Trifluoroacetate as a Bridging Ligand for Antimony(V): Crystal and Molecular Structures of μ-Fluoro-μ-trifluoroacetato-bis[tetrafluoroantimony(V)] (1) and of μ-Oxo-di-μ-trifluoroacetato-bis[trifluoroantimony(V)] (2)

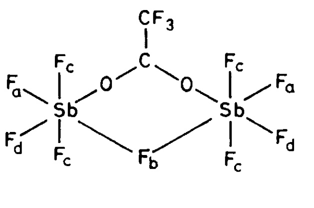
By **David P. Bullivant, Michael F. A. Dove,*** and **Martin J. Haley,** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Crystals of title compound (1), $Sb_2(O_2CCF_3)F_9$, are monoclinic. Space group $P2_1/c$ with a = 9.386(6), b = 15.119(8), c = 16.250(7) Å, β = 110.52(11)°, and Z = 8. The asymmetric unit contains two equivalent but crystallographically independent binuclear complexes in which the Sb atoms are bridged by a F atom (F_b) and by a trifluoroacetato-group. The distorted octahedral co-ordination at each Sb centre is completed by four terminal F atoms (F_t). The mean bond distances are: Sb–F_b 2.025(21), Sb–O 2.026(23), and Sb–F_t 1.836(24) Å. The heavy atoms have been located directly and full-matrix least-squares refinement with anisotropic thermal parameters for the Sb atoms has given R = 0.090 with 1 791 independent observed reflections. Title compound (2), $Sb_2O(O_2CCF_3)_2F_6$, crystallizes in the monoclinic space group Cc with a = 12.322(6), b = 13.867(8), c = 9.443(5) Å, β = 122.75(5)°, and Z = 4. The two Sb atoms are bridged by an oxygen atom (O_b) and by two trifluoroacetato-groups with the octahedral co-ordination at Sb completed by terminal fluorines (F_t). The binuclear complex has approximate C_{2v} symmetry and exhibits the following mean bond distances: Sb–O_b 1.893(21), Sb–O 2.064(16), and Sb–F_t 1.840(17) Å. The analysis is based on 1 760 independent observed reflections and refined by weighted full-matrix least-squares analysis to R = 0.043.

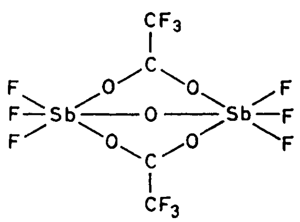
IN an attempt to prepare antimony(V) trifluoroacetate we have investigated the reaction between trifluoroacetic anhydride and SbF_5; mass-balance studies and ^{19}F n.m.r. spectroscopy showed that the reaction yields a new binuclear antimony complex (1), according to equation (i).[1a] We have now succeeded in characterizing

$$(CF_3CO)_2O + 2SbF_5 \longrightarrow CF_3COF + Sb_2(O_2CCF_3)F_9 \quad \text{(i)}$$

this compound by X-ray crystallography and thus can confirm the structure (1) inferred earlier from our ^{19}F n.m.r. spectroscopic study.[1a]



(1)



(2)

The other title compound (2), details of whose crystal structure are given in this paper, was originally produced by thermal decomposition of (1).[1a] We now have proof that compound (2) can be prepared from (1) by a stepwise reaction with trifluoroacetic anhydride. Evidence

$$Sb_2(O_2CCF_3)F_9 + (CF_3CO)_2O \longrightarrow CF_3COF + 2Sb(O_2CCF_3)F_4 \quad \text{(ii)}$$

$$2Sb(O_2CCF_3)F_4 + (CF_3CO)_2O \longrightarrow 2CF_3COF + Sb_2O(O_2CCF_3)_2F_6 \quad \text{(iii)}$$

for the course of the reaction, equations (ii) and (iii), and for the intermediate product of composition $Sb(O_2CCF_3)F_4$ will be presented in a later publication.

EXPERIMENTAL

Materials.—Antimony(V) fluoride was prepared by the fluorination of antimony metal (97% pure) in a stream of HF-free fluorine. Conversion of the mixed-oxidation-state antimony fluorides into SbF_5 was completed by distillation in a stream of fluorine. The clear viscous product was redistilled *in vacuo* into a glass storage vessel. Trifluoroacetic anhydride was prepared from the acid (Aldrich Chemical Co., 99% pure) by dehydration over P_4O_{10} and purified by distillation at 40—42 °C (lit.,[1b] 39.5—40.1 °C). The product was stored over P_4O_{10} and then distilled twice at −35 °C to remove traces of acid (lit., m.p. −15.25 °C). The purity of the anhydride was checked by i.r. and Raman spectroscopy.[2,3]

Preparation of μ-Fluoro-μ-trifluoroacetato-bis[tetrafluoroantimony(V)], (1).—Trifluoroacetic anhydride was distilled on to twice the molar quantity of antimony(V) fluoride *in vacuo*: the reaction was allowed to proceed at 0 °C (0.5 h) until a white solid product had formed. Trifluoroacetyl fluoride was removed from the reaction vessel *in vacuo* whilst keeping the solid product at 0 °C; CF_3COF was identified by ^{19}F n.m.r. spectroscopy {δ −15 (q) and +75 (d) p.p.m. [J(F–F) 6 Hz]}. The new moisture-sensitive antimony compound was purified by sublimation at 20 °C *in vacuo* on to a water-cooled surface at 10 °C (Found: C, 4.30, 4.30; F-on-Sb, 32.5, 32.75; Sb, 46.3, 46.05. Calc. for $C_2F_{12}O_2Sb_2$: C, 4.55; F-on-Sb, 32.6; Sb, 46.15%). Four single crystals obtained in this way were examined by X-ray photography and were found to be identical with the crystal of $Sb_2(O_2CCF_3)F_9$ isolated from the reaction described below.

