Determination of the Molecular Structure and Absolute Configuration of (*R*)-Tris(trifluoroacetato)antimony(III)

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

Crystals of the title compound are colourless and crystallise in the cubic space group $P4_332$ with a = 13.840(3) Å and Z = 8. The crystal structure has been solved by a combination of heavy-atom and direct methods and refined by weighted, anisotropic, full-matrix, least squares to a conventional R value of 0.0227 using 485 independent observed reflections measured on a four-circle diffractometer. The absolute configuration has been determined from a significance test applied to the ratio of the Hamilton-weighted R factors for the two enantiomorphs after the effects of anomalous dispersion had been included. The molecule is discrete and the geometry on Sb is pyramidal with crystallographic C_3 symmetry. The trifluoroacetato-groups function as unidentate ligands [Sb–O 2.043(4) Å and O–Sb–O 84.92(16)°]. The i.r. and Raman spectra of the solid are reported and shown to be consistent with the structure.

THE preparation of $Sb(O_2CCF_3)_3$ from the reaction of $SbCl_3$ and $Ag[O_2CCF_3]$ has been reported along with the preparations of the arsenic, bismuth, and phosphorus(III) analogues.[1] Pyramidal monomeric structures involving unidentate trifluoroacetato-groups were proposed for the phosphorus and arsenic compounds on the basis of their low melting points, appreciable volatility, and i.r. spectra. On the other hand the properties of the Sb compound were said to be indicative of significant molecular association *via* bridging trifluoroacetato-groups. In the course of our investigations of antimony(V) trifluoroacetate derivatives a more convenient preparation of the antimony(III) compound, from Sb_2O_3 and $(CF_3CO)_2O$, was successfully carried out. The i.r. spectrum of the moisture-sensitive compound was found to differ from that reported earlier[1] and so we report here the Raman spectrum as well as the results of a single-crystal *X*-ray determination of the structure of the compound.

EXPERIMENTAL

Materials.—Trifluoroacetic anhydride was prepared from the acid by treatment with P_4O_{10}.[2] Antimony(III) oxide (Harrington Bros. Ltd.) was used without further purification.

Tris(trifluoroacetato)antimony(III).—Trifluoroacetic anhydride (9.37 g, 44.6 mmol) was condensed on to Sb_2O_3 (1.02 g, 3.5 mmol) *in vacuo* at 77 K. The reaction mixture was heated at 120 °C for 2 d by which time all the solid, apart from a small amount of white residue, had dissolved. The mixture was cooled to 0 °C and the excess of anydride removed *in vacuo*, leaving a white residue [3.10 g; theoretical yield of $Sb(O_2CCF_3)_3$, 3.22 g]. The crude moisture-sensitive product was sublimed *in vacuo* at 80 °C to yield colourless, well faceted, block-like crystals (m.p. 114—117 °C) (Found: C, 15.2, 15.35. Calc. for $C_6F_9O_6Sb$: C, 15.65%).

A crystal of dimensions *ca.* 0.3 × 0.3 × 0.4 mm was sealed into a 0.3 mm Lindemann glass capillary; unit-cell dimensions obtained initially from Weissenberg photographs were later refined by least-squares analysis of the angle settings of 15 intense reflections measured with a Hilger and Watts four-circle diffractometer.

Crystal Data.—$C_6F_9O_6Sb$, Cubic, $M = 460.73$, $a =$ 13.840(3) Å, $U = 2\,651$ Å^3, $F(000) = 1\,728$, $Z = 8$, $D_c =$ 2.31 g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,7$ Å), μ(Mo-K_α) = 22.6 cm^{-1}. Systematically absent reflections: $h00$ with $h \neq 4n$, space group $P4_332$ (no. 212) or $P4_132$ (no. 210).

Reflection intensities were measured for the (hkl) octant out to a maximum θ of 25°. Each reflection was scanned for 24 s and stationary background counts made on either side (6 s). The intensities of three standard reflections were re-examined after every 100 reflections had been collected; changes in these standards were insignificant throughout the complete data-collection process. 2 688 Reflections were measured of which 2 431 had net counts in excess of $3\sigma(I)$. After averaging reflections equivalent by symmetry, 485 were retained as unique; these were corrected for Lorentz and polarisation but not for absorption effects.

