
10	14.2	12.9
11	0	1.6*
1, 4, L		
-11	7.8	6.8
-10	8.5	7.4
-9	11.1	9.1
-8	17.0	16.7
-7	4.8	3.2
-6	23.1	24.8
-5	0	0.9*
-4	0	0.6*
-3	11.2	9.6
-2	9.9	8.0
-1	10.5	10.7
0	7.5	6.8
1	23.6	23.4
2	14.2	14.1
3	30.9	34.6
4	17.6	17.7
5	3.9	3.7
6	27.1	31.6
7	0	2.5*
8	18.1	15.5
9	6.5	5.9
10	4.2	3.1
1, 5, L		
-11	0	2.4*
-10	9.2	8.7
-9	3.5	3.5
-8	0	1.4*
-7	13.1	12.1
-6	3.4	2.2
-5	23.3	24.6
-4	8.6	9.0
-3	14.7	14.7
-2	18.7	18.4
-1	17.5	19.0
0	21.3	22.8
1	11.4	10.5
2	21.9	22.1
3	12.6	11.7
4	11.1	10.9
5	12.6	11.5
6	9.5	8.2
7	16.6	14.6
8	0	1.8*
9	0	1.4*
10	8.6	9.5
1, 6, L		
-10	0	1.6*
-9	12.0	12.1
-8	4.4	2.9
-7	6.2	4.6
-6	24.1	24.6
-5	0	2.5*
-4	13.4	12.1
-3	16.6	16.7
-2	11.0	9.4
-1	14.7	15.9
0	12.5	12.1
1	21.7	23.5
2	25.2	25.7
3	22.0	24.1
4	3.5	2.7
5	4.6	3.5
6	17.2	15.4
7	0	0.8*
8	4.4	3.4
9	8.7	7.8
1, 7, L		
-9	4.6	4.8
-8	0	0.0*
-7	11.0	9.4
-6	6.0	4.0
-5	19.9	18.4
-4	0	1.8*
-3	20.5	20.6
-2	32.4	37.1
-1	0	0.3*
0	11.8	11.4
1	8.7	8.3
2	14.7	14.1
3	14.3	14.4
4	15.5	14.0
5	9.9	7.8
6	7.0	6.3
7	11.4	9.2
8	3.2	2.6
1, 8, L		
-8	3.8	4.0
-7	0	3.3*
-6	10.9	9.8
-5	8.9	8.0
-4	6.5	5.5
-3	10.6	8.5
-2	0	0.2*
-1	15.8	14.4
0	4.8	4.1
1	18.8	17.8
2	14.7	12.6
3	9.7	7.2
4	3.5	3.2
5	8.2	6.4
6	9.2	8.2
7	3.4	3.5
1, 9, L		
-6	0	0.8*
-5	10.6	9.6
-4	0	1.7*
-3	12.8	10.9
-2	6.2	6.2
-1	0	1.0*
0	3.4	3.6
1	5.8	4.5
2	5.6	5.7
3	7.7	6.7
4	0	2.0*
5	10.4	9.0
1,10, L		
-3	5.7	5.6
-2	4.8	4.1
-1	9.8	9.6
0	2.8	2.2
1	10.7	10.2
2	5.3	5.1
3	4.6	8.8
2, 0, L		
-12	14.3	13.1
-10	0	0.4*
-8	17.0	16.4
-6	20.6	21.7
-4	24.5	27.1**
-2	31.5	50.3**
2	40.3	41.0
4	20.0	22.3
6	7.3	7.1
8	0	1.8*
10	4.1	3.3
2, 1, L		
-12	3.3	3.1
-11	0	1.0*
-10	0	1.2*
-9	4.8	4.5
-8	26.2	27.7
-7	6.5	5.7
-6	40.5	41.0
-5	19.5	18.7
-4	30.4	32.6
-3	18.2	19.8
-2	18.5	19.9
-1	0	4.5*
1	12.4	11.3
2	36.1	40.6
3	9.3	9.2
4	27.9	29.4
5	0	0.9*
6	16.7	17.0
7	7.8	7.0
8	13.9	13.7
9	2.8	3.0
10	0	3.4*
11	0	2.0*
2, 2, L		
-12	10.8	10.7
-11	1.8	1.3
-10	0	1.4*
-9	4.7	5.0
-8	0	0.6*
-7	4.1	3.4
-6	4.0	2.5
-5	15.2	15.4
-4	17.7	14.5
-3	25.3	26.4
-2	28.4	28.7
-1	16.1	14.3
0	58.6	70.5
1	23.4	23.6
2	21.9	22.5
3	11.3	11.1
4	4.1	2.2
5	0	1.3*
6	3.5	2.9
7	17.6	18.5
8	5.6	6.2
9	0	1.6*
10	6.5	5.4
11	0	1.0*
2, 3, L		
-12	0	0.4*
-11	0	0.9*
-10	11.7	11.2
-9	0	1.9*
-8	18.5	18.4
-7	0	1.3*
-6	14.2	12.9
-5	17.4	18.0
-4	5.4	5.6
-3	3.2	2.0
-2	12.9	12.2
-1	14.3	15.8
0	48.6	49.7
1	14.1	14.7
2	7.4	6.2
3	0	1.3*
4	27.9	27.8
5	0	0.4*
6	31.6	34.3
7	6.1	5.5
8	11.7	11.0
9	0	2.6*
10	3.0	2.8
2, 4, L		
-11	0	1.3*
-10	4.1	3.5
-9	7.9	7.1
-8	8.1	6.9
-7	14.6	13.6
-6	8.1	8.9
-5	5.1	4.7
-4	16.6	16.4
-3	4.2	3.7
-2	13.2	12.9