Reaction of SbF_5 *with Excess of* $(CF_3CO)_2O$.—Trifluoroacetic anhydride (10.35 g, 49.3 mmol) was condensed *in vacuo* on to SbF_5 (3.17 g, 14.6 mmol) at 77 K. The reaction was allowed to proceed at room temperature for 1 h, the mixture was cooled to −25 °C, and the volatiles removed *in vacuo* leaving an off-white solid residue [3.80 g; theoretical yield of $Sb_2(O_2CCF_3)F_9$, 3.86 g]. The crude product was sublimed repeatedly *in vacuo* at 40 °C from one glass vessel to another: the final product consisted of a colourless liquid and crystals, several of which were transferred under dry N_2 into silica capillaries and four of these were examined by *X*-ray photography. Two distinct species [two of (1) and two of (2)] were characterized in this way.

RESULTS

Crystal Structure of $Sb_2(O_2CCF_3)F_9$ (1).—Crystals of $Sb_2(O_2CCF_3)F_9$ were found to be exceedingly moisture-sensitive and to react with Lindemann glass capillary tubes, in which their decomposition was apparent during preliminary *X*-ray photography. Some improvement in crystal stability was achieved with specimens which had been sealed into silica capillaries under an inert atmosphere and approximate unit-cell parameters for the primitive monoclinic crystal were determined from Weissenberg photographs. Several attempts to compute an orientation matrix based on 23 reflection positions, measured on a Hilger and Watts four-circle diffractometer, produced generally poor results. However, the best matrix gave the refined cell parameters $a = 16.310\ 6(12)$, $b = 15.160\ 1(14)$, $c = 9.414\ 6(14)$ Å, and $\beta = 110.53(10)°$. The diffractometer was set to collect intensity measurements with graphite-monochromated Mo-K_α radiation in the range $1 \leqslant \theta \leqslant 25°$ with three standard intensities which were examined after every 100 reflections. During the measurement of the first 1 000 reflections the standards had shown marked variations in intensities which sometimes exceeded 10%. The crystal then cracked and could not be reset before disintegration of the specimen occurred. 1 049 Reflections had been measured of which 811 had net counts in excess of $3\sigma(I)$ and were considered as observed. A fresh specimen was then sealed into a silica capillary tube and rapidly transferred to the diffractometer. An improved orientation matrix was achieved with the second crystal, which showed $h0l$ absences for odd l and weak $h0l$ intensities for odd h when re-indexed to give space group $P2_1/c$.

Crystal data. $Sb_2(O_2CCF_3)F_9$, M 527.5, Monoclinic, space group $P2_1/c$, $a = 9.386(6)$, $b = 15.119(8)$, $c = 16.250(7)$ Å, $\beta = 110.52(11)°$, $U = 2\ 160$ Å^3, $Z = 8$, $D_c = 3.24$ g cm^{-3}, $F(000) = 1\ 904$, μ(Mo-K_α) = 52.4 cm^{-1}. Systematically absent reflections: $0k0$ for k odd; $h0l$ for l odd.

Intensity measurements for the second specimen were collected in the range $1 \leqslant \theta \leqslant 25°$ beginning with $1kl$ reflections. Data collection proceeded reasonably well until $4kl$ at which point standard reflection intensities again indicated crystal instability and during measurements made on $5kl$ the second crystal finally disintegrated. The total number of independent observed reflections [$I > 3\sigma(I)$] measured for this specimen was 1 395. Because of the likelihood that other crystals of $Sb_2(O_2CCF_3)F_9$ would be equally difficult to measure, it was decided to attempt to solve the structure using the data so far collected which were then corrected for Lorentz and polarization effects and for the variations in standard intensities.

Solution and refinement of the structure. The structure was solved directly using the automatic centrosymmetric routine in SHELX [4] with E values $\geqslant 1.7$ which were calculated from the re-indexed data collected from the first crystal. Four E maps were computed and on the map which eventually led to the structure the four highest peaks could be sorted into two pairs each separated by *ca.* 4.04 Å. These positions were consistent with the Patterson function: the Sb–Sb separations suggested an asymmetric unit comprising two crystallographically independent, bridged, binuclear complexes rather than four mononuclear species or the tetranuclear configuration observed in $SbCl_4F$.[5] Two cycles of full-matrix least-squares isotropic refinement of the four Sb positions with the 1 395 independent observed reflections in the data set collected for the second crystal reduced R to 0.280 and a difference synthesis then revealed atomic positions in the octahedral environments at each Sb centre. Two further cycles of refinement in which each of the non-antimony atoms was assigned the scattering power of F, followed by a difference synthesis, enabled the atoms in the trifluoroacetato-groups to be located and the atoms co-ordinated to Sb could then be given their appropriate scattering power. Both sets of data were then combined, after scaling based on a comparison of the 100 strongest reflections common to both sets, thereby increasing the total number of reflections to 1 791. After four final cycles, with anisotropic Sb parameters, the refinement had converged with an R value of 0.090.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for $Sb_2(O_2CCF_3)F_9$