Solution and Refinement of the Structure.—The Patterson function revealed the presence of a single Sb atom located on a special position with three-fold site symmetry. At the same time attempts were made to solve the structure directly. For computational convenience the orthorhombic space group $P2_12_12_1$ was used in direct methods, since it was appropriate to the form in which the data had been collected, although it required the removal of some additional weak intensities required to be systematically absent in the subgroup. The positions of the two Sb atoms which are present as a result of the use of $P2_12_12_1$ were found in the best E map[3] and their atomic co-ordinates could be sensibly related to the Sb position deduced from the Patterson function. After two cycles of isotropic full-matrix refinement a difference synthesis gave the positions of the atoms in the six trifluoroacetato-ligands, and two further cycles of refinement, calculated for the complete structure, reduced R to 0.090 4. When the positions of the Sb atoms in $P2_12_12_1$ symmetry were then compared with the equivalent positions in the cubic space groups, deduced from the Patterson map, it became clear that the direct solution had arbitrarily chosen the enantiomorph belonging to the space group $P4_132$. This choice of space group was unaltered when refinement was continued in the cubic system using the symmetry-averaged data set. With anisotropic temperature factors, full-matrix refinement converged at $R = 0.024\,1$. In the final two cycles the weighting scheme $w = 1$ for $F_{obs.} < A$ and $w = (A/F_{obs.})^2$ for $F_{obs.} \geqslant A$, with $A = 125$, was applied whereupon R fell to 0.022 1.

Determination of the Absolute Configuration.—The relation of mirror symmetry between the two possible space groups

$P4_132$ and $P4_332$ indicates that the molecule is chiral. In order to determine the absolute configuration, structure factors were calculated in which the anomalous dispersion effects of the Sb atom were included after weighted, full-matrix, least squares had converged. Conventional and Hamilton-weighted R values of 0.023 1 and 0.026 3 respectively were obtained with $P4_132$. The corresponding structure factors for space group $P4_332$ were 0.022 7 and 0.025 9, respectively. The statistical significance of the change in the weighted R factor was examined using the linear hypothesis test described by Hamilton.[4] For the 485 reflections and 67 least-squares parameters used in the analysis the one-dimensional hypothesis that the absolute configuration resulting from a choice of space groups $P4_132$ is correct can confidently be rejected at the significance level $\alpha = 0.005$. The enantiomorphic form of the compound present in the crystal examined belongs, therefore, to space group $P4_332$ and in the illustration of the molecular structure (Figure 1) the correct absolute configuration is shown.

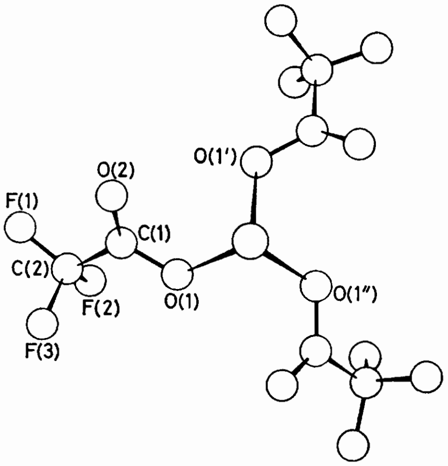

FIGURE 1 The molecule viewed down the C_3 axis

Positional parameters are listed in Table 1 and bond lengths and angles appear in Table 2. Estimated standard deviations were derived from inversion of the full variance–covariance matrix and are shown in parentheses. Scattering curves were taken from ref. 5: calculations, other than direct methods, were performed using CRYSTALS.[6] Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22624 (9 pp.).*

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Sb(1)	−694.9(3)	−694.9(3)	−694.9(3)
O(1)	−66(3)	−1 108(3)	601(3)
O(2)	702(3)	−2 150(3)	−219(3)
C(1)	507(4)	−1 741(4)	512(4)
C(2)	926(6)	−2 084(6)	1 483(5)
F(1)	1 666(3)	−2 635(4)	1 353(4)
F(2)	1 172(4)	−1 361(5)	2 045(4)
F(3)	260(4)	−2 581(4)	1 937(3)