-1	3.7	3.8
0	31.4	34.3
1	23.0	22.3
2	35.4	39.7
3	4.4	4.0
4	0	0.3*
5	15.9	16.4
6	0	3.2*
7	6.7	6.2
8	12.4	11.8
9	0	1.4*
10	4.9	5.4
2, 5, L		
-11	5.2	5.5
-10	6.0	5.6
-9	3.9	3.7
-8	17.5	16.5
-7	11.1	11.4
-6	12.9	11.5
-5	0	0.5*
-4	16.4	16.0
-3	3.2	2.8
-2	12.3	11.9
-1	27.8	29.0
0	0	1.1*
1	28.7	28.9
2	0	2.5*
3	9.9	9.6
4	20.2	21.0
5	0	1.1*
6	17.2	15.0
7	2.9	3.8
8	10.2	9.2
9	0	1.5*
2, 6, L		
-10	0	1.4*
-9	5.7	5.5
-8	6.3	5.7
-7	20.4	18.4
-6	0	2.0*
-5	8.1	7.5
-4	20.0	21.3
-3	6.6	6.3
-2	16.7	15.5
-1	2.4	2.5
0	31.3	32.1
1	4.6	4.0
2	4.0	4.0
3	4.6	4.3
4	6.4	5.6
5	20.7	18.0
6	0	1.3*
7	4.2	3.2
8	6.4	7.2
9	0	3.6*
2, 7, L		
-9	0	1.3*
-8	10.5	9.8
-7	4.2	4.0
-6	15.4	12.9
-5	0	0.5*
-4	17.4	18.2
-3	10.1	10.2
-2	5.2	5.0
-1	25.3	26.1
0	25.4	26.8
1	10.7	10.3
2	3.5	3.8
3	0	0.3*
4	14.8	13.6
5	0	1.7*
6	0	0.6*
7	0	0.2*
8	0	6.0*
2, 8, L		
-8	3.6	4.0
-7	11.8	11.7
-6	5.6	4.5
-5	13.7	12.8
-4	13.3	13.0
-3	4.8	4.1
-2	7.9	6.7
-1	0	1.1*
0	17.4	17.3
1	0	1.3*
2	0	2.8*
3	3.9	4.0
4	0	1.3*
5	11.7	10.5
6	3.0	3.1
2, 9, L		
-6	2.8	3.5
-5	0	0.5*
-4	4.1	3.8
-3	11.3	10.8
-2	0	1.4*
-1	14.5	14.0
0	3.9	4.6
1	10.5	9.1
2	6.0	5.7
3	5.7	5.9
4	7.6	7.8
5	0	0.6*
2,10, L		
-3	0	1.8*
-2	0	0.9*
-1	0	0.4*
0	2.6	2.3
1	0	0.2*
2	0	7.9*
3, 0, L		
-12	1.9	2.0
-10	0	3.2*
-8	8.9	9.2
-6	38.7	55.4**
-4	19.0	25.2**
2	26.5	27.1
4	33.7	37.7
6	17.4	20.6
8	13.1	13.3
10	0	1.3*
3, 1, L		
-12	7.9	7.1
-11	0	1.0*
-10	17.0	15.4
-9	4.2	3.6
-8	13.7	13.1
-7	7.7	8.5
-6	23.1	24.8
-5	10.1	10.0
-4	4.7	4.5
-3	9.5	7.8
-2	25.4	23.1
-1	0	20.3*
1	14.3	13.8
2	23.7	23.0
3	13.4	12.8
4	9.5	9.0
5	9.6	9.4
6	15.8	17.0
7	0	0.4*
8	5.9	4.7
9	5.2	4.9
10	7.6	8.4
3, 2, L		
-12	7.1	7.3
-11	5.2	4.6
-10	2.7	2.3
-9	6.3	5.6
-8	6.0	6.6
-7	0	0.8*
-6	28.0	29.3
-5	13.6	14.1
-4	13.8	12.9
-3	24.9	25.2
-2	8.2	6.9
-1	19.7	17.5
0	37.0	32.9
1	12.8	12.0
2	15.5	14.8
3	8.3	8.6
4	4.6	3.7
5	3.8	4.0
6	16.9	18.1
7	7.4	6.7
8	8.8	8.0
9	4.9	4.4
10	0	2.0*
3, 3, L		
-12	8.6	9.6
-11	2.5	2.7
-10	0	2.4*
-9	4.7	4.1
-8	15.8	16.7
-7	6.8	7.0
-6	7.1	6.2
-5	3.1	2.7
-4	11.8	11.2
-3	7.3	6.8
-2	7.6	5.9
-1	17.1	15.9
0	49.1	49.0
1	6.1	4.9
2	36.6	38.7
3	9.0	8.0
4	8.1	7.7
5	5.6	5.7
6	21.6	22.9
7	3.2	2.6
8	9.3	8.4
9	3.6	3.7
10	0	6.9*
3, 4, L		
-11	4.5	3.7
-10	3.5	3.6
-9	0	0.9*
-8	6.4	6.3
-7	11.7	11.5
-6	14.4	14.6
-5	0	2.3*
-4	5.6	4.7
-3	6.9	5.3
-2	19.6	20.6
-1	7.1	6.3
0	21.3	21.7
1	9.3	9.8
2	9.0	9.0
3	7.3	6.9
4	19.5	22.7
5	14.3	13.9
6	15.8	14.9
7	7.0	6.6
8	6.2	5.3
9	0	1.0*
3, 5, L		
-11	0	1.5*
-10	5.5	4.8
-9	2.5	2.3
-8	7.4	6.6
-7	0	1.2*
-6	10.0	10.0
-5	22.2	25.0
-4	4.4	4.1
-3	4.3	4.0
-2	15.0	17.4
-1	9.2	9.1