Atom	x/a	y/b	z/c
Sb(1)	5 557(3)	1 657(2)	3 650(2)
Sb(2)	4 278(3)	2 797(2)	1 404(2)
O(1)	5 553(29)	2 987(15)	3 752(16)
O(2)	4 720(28)	3 659(16)	2 414(12)
C(1)	5 233(38)	3 609(21)	3 200(22)
C(2)	5 363(57)	4 525(31)	3 721(34)
F(1)	4 920(23)	1 867(13)	2 319(13)
F(2)	7 519(28)	1 781(15)	3 651(17)
F(3)	3 489(27)	1 756(15)	3 461(16)
F(4)	5 447(26)	470(14)	3 416(16)
F(5)	6 143(27)	1 647(15)	4 818(16)
F(6)	6 349(27)	2 881(15)	1 606(16)
F(7)	4 030(27)	1 906(15)	638(16)
F(8)	3 720(24)	3 689(13)	626(14)
F(9)	2 333(29)	2 606(16)	1 424(17)
F(10)	4 202(28)	5 024(16)	3 378(17)
F(11)	6 487(30)	4 978(17)	3 453(18)
F(12)	5 817(39)	4 473(22)	4 516(25)
Sb(3)	503(3)	3 522(2)	3 589(2)
Sb(4)	−671(3)	4 647(2)	1 336(2)
O(3)	9 866(27)	2 659(15)	2 587(15)
O(4)	9 157(28)	3 309(15)	1 240(16)
C(3)	9 355(37)	2 689(20)	1 800(21)
C(4)	9 107(52)	1 755(28)	1 285(30)
F(13)	−2(24)	4 444(14)	2 669(14)
F(14)	1 009(27)	4 398(15)	4 387(16)
F(15)	913(26)	2 626(14)	4 374(15)
F(16)	8 432(27)	3 594(15)	3 417(16)
F(17)	2 430(32)	3 532(17)	3 509(19)
F(18)	1 364(26)	4 452(14)	1 518(15)
F(19)	7 387(30)	4 641(16)	1 382(18)
F(20)	363(29)	826(16)	343(18)
F(21)	8 667(28)	4 643(16)	153(17)
F(22)	455(28)	1 285(16)	1 622(17)
F(23)	8 785(37)	1 816(21)	495(24)
F(24)	8 190(30)	1 329(17)	1 571(18)

In view of the limited quality of the data no further attempts were made to improve the refinement. The atomic co-ordinates are listed in Table 1 and estimated standard deviations derived from the full variance–covariance matrix are indicated in parentheses.

Crystal Structure of $Sb_2O(O_2CCF_3)_2F_6$ (2).—A crystal of the moisture-sensitive complex was sealed into a 0.3 mm diameter silica capillary tube under an atmosphere of dry nitrogen. Approximate unit-cell dimensions were obtained from Weissenberg photographs and later refined on the diffractometer using the positions of 21 intense reflections.

None of the problems of crystal instability observed in the previous determination was encountered with this compound although the specimen chosen for diffractometry was found to be twinned. A unique set of reflections could, however, be resolved using the diffractometer, with the exception of the $0kl$ reflections.

Crystal data. $Sb_2O(O_2CCF_3)_2F_6$, M 599.5, Monoclinic, space group Cc, $a = 12.332(6)$, $b = 13.867(8)$, $c = 9.443(5)$ Å, $\beta = 122.75(5)°$, $U = 1\,358$ Å^3, $F(000) = 1\,096$, $Z = 4$, $D_c = 2.93$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,7$ Å), μ(Mo-K_α) = 42.0 cm^{-1}. Systematically absent reflections: hkl for $h + k$ odd; $h0l$ for l odd (h odd); $0k0$ for k odd.

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) for $Sb_2O(O_2CCF_3)_2F_6$ *

Atom	x/a	y/b	z/c
Sb(1)	60 760 †	31 401(9)	65 449 †
Sb(2)	56 756(7)	31 320(10)	26 412(9)
O(1)	7 233(16)	4 171(11)	6 525(19)
O(2)	7 246(19)	4 067(13)	4 071(24)
O(3)	4 577(17)	4 032(11)	5 010(21)
O(4)	4 480(18)	4 184(14)	2 653(22)
O(5)	5 891(27)	2 572(4)	4 612(30)
C(1)	7 641(15)	4 350(10)	5 564(18)
C(2)	8 829(22)	4 972(18)	6 258(29)
C(3)	4 125(15)	4 346(14)	3 569(26)
C(4)	2 949(16)	5 060(14)	2 815(22)
F(1)	7 538(21)	2 485(15)	8 024(22)
F(2)	4 982(25)	2 358(15)	6 726(26)
F(3)	6 218(15)	3 880(11)	8 215(15)
F(5)	4 188(23)	2 398(15)	1 246(26)
F(6)	6 795(21)	2 269(12)	2 635(25)
F(7)	5 481(18)	3 908(12)	870(21)
F(8)	8 605(18)	5 773(13)	6 702(21)
F(9)	9 769(14)	4 613(15)	7 550(26)
F(10)	9 063(15)	5 352(9)	5 201(18)
F(11)	3 262(15)	5 840(9)	2 173(19)
F(12)	1 959(15)	4 614(13)	1 494(12)
F(13)	2 655(21)	5 166(20)	3 858(25)

*Anisotropic temperature factors for these atoms, in the form $T = \exp[-2\pi^2(h^2a^{*2}U + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$, are deposited in SUP 22635. † Parameter fixed to define origin.