0	16.8	18.4
1	19.6	21.7
2	17.1	17.0
3	6.6	7.5
4	0	0.4*
5	7.0	6.4
6	13.9	13.7
7	7.1	6.5
8	2.8	3.1
3, 6, L		
-10	4.8	5.3
-9	3.3	3.2
-8	9.9	8.4
-7	12.3	11.9
-6	23.6	24.0
-5	3.9	2.9
-4	4.5	3.4
-3	5.7	6.1
-2	13.0	13.5
-1	7.2	7.5
0	9.6	10.7
1	11.0	12.0
2	13.2	14.8
3	2.2	1.6
4	5.5	1.4
5	10.8	10.5
6	14.3	14.0
7	5.5	5.0
8	4.6	6.1
3, 7, L		
-9	3.3	4.5
-8	0	0.5*
-7	8.7	8.3
-6	9.5	8.1
-5	15.2	14.2
-4	12.4	12.5
-3	0	1.0*
-2	24.1	26.6
-1	14.0	14.5
0	0	1.2*
1	10.6	10.8
2	4.5	3.8
3	3.6	3.4
4	0	1.2*
5	2.9	2.7
6	0	2.8*
7	5.1	7.8
3, 8, L		
-8	5.0	6.8
-7	5.0	4.7
-6	12.5	11.3
-5	10.6	10.3
-4	4.1	3.4
-3	5.2	5.5
-2	6.9	7.0
-1	3.4	2.9
0	0	1.3*
1	14.2	13.7
2	12.2	12.5
3	5.7	4.5
4	0	0.9*
5	0	0.5*
3, 9, L		
-6	2.0	2.0
-5	5.0	4.8
-4	4.9	5.4
-3	5.7	5.4
-2	9.6	9.6
-1	7.6	7.5
0	8.1	7.4
1	6.0	6.0
2	6.5	5.7
3	3.6	4.3
4, 0, L		
-12	11.2	10.9
-10	0	0.2*
-8	5.1	5.9
-6	24.6	30.7**
-4	33.3	48.6**
-2	0	7.8*
0	9.0	9.4
2	14.9	14.1
4	12.4	12.5
6	3.9	3.6
8	14.9	15.2
4, 1, L		
-12	5.7	5.3
-11	0	1.1*
-10	11.0	9.9
-9	0	0.6*
-8	24.5	27.7
-7	7.6	7.4
-6	12.0	12.3
-5	2.2	1.9
-4	15.1	15.0
-3	3.3	1.8
-2	33.1	34.2
-1	0	0.9*
0	37.2	38.5
1	3.1	2.0
2	5.5	4.1
3	10.9	9.5
4	28.5	31.0
5	0	0.9*
6	10.9	10.1
7	6.5	6.5
8	4.6	4.8
9	2.4	2.6
4, 2, L		
-12	5.9	6.2
-11	0	1.0*
-10	4.2	3.3
-9	9.4	9.7
-8	5.6	4.7
-7	8.9	9.3
-6	13.7	14.5
-5	4.8	4.5
-4	20.1	19.9
-3	26.8	25.1
-2	30.4	27.2
-1	17.1	16.1
0	29.9	33.2
1	3.4	3.5
2	7.5	5.9
3	14.3	14.6
4	14.3	15.6
5	7.6	7.2
6	11.7	12.0
7	9.2	8.7
8	13.0	12.9
9	6.3	6.8
4, 3, L		
-12	2.8	3.0
-11	0	0.2*
-10	11.4	11.5
-9	3.1	2.4
-8	6.7	6.3
-7	5.8	5.3
-6	7.6	7.2
-5	4.8	4.1
-4	19.5	21.5
-3	8.8	8.2
-2	17.5	15.3
-1	9.4	8.3
0	10.9	9.4
1	2.6	2.7
2	36.2	37.5
3	7.1	6.0
4	19.7	-22.0
5	5.4	5.2
6	11.6	10.1
7	7.6	7.2
8	0	0.2*
9	2.6	4.0
4, 4, L		
-11	4.2	3.2
-10	2.6	2.3
-9	6.1	5.9
-8	5.2	4.5
-7	8.7	8.3
-6	5.5	5.2
-5	4.6	3.7
-4	6.8	5.8
-3	0	1.7*
-2	23.3	24.9
-1	16.3	17.1
0	37.3	37.1
1	13.2	13.2
2	12.3	3.7
3	10.7	11.1
4	11.8	12.5
5	8.5	7.8
6	10.8	11.1
7	0	1.8*
8	9.9	10.9
4, 5, L		
-11	1.2	1.6
-10	7.6	7.8
-9	4.2	3.5
-8	11.9	11.4
-7	0	0.4*
-6	8.4	7.3
-5	12.3	12.7
-4	9.7	11.1
-3	18.6	21.4
-2	11.4	11.1
-1	13.2	14.0
0	9.5	9.0
1	0	1.0*
2	12.8	13.6
3	16.5	17.1
4	17.0	16.0
5	7.4	6.8
6	9.6	8.9
7	0	1.5*
8	0	2.4*
4, 6, L		
-10	1.7	1.9
-9	6.0	5.8
-8	2.7	2.5
-7	14.9	14.0
-6	11.7	10.7
-5	5.0	4.2
-4	17.9	20.0
-3	0	0.2*
-2	2.5	2.1
-1	16.2	17.6
0	13.2	12.8
1	11.8	12.1
2	3.6	3.3
3	9.3	8.4
4	0	1.6*
5	10.4	9.3
6	0	0.1*
7	0	1.0*
4, 7, L		
-9	0	0.1*
-8	13.7	14.1
-7	6.0	5.5
-6	8.6	8.1
-5	12.4	11.5
-4	4.7	1.2
-3	13.0	12.7
-2	6.7	6.5
-1	13.6	13.1
0	15.9	15.7
1	0	1.3*
2	8.3	7.8
3	0	0.9*
4	11.8	11.6
5	4.4	4.1
6	2.5	3.6
4, 8, L		
-7	4.2	5.2
-6	7.6	8.0
-5	4.3	4.1
-4	8.1	8.1
-3	7.4	6.9
-2	3.6	3.2
-1	0	1.4*
0	8.6	8.0
1	4.6	4.8
2	2.6	2.5
3	11.5	12.9
4	0	0.7*
4, 9, L		
-5	4.5	6.5
-4	7.3	7.2
-3	7.9	8.6
-2	0	0.5*
-1	10.1	10.9
0	4.9	5.8
1	5.6	6.4
2	2.2	3.0
5, 0, L		
-12	5.3	5.1
-10	14.5	15.4
-8	13.0	14.6
-6	23.2	30.1**
-4	6.0	6.8
-2	?	54.9*
0	16.7	17.9
2	25.9	26.0
4	4.0	3.1
6	24.1	24.9
8	5.5	6.3
5, 1, L		
-12	7.7	8.7
-11	2.6	2.3
-10	4.7	4.4
-9	3.6	3.3
-8	26.4	26.8
-7	8.2	8.5
-6	31.9	33.1
-5	10.9	10.1
-4	9.7	9.7
-3	10.7	11.0
-2	14.0	16.5
-1	5.9	4.8
0	31.5	24.8
1	3.0	1.9
2	15.6	16.3
3	6.8	6.3
4	10.7	9.9
5	10.9	11.0
6	23.3	24.8
7	0	1.8*
8	7.1	8.9
5, 2, L		
-12	6.3	8.1
-11	1.5	1.3
-10	5.1	4.8
-9	7.1	6.2
-8	12.7	12.1
-7	9.4	9.7
-6	30.7	31.5
-5	2.0	1.9
-4	4.9	5.3
-3	5.9	2.6
-2	26.9	28.2
-1	9.4	7.5
0	41.3	40.5
1	28.4	25.3
2	25.4	23.4
3	2.4	3.2
4	9.3	9.0
5	13.7	14.4
6	15.2	15.1
7	6.8	7.1
8	3.7	4.7
5, 3, L		
-12	2.2	4.6
-11	3.0	3.2
-10	2.3	1.8
-9	0	0.2*
-8	14.5	13.6
-7	12.2	12.2
-6	10.9	9.6
-5	4.4	3.8
-4	14.3	13.6
-3	3.6	0.7
-2	37.0	33.5
-1	22.9	19.8
0	27.4	25.6
1	14.2	13.9
2	12.5	12.0
3	8.4	7.9
4	21.6	21.1
5	9.2	8.7
6	17.4	17.3
7	3.0	2.5
8	2.7	5.5
5, 4, L		
-11	2.0	2.0
-10	0	0.3*
-9	4.2	2.8
-8	9.6	8.9
-7	14.4	13.5
-6	21.2	22.2
-5	11.6	11.2
-4	7.3	7.9
-3	8.4	8.3
-2	5.3	4.3
-1	17.5	17.7
0	35.2	37.9
1	4.7	4.5
2	16.5	16.2
3	4.0	3.3
4	12.5	11.7
5	11.6	10.8
6	7.8	7.1
7	5.5	6.1
5, 5, L		
-10	2.4	2.1
-9	7.9	7.4
-8	9.1	8.2
-7	9.2	8.7
-6	12.3	11.4
-5	19.9	21.3
-4	6.8	5.4
-3	18.2	19.1
-2	17.9	20.0
-1	22.7	24.6
0	10.0	10.7
1	17.3	17.5
2	10.6	8.9
3	3.7	2.9
4	7.9	7.0
5	0	0.2*
6	11.9	12.5
5, 6, L		
-10	0	7.7*
-9	4.5	4.3
-8	6.9	6.1
-7	14.0	12.5
-6	10.7	9.9
-5	13.9	13.3
-4	3.7	3.1
-3	9.2	8.5
-2	10.9	9.8
-1	12.3	11.9
0	0	1.5*
1	7.7	6.9
2	13.2	11.6
3	3.1	3.5
4	4.5	4.0
5	6.5	6.7
6	0.0	9.3**
5, 7, L		
-8	5.5	5.3
-7	9.2	9.3
-6	11.0	11.1
-5	8.5	8.5
-4	4.5	4.2
-3	7.6	7.5
-2	5.8	5.2
-1	12.6	13.2
0	1.7	0.8
1	12.1	12.1
2	3.4	3.3
3	6.1	6.0
4	3.1	3.3
5, 8, L		
-7	3.3	8.7
-6	4.5	4.6
-5	5.3	6.0
-4	2.2	2.2
-3	6.6	6.5
-2	3.8	3.9
-1	7.6	8.1
0	1.9	2.2
1	13.1	15.3
2	6.8	8.3
3	0	0.4*
5, 9, L		
-3	0	2.5*
-2	3.4	5.4
-1	3.7	8.1
6, 0, L		
-12	5.0	7.1
-10	0	0.8*
-8	13.1	13.0
-6	16.9	26.7**
-4	12.7	23.4**
-2	0	11.2*
0	17.0	17.0
2	17.7	18.1
4	10.3	8.7
6	7.9	8.6
6, 1, L		
-12	6.3	10.9
-11	0	0.1*
-10	11.5	11.1
-9	0	1.3*
-8	17.5	16.6
-7	2.2	2.0
-6	4.3	3.8
-5	3.4	3.1
-4	6.1	6.4
-3	1.7	1.6
-2	2.4	3.2
-1	15.6	16.0
0	28.3	27.4
1	6.8	6.4
2	17.9	17.0