A total of 2 066 intensity measurements were made in the range $0 \leqslant \theta \leqslant 27.5°$ with Mo-K_α radiation and standard intensities measured as above: 1 760 reflections having $I > 3\sigma(I)$ were observed and corrected for Lorentz and polarization effects but not for absorption.

Solution and refinement of the structure. From the Patterson function the asymmetric unit apparently contained only one heavy atom implying that the complex was mononuclear and that the eight Sb atoms in the cell would occupy the eight-fold general positions in the space group $C2/c$. The failure of attempts to refine the heavy-atom position and the appearance of a subsequent difference synthesis showed this assumption to be incorrect. It was decided, therefore, to solve the structure by direct methods, using MULTAN,[6] in the alternative space group Cc. The E map based on the set with the best combined factor of merit showed the two strongest peaks to have almost identical y co-ordinates which agreed with the Patterson vectors and explained their earlier misinterpretation. Furthermore, these peaks were separated by 3.4 Å suggesting the presence of bridging ligands in a binuclear complex.

Two cycles of full-matrix least-squares refinement, with a separate scale factor applied to the $0kl$ reflections, reduced R to 0.250 and the atoms co-ordinated to Sb were readily located by a difference synthesis; one of these atoms appeared to be linked to both Sb centres. The two bridging trifluoroacetato-groups became recognisable by repeating the procedure with each co-ordinated atom considered as F and, after refinement of the completed structure, the difference map was entirely featureless with the exception of some residual electron density close to the heavy atoms. At this stage it became necessary to reconsider the identity of the single bridging atom since otherwise the complex would not have been electronically neutral. An isotropic refinement with a bridging O rather than F gave an R value at convergence of 0.053. Unit weights were then replaced by those of a weighting scheme based on a Chebychev series and used in the final stages of refinement.

The only anomalous feature of the refinement appeared to be in the significant difference between the two chemically equivalent C–C bond lengths in the trifluoroacetato-groups [C(1)–C(2) 1.47(3), C(3)–C(4) 1.62(3) Å]. With these distances both constrained to a value of 1.5(3) Å, anisotropic refinement gave a final R value of 0.043. Atomic co-ordinates are listed in Table 2. Unless where otherwise stated, calculations were performed using the CRYSTALS[7] set of programs in both analyses; scattering curves were taken from ref. 8. Observed and calculated structure factors and thermal parameters for both compounds are listed in Supplementary Publication No. SUP 22635 (40 pp.).*

DISCUSSION

The asymmetric unit of compound (1) contains two equivalent but crystallographically independent binuclear complexes, for which the atom-numbering scheme is shown in Figure 1. Since there are no intermolecular

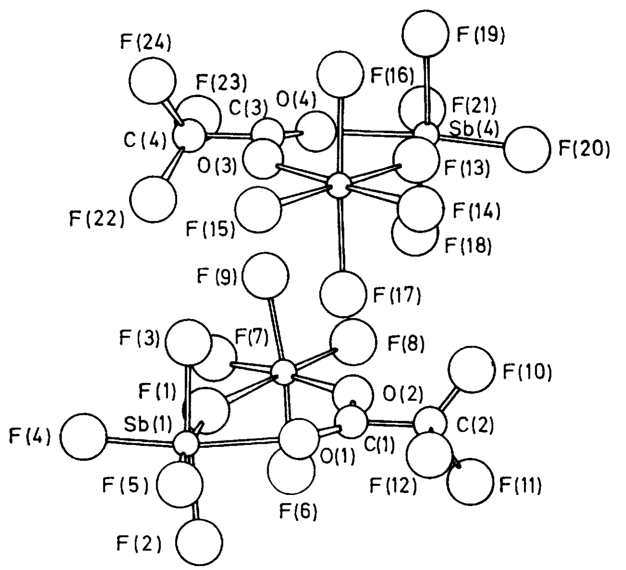


FIGURE 1 Atom-numbering scheme for the two independent molecules of $Sb_2(O_2CCF_3)F_9$ (1)

contacts less than 3.5 Å involving the Sb atoms it is evident that the structure is indeed molecular. Table 3 lists the bond lengths and angles for the two molecules. Each Sb is approximately octahedrally co-ordinated by five F atoms and one O atom [Figure 2(*a*) and Table 4, planes (3)—(10)]. The Sb atoms are bridged by a

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 3

Bond lengths (Å) and angles (°) for $Sb_2(O_2CCF_3)F_9$

(a) Bond lengths

Sb(1)–O(1)	2.024(23)	Sb(2)–O(2)	2.029(25)
Sb(1)–F(1)	2.064(21)	Sb(2)–F(1)	1.987(20)
Sb(1)–F(2)	1.856(25)	Sb(2)–F(6)	1.865(24)
Sb(1)–F(3)	1.867(24)	Sb(2)–F(7)	1.799(24)
Sb(1)–F(4)	1.835(22)	Sb(2)–F(8)	1.802(21)
Sb(1)–F(5)	1.788(25)	Sb(2)–F(9)	1.865(26)
C(1)–O(1)	1.265(37)	C(2)–F(10)	1.285(50)
C(1)–O(2)	1.204(39)	C(2)–F(11)	1.453(51)
C(1)–C(2)	1.609(54)	C(2)–F(12)	1.218(53)
Sb(3)–O(3)	2.015(23)	Sb(4)–O(4)	2.036(23)
Sb(3)–F(13)	1.982(22)	Sb(4)–F(13)	2.065(22)
Sb(3)–F(14)	1.802(24)	Sb(4)–F(18)	1.857(23)
Sb(3)–F(15)	1.813(22)	Sb(4)–F(19)	1.856(27)
Sb(3)–F(16)	1.873(24)	Sb(4)–F(20)	1.831(24)
Sb(3)–F(17)	1.864(28)	Sb(4)–F(21)	1.807(26)
C(3)–O(3)	1.203(37)	C(4)–F(22)	1.390(47)
C(3)–O(4)	1.278(36)	C(4)–F(23)	1.219(51)
C(3)–C(4)	1.621(50)	C(4)–F(24)	1.290(46)

(b) Bond angles

F(1)–Sb(1)–F(2)	84.7(10)	F(1)–Sb(2)–F(6)	83.8(9)
F(1)–Sb(1)–F(3)	85.0(10)	F(1)–Sb(2)–F(7)	85.5(9)
F(1)–Sb(1)–F(4)	87.6(9)	F(1)–Sb(2)–F(8)	176.5(9)
F(1)–Sb(1)–F(5)	171.6(9)	F(1)–Sb(2)–F(9)	85.3(10)
F(1)–Sb(1)–O(1)	85.7(9)	F(1)–Sb(2)–O(2)	85.7(9)
F(2)–Sb(1)–F(3)	166.4(11)	F(6)–Sb(2)–F(7)	92.7(11)
F(2)–Sb(1)–F(4)	94.7(10)	F(6)–Sb(2)–F(8)	95.8(10)
F(2)–Sb(1)–F(5)	93.7(11)	F(6)–Sb(2)–F(9)	168.4(12)
F(3)–Sb(1)–F(4)	93.7(10)	F(7)–Sb(2)–F(8)	98.0(10)
F(3)–Sb(1)–F(5)	95.2(11)	F(7)–Sb(2)–F(9)	90.4(11)
F(4)–Sb(1)–F(5)	100.8(11)	F(8)–Sb(2)–F(9)	94.8(10)
F(2)–Sb(1)–O(1)	86.0(10)	F(6)–Sb(2)–O(2)	84.7(10)
F(3)–Sb(1)–O(1)	84.4(10)	F(7)–Sb(2)–O(2)	171.0(11)
F(4)–Sb(1)–O(1)	173.2(10)	F(8)–Sb(2)–O(2)	90.8(10)
F(5)–Sb(1)–O(1)	86.0(10)	F(9)–Sb(2)–O(2)	90.5(11)
F(10)–C(2)–F(11)	100.9(38)	O(1)–C(1)–O(2)	135.4(32)
F(10)–C(2)–F(12)	115.4(45)	O(1)–C(1)–C(2)	108.2(31)
F(11)–C(2)–F(12)	109.3(42)	O(2)–C(1)–C(2)	115.8(32)
F(10)–C(2)–C(1)	112.5(38)	Sb(1)–F(1)–Sb(2)	143.0(11)
F(11)–C(2)–C(1)	100.3(33)	Sb(1)–O(1)–C(1)	133.7(23)
F(12)–C(2)–C(1)	116.1(42)	Sb(2)–O(2)–C(1)	135.7(23)
F(13)–Sb(3)–F(14)	87.7(10)	F(13)–Sb(4)–F(18)	83.8(9)
F(13)–Sb(3)–F(15)	176.2(10)	F(13)–Sb(4)–F(19)	84.1(10)
F(13)–Sb(3)–F(16)	83.4(10)	F(13)–Sb(4)–F(20)	87.5(10)
F(13)–Sb(3)–F(17)	85.5(11)	F(13)–Sb(4)–F(21)	171.0(9)
F(13)–Sb(3)–O(3)	85.4(9)	F(13)–Sb(4)–O(4)	85.4(9)
F(14)–Sb(3)–F(15)	96.1(11)	F(18)–Sb(4)–F(19)	165.6(11)
F(14)–Sb(3)–F(16)	93.7(10)	F(18)–Sb(4)–F(20)	92.5(11)
F(14)–Sb(3)–F(17)	91.6(11)	F(18)–Sb(4)–F(21)	96.9(11)
F(15)–Sb(3)–F(16)	95.9(11)	F(19)–Sb(4)–F(20)	94.7(11)
F(15)–Sb(3)–F(17)	94.8(11)	F(19)–Sb(4)–F(21)	93.9(11)
F(16)–Sb(3)–F(17)	167.5(12)	F(20)–Sb(4)–F(21)	101.4(11)
F(14)–Sb(3)–O(3)	173.1(10)	F(18)–Sb(4)–O(4)	84.5(10)
F(15)–Sb(3)–O(3)	90.9(10)	F(19)–Sb(4)–O(4)	86.9(10)
F(16)–Sb(3)–O(3)	85.3(10)	F(20)–Sb(4)–O(4)	172.5(11)
F(17)–Sb(3)–O(3)	88.2(11)	F(21)–Sb(4)–O(4)	85.8(10)
F(22)–C(4)–F(23)	108.2(39)	O(3)–C(3)–O(4)	133.9(31)
F(22)–C(4)–F(24)	103.5(36)	O(3)–C(3)–C(4)	116.8(30)
F(23)–C(4)–F(24)	108.1(43)	O(4)–C(3)–C(4)	108.3(29)
F(22)–C(4)–C(3)	107.3(32)	Sb(3)–F(13)–Sb(4)	143.7(12)
F(23)–C(4)–C(3)	114.8(38)	Sb(3)–O(3)–C(3)	137.3(23)
F(24)–C(4)–C(3)	104.1(33)	Sb(4)–O(4)–C(3)	133.7(22)