3	0	0.8*
4	24.1	26.2
5	4.0	4.0
6	6.1	6.4
7	4.6	5.8
6, 2, L		
-11	2.5	2.7
-10	0	0.7*
-9	6.0	5.5
-8	5.2	3.9
-7	8.9	7.3
-6	22.5	22.8
-5	14.3	14.5
-4	29.2	28.3
-3	5.1	4.3
-2	18.8	18.6
-1	7.3	6.2
0	22.2	18.6
1	17.7	16.2
2	0	1.0*
3	17.7	17.7
4	5.8	5.5
5	2.1	2.7
6	8.4	8.9
7	0	0.5*
6, 3, L		
-11	2.2	2.4
-10	9.6	9.9
-9	0	0.9*
-8	10.9	9.3
-7	3.0	2.0
-6	14.9	14.0
-5	14.4	12.8
-4	16.5	16.9
-3	11.2	10.7
-2	21.3	19.7
-1	14.3	13.2
0	26.1	23.7
1	7.4	7.3
2	22.6	22.4
3	0	1.4*
4	12.0	11.6
5	3.0	3.0
6	4.6	4.6
6, 4, L		
-11	2.4	5.6
-10	0	0.4*
-9	5.9	5.9
-8	0	0.3*
-7	10.1	9.3
-6	16.0	14.1
-5	3.1	3.0
-4	24.7	23.6
-3	0	0.4*
-2	15.6	13.8
-1	11.7	10.5
0	18.7	18.4
1	13.1	12.4
2	9.2	7.7
3	7.7	7.1
4	4.1	4.2
5	7.1	6.7
6	5.1	7.9
6, 5, L		
-10	4.7	6.5
-9	2.0	1.4
-8	7.5	6.6
-7	10.7	9.4
-6	0	5.8*
-5	18.2	16.8
-4	5.9	6.0
-3	19.8	19.7
-2	9.9	9.1
-1	1.2	1.4
0	16.7	14.5
1	1.7	1.5
2	11.5	11.9
3	2.2	2.1
4	10.6	10.1
5	0	0.3*
6, 6, L		
-9	4.0	6.1
-8	6.6	7.0
-7	8.9	9.5
-6	8.2	7.3
-5	1.2	1.3
-4	9.7	9.0
-3	2.4	1.8
-2	0	0.5*
-1	11.9	11.4
0	10.1	9.0
1	9.7	8.5
2	4.4	3.9
3	8.3	8.7
4	5.4	6.4
6, 7, L		
-7	6.2	7.8
-6	2.3	1.8
-5	10.8	11.2
-4	2.9	2.9
-3	9.6	10.5
-2	0	1.3*
-1	8.3	8.6
0	9.0	8.4
1	3.8	4.1
2	0	0.5*
3	0	2.2*
6, 8, L		
-5	3.3	5.5
-4	1.9	1.6
-3	1.8	1.9
-2	1.0	0.7
-1	3.1	3.8
0	1.9	2.3
7, 0, L		
-10	9.2	10.6
-8	5.8	5.2
-6	14.3	15.8
-4	0	1.8*
-2	7.2	11.3
0	8.3	7.2
2	19.0	18.0
4	6.8	7.1
7, 1, L		
-11	0	0.1*
-10	2.1	2.7
-9	2.9	2.7
-8	13.7	13.0
-7	7.5	6.3
-6	13.2	11.3
-5	3.0	3.1
-4	4.5	3.5
-3	5.4	7.9
-2	12.9	16.1
-1	5.9	5.0
0	26.3	22.2
1	9.3	7.7
2	3.4	4.3
3	2.6	3.3
4	5.5	5.4
5	0	0.1*
7, 2, L		
-11	0	0.5*
-10	5.4	5.5
-9	0	0.8*
-8	11.4	10.7
-7	2.5	2.3
-6	19.9	18.7
-5	9.9	8.3
-4	5.1	2.5
-3	18.5	14.9
-2	19.5	14.1
-1	14.2	10.9
0	18.0	14.7
1	9.8	8.8
2	12.3	11.2
3	5.5	5.4
4	5.5	5.4
5	5.9	8.4
7, 3, L		
-10	3.5	4.0
-9	2.3	2.3
-8	11.1	10.9
-7	10.7	9.5
-6	12.4	11.3
-5	6.2	5.9
-4	15.4	12.7
-3	1.9	2.0
-2	24.8	19.1
-1	10.0	8.5
0	2.6	2.5
1	4.9	4.9
2	7.0	6.1
3	3.9	3.9
4	8.9	9.9
5	1.6	2.7
7, 4, L		
-10	1.4	2.1
-9	2.3	2.4
-8	10.3	10.4
-7	6.2	6.4
-6	15.7	13.6
-5	7.1	5.6
-4	5.5	3.4
-3	2.5	2.2
-2	14.0	12.4
-1	11.0	8.9
0	17.6	16.3
1	5.1	4.9
2	9.1	8.6
3	2.0	2.1
4	3.3	3.9
7, 5, L		
-9	4.9	8.2
-8	7.1	7.4
-7	5.8	6.4
-6	10.7	9.2
-5	6.4	5.4
-4	6.6	6.0
-3	12.2	11.2
-2	16.2	13.9
-1	5.1	4.5
0	2.0	1.8
1	1.7	1.8
2	1.9	1.9
3	2.2	2.1
7, 6, L		
-8	0	1.2*
-7	4.0	5.2
-6	3.1	2.6
-5	7.7	7.8
-4	0	0.7*
-3	0	0.5*
-2	7.6	6.7
-1	9.6	9.0
0	5.8	5.7
1	4.8	5.7
2	7.6	11.7
7, 7, L		
-6	0	6.5*
-5	2.6	4.0
-4	1.7	1.7
-3	3.2	4.0
-2	3.7	3.5
-1	3.6	4.8
0	2.3	3.9

[a] The F_o values are given on an absolute scale. Unobserved reflections are marked with one asterisk. The reflections denoted by two asterisks were excluded from the final refinements as their intensities could not be accurately measured (because of unfavorable spot shape or large intensity on the last film). Two reflections, 104 and 502, were not measured because of very large spot deformation.

mean value of the S–O distances in these investigations is 1.446 (4) Å (the S–OH distances are not included in this value). The two longest S–O distances in the present investigation involve the two oxygen atoms O(1) and O(2) which are engaged in hydrogen bonding. The O–S–O angles (112.4, 116.0, and 115.7°) are all larger than the tetrahedral value.

The S–O distances clearly show that no hydrogen atoms are attached to the oxygen atoms in the fluorosulfate group. The distortion of the sulfate tetrahedron

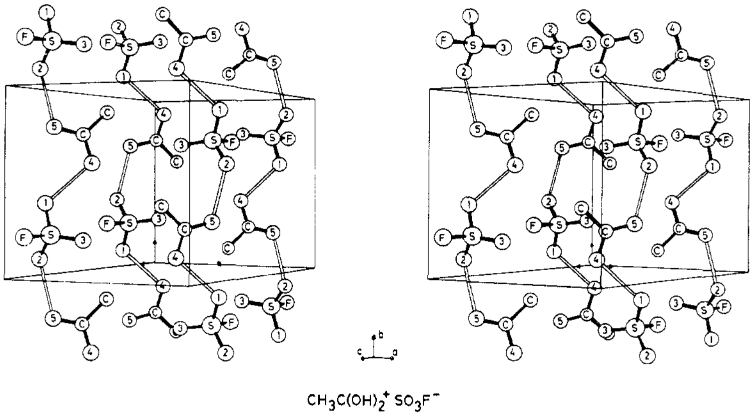

Figure 1.—A stereoscopic pair of drawings showing the structure of $CH_3C(OH)_2^+SO_3F^-$. Covalent bonds are filled; hydrogen bonds are open. The oxygen atoms are numbered 1–5.

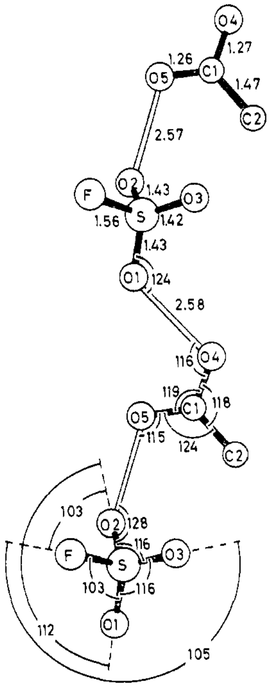

Figure 2—Bond angles and distances.

Table VI

Distances and Angles[a]

Distances	Å	Å	Angles	Deg
A. Covalent Bonds within the SO_3F^- Ion				
S–O(1)	1.432 (4)	[1.444]	O(1)–S–O(2)	112.4 (3)
S–O(2)	1.429 (4)	[1.442]	O(1)–S–O(3)	116.0 (3)
S–O(3)	1.418 (5)	[1.435]	O(1)–S–F	102.9 (3)
S–F	1.561 (4)	[1.581]	O(2)–S–O(3)	115.7 (3)
			O(2)–S–F	103.0 (3)
			O(3)–S–F	104.7 (3)
B. Covalent Bonds within the $CH_3C(OH)_2^+$ Ion				
C(1)–C(2)	1.469 (8)	[1.475]	C(2)–C(1)–O(4)	117.6 (5)
C(1)–O(4)	1.273 (7)	[1.284]	C(2)–C(1)–O(5)	123.6 (5)
C(1)–O(5)	1.261 (7)	[1.268]	O(4)–C(1)–O(5)	118.8 (5)
C. Hydrogen Bonds				
O(4)–H···O(1)	2.583 (6)		C(1)–O(4)···O(1)	116.2 (4)
O(5)–H···O(2)	2.568 (6)		C(1)–O(5)···O(2)	115.1 (4)
			S–O(1)···O(4)	123.9 (3)
			S–O(2)···O(5)	127.9 (3)

[a] Standard deviations are given in parentheses. Distances corrected for thermal riding motion are given within brackets.

when fluorine is introduced may be explained by the increase in double-bond character of the S–O bonds.[13] The S–F bond length (1.561 Å) is shorter than the single-bond length of 1.625 Å calculated by the formula given by Schomaker and Stevenson.[14]

The S–F distance is very similar to the S–OH distances found in earlier investigations. The mean S–OH bond length of five recent studies is 1.56 (1) Å. References are given by Jönsson and Olovsson.[2]

The Acetate Acidium Ion.—The heavy atoms in the acetate acidium ion deviate at the most 0.002 Å from the least-squares plane through these atoms (calculated according to Blow[15]). The hydrogen atoms H(4) and H(5) in the acetate acidium ion and oxygen O(2) in a neighboring fluorosulfate group are all less than 0.06 Å away from this plane (Table VII).