trifluoroacetato-group and by an F atom (F_b) in such a way that the Sb centres, F_b, and the carboxylato-function form an approximately planar six-membered ring [planes (1) and (2) Table 4]. The mean SbF_bSb angle (143.4°) is intermediate between the value (146°) [9] found in $[ClO_2][Sb_2F_{11}]$ and the smaller of the two angles (141 and 170°) [10] reported for SbF_5. Furthermore the average C–O bond length and O–C–O bond angle are comparable with the results for compound (2) and the other known structures (Table 5). It is interesting that the trends in the M–O–C and O–C–O angles both follow that in the metal–metal distance: of the two, the M–O–C angles are more sensitive to changes in the M–M distance. Evidently there is little strain in the double bridge between the Sb atoms of (1). This can be confirmed by examining the co-ordination of the Sb atoms in (1) [Figure 2(a)] which is quite comparable with that in the tetrameric $SbCl_4F$ [5] [Figure 2(b)] and in other fluorine-bridged compounds such as $(SbCl_3F_2)_4$,[16] $Sb_4Cl_{13}F_7$,[17] and the trinuclear $Sb_3Cl_{10.7}F_{4.3}$.[18]

The Sb–F bond lengths in compound (1) provide slight evidence for a *trans* effect; thus Sb(1)–F(4) and Sb(1)–F(5) are shorter than Sb(1)–F(2) or Sb(1)–F(3),

TABLE 4

Least-squares planes for $Sb_2(O_2CCF_3)F_9$. Displacements (Å) of atoms from the plane are given in square brackets. The plane is defined, in direct space, by the equation $PX + QY + RZ = S$

Plane	Atoms	P	Q	R	S
(1)	Sb(1), F(1), Sb(2), O(2), C(1), O(1)	9.361	0.870	−5.015	3.560
(2)	Sb(3), F(13), Sb(4), O(4), C(3), O(3)	9.373	−0.640	−5.202	−1.648
(3)	O(1), C(1), O(2), C(2)	9.358	1.086	−5.267	3.560
(4)	O(3), C(3), O(4), C(4)	9.375	−0.402	−5.105	−1.576
(5)	Sb(1), Sb(2), F(2), F(3), F(6), F(9)	0.835	−13.551	−7.117	−4.436
(6)	Sb(3), Sb(4), F(16), F(17), F(18), F(19)	−0.238	−13.566	−6.563	−7.125
(7)	Sb(1), O(1), F(4), F(5), F(1)	−9.359	−0.215	4.563	−3.568
(8)	Sb(2), O(2), F(7), F(8), F(1)	9.335	1.448	−5.063	3.699
(9)	Sb(3), O(3), F(14), F(15), F(13)	−9.381	0.454	5.523	1.675
(10)	Sb(4), O(4), F(20), F(21), F(13)	−9.351	1.121	5.034	1.815

Displacements:

Plane (1): [Sb(1) −0.045, F(1) 0.044, Sb(2) −0.017, O(2) −0.034, C(1) 0.047, O(1) 0.016]

Plane (2): [Sb(3) 0.027, F(13) −0.027, Sb(4) 0.027, O(4) 0.001, C(3) −0.065, O(3) 0.006]

Plane (3): [O(1) −0.016, C(1) 0.043, O(2) −0.018, C(2) −0.010, Sb(1) −0.103, Sb(2) 0.007, F(1) 0.025]

Plane (4): [O(3) 0.023, C(3) −0.055, O(4) 0.020, C(4) 0.013, Sb(3) 0.074, Sb(4) 0.078, F(13) 0.032]

Plane (5): [Sb(1) 0.056, Sb(2) 0.004, F(2) 0.052, F(3) −0.116, F(6) −0.081, F(9) 0.085]

Plane (6): [Sb(3) −0.021, Sb(4) −0.039, F(16) 0.044, F(17) −0.027, F(19), 0.057, F(19) −0.015]

Plane (7): [Sb(1) −0.002, O(1) 0.019, F(4) 0.019, F(5) −0.018, F(1) −0.018]

Plane (8): [Sb(2) −0.012, O(2) 0.015, F(7) 0.016, F(8) −0.009, F(1) −0.010]

Plane (9): [Sb(3) −0.005, O(3) 0.000, F(14) 0.000, F(15) 0.003, F(13) 0.003]

Plane (10): [Sb(4) 0.005, O(4) 0.032, F(20) −0.031, F(21) 0.029, F(13) 0.029]

Interplanar angles (°): (3)—(5) 88.96, (4)—(6) 90.09, (7)—(8) 174.94, (9)—(10) 3.09, (3)—(4) 5.76

TABLE 5

Intramolecular metal–metal distances and μ-trifluoroacetato-group parameters in bi- and tri-nuclear complexes

Compound	Distance/Å		Angle (°)		Ref.
	M–M	C–O	O–C–O	M–O–C	
(1) $Sb_2(O_2CCF_3)F_9$	3.844(5)	1.238(39)	134.6(32)	135.1(23)	
(2) $Sb_2O(O_2CCF_3)_2F_6$	3.446(3)	1.245(24)	131.1(3)	131.3(14)	
$[\{Cu(O_2CCF_3)_2(C_9H_7N)\}_2]$	2.886(4)	1.242(10)	129.3(7)	124.7(6)	11
$[\{Mo(O_2CCF_3)_2(C_5H_5N)\}_2]$	2.129(2)	1.26(1)	126.1(10)	115.3(6)	12
$[\{V(O_2CCF_3)_2(\eta\text{-}C_5H_5)\}_2]$	3.70	1.26	124	134	13
$[Pt_2(O_2CCF_3)_2(CH_3)_4(C_6H_7N)_2]$	2.557(1)	1.28(2)	127(2)	118.3(10)	14
$[Cr_3(O_2CCF_3)_6(\eta\text{-}C_5H_5)_2]$	3.717(1)	1.239(7)	129.9(5)	135.0(4)	15

which are in turn shorter than Sb(1)–F(1), where F(1) is a bridging atom and F(2) and F(3) are terminal fluorines *trans* to one another. Although there is no evidence of disordering in the positions of the trifluoromethyl fluorines and their thermal parameters are considerably less than is usual in trifluoroacetates, the C–F bond lengths (1.21—1.55 Å) range around the value, 1.325(6) Å, measured in $K[H(O_2CCF_3)_2]$.[19]

Although the antimony atoms in the triply bridged binuclear species (2) are crystallographically independent the molecular symmetry approximates to C_{2v} symmetry, if the F-on-C atoms are neglected. The co-ordination around each Sb is distorted octahedral [Figure 2(*c*) and Table 6, planes (3)—(8)] and there are no intermolecular contacts less than 3.5 Å involving them. The molecular unit and the atom-numbering scheme are shown in Figure 3: bond lengths and angles are listed in Table 7. The bridge angle at O(5) (131.1°) is similar to those in

TABLE 6

Least-squares planes for $Sb_2O(O_2CCF_3)_2F_6$

Plane (1): C(2), C(1), O(1), O(2), Sb(1), Sb(2)

P	Q	R	S
−6.947	10.587	0.350	−0.555

[C(2) −0.096, C(1) 0.046, O(1) 0.174, O(2) −0.031, Sb(1) −0.113, Sb(2) 0.020]

Plane (2): C(4), C(3), O(3), O(4), Sb(1), Sb(2)

−7.194	−10.379	0.455	−7.300

[C(4) 0.055, C(3) −0.016, O(3) 0.050, O(4) −0.144, Sb(1) −0.032, Sb(2) 0.087]

Plane (3): F(1), F(2), O(3), O(1), Sb(1)

4.767	−6.799	−8.181	−4.674

[F(1) 0.013, F(2) −0.057, O(3) 0.015, O(1) −0.052, Sb(1) 0.081]

Plane (4): F(3), O(5), F(1), O(3), Sb(1)

9.913	9.279	−4.200	5.806

[F(3) 0.027, O(5) 0.027, F(1) 0.019, O(3) 0.014, Sb(1) −0.088]

Plane (5): F(3), O(5), F(2), O(1), Sb(1)

−6.581	7.897	−2.263	−2.931

[F(3) 0.045, O(5) 0.042, F(2) −0.007, O(1) −0.011, Sb(1) −0.068]

Plane (6): F(5), F(6), O(2), O(4), Sb(2)

4.708	5.764	−8.510	2.268

[F(4) 0.025, F(6) −0.004, O(2) 0.022, O(4) −0.005, Sb(2) −0.038]

Plane (7): F(7), O(5), F(5), O(2), Sb(2)

−9.091	9.316	4.320	−1.022

[F(7) 0.056, O(5) 0.054, F(5) −0.013, O(2) −0.018, Sb(2) −0.079]

Plane (8): F(7), O(4), F(6), O(5), Sb(2)

6.659	8.009	2.127	6.916

[F(7) 0.049, O(4) −0.018, F(6) −0.013, O(5) 0.048, Sb(2) −0.066]

Interplanar angles (°): (1)—(2) 98.23, (3)—(6) 53.94, (4)—(5) 88.88, (6)—(7) 95.78, (4)—(8) 41.11, (7)—(8) 88.05

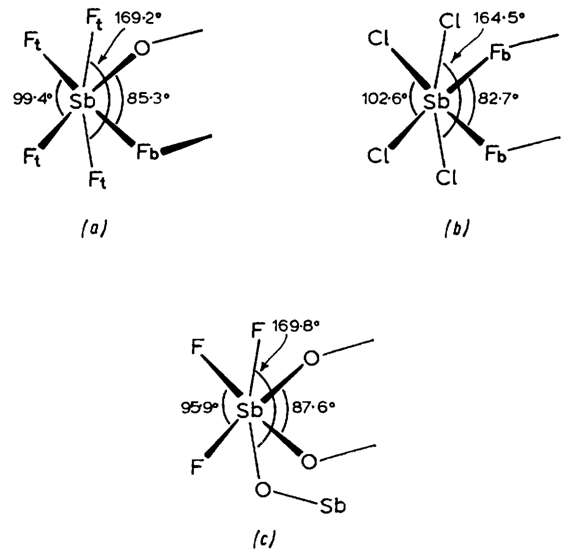


FIGURE 2 The distorted octahedral co-ordination of Sb in (*a*) compound (1), (*b*) $(SbCl_4F)_4$, and (*c*) compound (2)