Table VII

Deviations from the Least-Squares Plane Through the Heavy Atoms in the Acetate Acidium Ion

Atom	Dev, Å	Atom	Dev, Å
C(1)	−0.002	H(4)	0.013
C(2)	0.000	H(5)	−0.057
O(4)	0.001	O(1)	−0.499
O(5)	0.001	O(2)	0.057

The C–OH distances (Table VI) within the ion are almost identical and slightly shorter than the mean value (1.29 Å) found in structures containing CH_3COOH molecules.[16,17]

The C–C distance (1.469 (8) Å) is significantly shorter than the value 1.505 Å estimated by Brown[18] for a bond between sp^3–sp^2 hybridized carbon atoms. The shortening may be caused by a delocalization of the ionic charge.

The C–C–O angles are rather different, 117.6 (5) and 123.6 (5)°, which may, at least partly, be due to the repulsion between two of the methyl hydrogen atoms H(1) and H(3) and the hydrogen atom attached to

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(13) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

(14) V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

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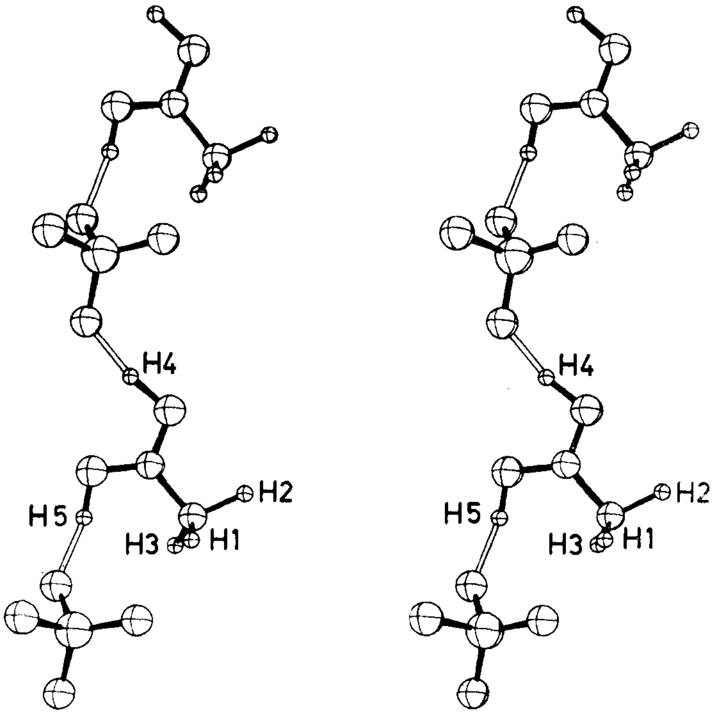

Figure 3.—A stereoscopic pair of drawings showing the hydrogen positions.

O(5) (see Figure 3). Further discussion of this point is made below.

The acetate acidium ion has been described earlier by Jönsson and Olovsson.[2] The present results are in close agreement with those of the previous investigation. A comparison is made in Table VIII.

TABLE VIII

COMPARISON OF DISTANCES AND ANGLES OF THE $CH_3C(OH)_2^+$ ION FOUND IN $CH_3C(OH)_2{}^+HSO_4{}^-$ AND IN $CH_3C(OH)_2{}^+SO_3F^-$

	Present work	$CH_3C(OH)_2{}^+HSO_4{}^-$ [2]
C(1)–C(2), Å	1.469 (8)	1.480 (8)
C(1)–O(4), Å	1.273 (7)	1.272 (6)
C(1)–O(5), Å	1.261 (7)	1.265 (6)
C(2)–C(1)–O(4), deg	117.6 (5)	118.2 (5)
C(2)–C(1)–O(5), deg	123.6 (5)	123.5 (5)
O(4)–C(1)–O(5), deg	118.8 (5)	118.4 (5)
O(4)–H···O(1), Å	2.583 (6)	2.521 (6)
O(5)–H···O(2), Å	2.568 (6)	2.522 (6)

Hydrogen Bonds.—The two hydrogen bonds in acetate acidium fluorosulfate (2.568 (6), 2.583 (6) Å) are significantly longer than the corresponding hydrogen bonds in acetate acidium hydrogen sulfate (2.521 (6), 2.522 (6) Å). The oxygen atoms of the sulfate group apparently become weaker hydrogen-bond acceptors when replacing OH by F. As mentioned previously the S–O distances in the present compound are somewhat shorter than in $CH_3C(OH)_2{}^+HSO_4{}^-$. It is possible that the difference in hydrogen-bond lengths is related to this effect.

The fluorine atom does not participate in any hydrogen bonding. This is not surprising as earlier investigations have shown that covalently bonded fluorine does not have any strong tendency for hydrogen bonding.

Hydrogen bonds between carbon and oxygen with distances up to 3.3 Å have been considered by Sutor.[19] In the present investigation there is a short distance between the methyl carbon atom and O(3) in the fluorosulfate group: 3.266 (8) Å. As the C–H···O angle (110°) is not favorable for hydrogen bonding, it does not seem justified to consider it as a hydrogen bond.

Hydrogen Positions.—Four of the five hydrogen atoms could easily be found from the difference synthesis as described above. The fifth hydrogen atom, H(2), has a more uncertain position and the C–H(2) distance, 1.22 Å, deviates considerably from the expected value. The average C–H distance involving the other two methyl hydrogen atoms is 1.03 Å. The hydrogen atoms participating in hydrogen bonding have an average O–H distance of 1.06 Å.

If the distances between the hydrogen atom H(5) attached to O(5) and the methyl hydrogen atoms are calculated for various orientations of the methyl group, it is found that the shortest distance varies between 2.1 and 2.5 Å. (In the calculations a C–H bond distance of 1.09 Å and an angle C(1)–C(2)–H of 109.5° were used.) The sum of the van der Waals radii for two hydrogen atoms is 2.4 Å according to Pauling. The orientation of the methyl group which corresponds to the smallest repulsion with H(5) is, within the experimental error, the one actually found in this investigation (see Figure 3). Naturally the errors in the hydrogen positions are rather large. The deviation in the C–C–O angles from 120° may be another result of this interaction between the hydrogen atoms (see above).

Other Intermolecular Contacts.—Excluding the hydrogen bonds, only one intermolecular distance within the chain is shorter than the sum of the van der Waals

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[19] D. J. Sutor, *J. Chem. Soc.*, 1105 (1963).

radii, namely, C(1)···O(3) = 2.911 (8) Å. The distances between the different hydrogen-bonded chains are all somewhat larger than this sum.

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The Stereochemistry of Base Hydrolysis of $Co(NH_3)_5X^{2+}$ and $Co(en)_2LX^{n+}$ Ions

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The stereochemistry of base hydrolysis of $Co(NH_3)_5X^{2+}$ and $Co(en)_2LX^{n+}$ complexes is examined in terms of the SN1CB mechanism. Stereochemical results reported for the $[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ complexes support the conclusion that the leaving group, X^-, leaves from a position *cis* to an amido group to form a trigonal-bipyramidal intermediate and that H_2O enters the intermediate by the microscopic reverse of this process. It is argued that for the base hydrolysis reactions of $Co(en)_2LX^{n+}$ complexes only two of a possible four (or three of a possible five where L = NH_3) trigonal-bipyramidal intermediates will be important. Assuming that only these two intermediates are important, the retention of optical activity in the base hydrolysis of active *cis*-$Co(en)_2LX^{n+}$ can be predicted from the yield of *trans* product from *cis*- and from *trans*-$Co(en)_2LX^{n+}$.

A wealth of evidence has been put forward recently to support the conclusion that cobalt(III) complexes of the type $Co(NH_3)_5X^{2+}$ and $Co(en)_2LX^{n+}$ undergo base hydrolysis by way of an SN1CB mechanism involving a five-coordinate intermediate.[1-7] A portion of this evidence involves the observation that the products of base hydrolysis reactions generally possess stereochemistry which is independent of the leaving group, X^-.[3,5,7] This observation supports the conclusion that the reactions of complexes differing only in their leaving group proceed through a common intermediate or set of intermediates.

It has been recognized previously that several intermediates may be important for the base hydrolysis of *cis*-$Co(en)_2LX^{n+}$ complexes.[8,9] For reactions in which more than one intermediate is possible, an SN1CB mechanism does not demand that the stereochemistry of products be independent of leaving group since the leaving group may influence the relative rates of formation of the intermediates which in turn will affect the product distribution. Thus, the observation that the stereochemistry of products is independent of leaving group indicates that not only is the decomposition of the intermediate independent of the leaving group but also its formation is independent of the leaving group. This being the case, it seems worthwhile to investigate the principles which govern the formation and the decomposition of the five-coordinate intermediate.

The stereochemistry of base hydrolysis of $Co(en)_2LX^{n+}$ complexes has been found to be compatible with a proposed reaction scheme in which the five-coordinate intermediate has a trigonal-bipyramidal structure.[9] The purpose of this paper is to show that the results of a recent stereochemical investigation of the base hydrolysis of $Co(NH_3)_4(^{15}NH_3)X^{2+}$ complexes[5] suggest a specific steric course for the formation and decomposition of a trigonal-bipyramidal intermediate. An examination of the reported stereochemistry for reactions of $Co(en)_2LX^{n+}$ complexes suggests that the same principles apply to these complexes also.

$Co(NH_3)_5X^{2+}$ Complexes.—It has recently been reported that base hydrolysis of *trans*-$Co(NH_3)_4(^{15}NH_3)Cl^{2+}$ gives 50% *cis*- and 50% *trans*-$Co(NH_3)_4(^{15}NH_3)OH^{2+}$.[5] The same distribution of products also results from the base hydrolysis of the bromo- and nitratopentaammine complexes.[5] This result can be explained in terms of a detailed mechanism.

According to the SN1CB mechanism the following sequence of steps occurs for $Co(NH_3)_5X^{2+}$

$$Co(NH_3)_5X^{2+} + OH^- \overset{\text{rapid}}{\rightleftharpoons} Co(NH_3)_4NH_2X^+ + H_2O \quad (1)$$

$$Co(NH_3)_4NH_2X^+ \xrightarrow{\text{slow}} Co(NH_3)_4(NH_2)^{2+} + X^- \quad (2)$$

$$Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_4NH_2H_2O^{2+} \quad (3)$$

$$Co(NH_3)_4NH_2H_2O^{2+} \xrightarrow{\text{fast}} Co(NH_3)_5OH^{2+} \quad (4)$$

We are concerned with the stereochemistry of the formation (step 2) and decomposition (step 3) of the five-coordinated intermediate.

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(1) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Son, Inc., New York, N. Y., 1967, pp 177–193.

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