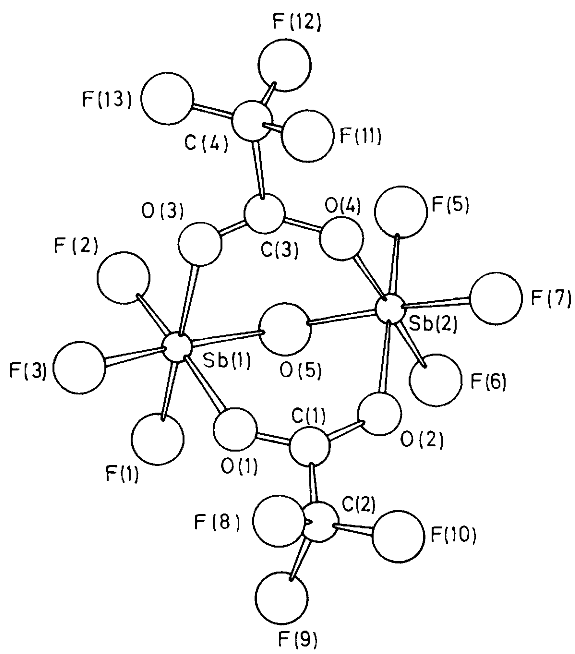


FIGURE 3 Molecular unit and atom-numbering scheme for $Sb_2O(O_2CCF_3)_2F_6$ (2)

TABLE 7

Bond lengths (Å) and angles (°) for $Sb_2O(O_2CCF_3)_2F_6$

(*a*) Bond lengths

Sb(1)–O(1)	2.028(15)	Sb(2)–O(2)	2.107(19)
Sb(1)–O(3)	2.041(17)	Sb(2)–O(4)	2.078(14)
Sb(1)–O(5)	1.886(20)	Sb(2)–O(5)	1.899(22)
Sb(1)–F(1)	1.821(18)	Sb(2)–F(5)	1.880(20)
Sb(1)–F(2)	1.809(18)	Sb(2)–F(6)	1.829(15)
Sb(1)–F(3)	1.809(14)	Sb(2)–F(7)	1.892(15)
C(1)–O(1)	1.277(19)	C(3)–O(3)	1.239(26)
C(1)–O(2)	1.280(22)	C(3)–O(4)	1.182(28)
C(1)–C(2)	1.511(20)	C(3)–C(4)	1.574(17)
C(2)–F(8)	1.268(33)	C(4)–F(11)	1.392(18)
C(2)–F(9)	1.248(27)	C(4)–F(12)	1.337(25)
C(2)–F(10)	1.292(26)	C(4)–F(13)	1.228(22)

(*b*) Bond angles

F(1)–Sb(1)–F(2)	96.3(11)	F(5)–Sb(2)–F(6)	95.5(10)
F(1)–Sb(1)–F(3)	91.3(8)	F(5)–Sb(2)–F(7)	94.4(9)
F(2)–Sb(1)–F(3)	89.2(8)	F(6)–Sb(2)–F(7)	96.1(8)
F(1)–Sb(1)–O(1)	87.0(9)	F(5)–Sb(2)–O(2)	174.7(9)
F(2)–Sb(1)–O(1)	171.1(8)	F(6)–Sb(2)–O(2)	88.3(9)
F(3)–Sb(1)–O(1)	82.5(6)	F(7)–Sb(2)–O(2)	81.5(7)
F(1)–Sb(1)–O(3)	172.6(9)	F(5)–Sb(2)–O(4)	87.5(9)
F(2)–Sb(1)–O(3)	89.7(10)	F(6)–Sb(2)–O(4)	176.3(8)
F(3)–Sb(1)–O(3)	84.3(6)	F(7)–Sb(2)–O(4)	81.5(7)
O(1)–Sb(1)–O(3)	86.5(7)	O(2)–Sb(2)–O(4)	88.6(8)
O(5)–Sb(1)–F(1)	95.0(9)	O(5)–Sb(2)–F(5)	91.9(9)
O(5)–Sb(1)–F(2)	97.7(9)	O(5)–Sb(2)–F(6)	91.6(9)
O(5)–Sb(1)–F(3)	170.1(6)	O(5)–Sb(2)–F(7)	169.5(6)
O(5)–Sb(1)–O(3)	88.6(8)	O(5)–Sb(2)–O(2)	91.6(8)
O(5)–Sb(1)–O(1)	90.3(7)	O(5)–Sb(2)–O(4)	90.4(7)
F(8)–C(2)–F(9)	106.2(24)	F(11)–C(4)–F(12)	106.7(17)
F(8)–C(2)–F(10)	94.5(16)	F(11)–C(4)–F(13)	121.8(20)
F(8)–C(2)–C(1)	108.1(22)	F(11)–C(4)–C(3)	106.4(12)
F(9)–C(2)–F(10)	116.2(24)	F(12)–C(4)–F(13)	106.7(17)
F(9)–C(2)–C(1)	111.7(18)	F(12)–C(4)–C(3)	106.8(16)
F(10)–C(2)–C(1)	117.7(17)	F(13)–C(4)–C(3)	108.1(16)
O(1)–C(1)–O(2)	131.4(15)	O(3)–C(3)–O(4)	127.8(17)
O(1)–C(1)–C(2)	117.6(16)	O(3)–C(3)–C(4)	118.5(19)
O(2)–C(1)–C(2)	111.0(15)	O(4)–C(3)–C(4)	113.7(16)
Sb(1)–O(1)–C(1)	133.8(11)	Sb(1)–O(3)–C(3)	133.8(13)
Sb(2)–O(2)–C(1)	124.7(11)	Sb(2)–O(4)–C(3)	132.9(14)
Sb(1)–O(5)–Sb(2)	131.1(3)		

$Rb_2[Sb_2OF_{10}]$ [20] and $Cs_3[Sb_3O_3F_{12}]$,[21] 133.2 and 133.5° respectively. The Sb–O(5) bond length (1.893 Å) is also similar to the corresponding distances in these two anions, 1.88 and 1.94 Å.

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