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses †

Distances

Sb(1)–O(1)	2.043(4)	C(1)–C(2)	1.539(9)
Sb(1)–O(2)	2.869(5)	C(2)–F(1)	1.289(8)
Sb(1)–O(2*)	3.039(4)	C(2)–F(2)	1.313(8)
C(1)–O(1)	1.282(7)	C(2)–F(3)	1.310(8)
C(1)–O(2)	1.192(7)		

Angles

O(1)–Sb(1)–O(1′)	84.92(16)	O(1)–C(1)–O(2)	126.34(55)
O(2)–Sb(1)–O(2′)	118.67(04)	C(2)–C(1)–O(1)	113.01(58)
O(2*)–Sb(1)–O(2*′)	102.70(10)	C(2)–C(1)–O(2)	120.62(57)
O(1)–Sb(1)–O(2)	50.04(14)	C(1)–C(2)–F(1)	111.12(62)
O(1)–Sb(1)–O(2*)	68.80(14)	C(1)–C(2)–F(2)	112.31(67)
O(2)–Sb(1)–O(2*)	73.88(09)	C(1)–C(2)–F(3)	108.37(64)
Sb(1)–O(1)–C(1)	110.51(37)	F(1)–C(2)–F(2)	109.13(78)
		F(1)–C(2)–F(3)	108.39(69)
		F(2)–C(2)–F(3)	107.39(65)

† Unprimed, singly and doubly primed O atoms are designated in Figure 2 and are related to one another by the transformations $x,y,z \rightarrow z,x,y \rightarrow y,z,x$, respectively. O(2*) is related to O(2) by the transformation $x,y,z \rightarrow -\frac{1}{4} + x, -\frac{1}{4} - z, \frac{1}{4} + y$.

TABLE 3

Vibrational spectra (cm^{-1}) of solid $Sb(O_2CCF_3)_3$

I.r.*	Raman	Assignment
1 695s, br	1 704m	CO_2 antisym str.
1 570w		
1 402s	1 410m	CO_2 sym str.
1 200s, br		C–F str.
	1 154vw, br	
868m	863s	C–C str.
850w (sh)		
787m		OCO def.
737m	730w	
618m	616m	CF_3 def.
603 (sh)		
	532m	
526m	524m	
	419w	CCO def.
	307s	
	280s	CCF_3 o.o.p. rock
	214m	M–O str. CF_3 rock and wag and lattice modes
	208m	
	176m	
	157m	

* Nujol mull. s = Strong, m = medium, w = weak, sh = shoulder, br = broad, v = very, str. = stretch, def. = deformation, o.o.p. = out of plane, and sym = symmetric.

Vibrational Spectroscopy.—Infrared spectra were obtained for Nujol and halogenocarbon mulls of the solid between AgCl windows in the region 400—4 000 cm^{-1} on a Perkin-Elmer 457 spectrometer. Raman spectroscopy was carried out on the sublimed bulk solid at room temperature using a Cary 81 spectrometer with Anaspec modification.

DISCUSSION

In principle it should be possible to distinguish between a unidentate trifluoroacetato-group (C_s symmetry) on the one hand and an ionic or bidentate or bridging group (C_{2v}) on the other by means of the carboxylato-stretching frequencies.[7] A unidentate ligand tends to give rise to a higher value (cm^{-1}) for the antisymmetric stretch and a larger separation between the antisymmetric and symmetric stretches ($\Delta\nu$). A notable feature of our i.r. spectra (Table 3) is that the carboxylato-stretching frequencies correspond to those expected for a unidentate ligand and, moreover, differ from the published values of

---

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

1 662 and 1 435 cm^{-1} ($\Delta\nu = 227$).[1] Our $\Delta\nu$ value of 293 cm^{-1} compares well with that of 271 cm^{-1} reported for $[AsPh_4]_2[Co(O_2CCF_3)_4]$ in which the trifluoroacetato-group has been shown to be unidentate by *X*-ray diffraction studies.[8] Similarly large values of $\Delta\nu$, 278 and 289 cm^{-1}, occur in the i.r. spectra of $[Mn(CO)_5(O_2CCF_3)]$ [9] and $[Au(PPh_3)(O_2CCF_3)]$ [10] respectively, for which unidentate groups have been confidently predicted. On the other hand these $\Delta\nu$ values are significantly higher than those, $\Delta\nu = 143$ and 129 cm^{-1}, we have found for $M_2(O_2CCF_3)F_9$, M = Sb or Nb respectively, in which the metal atoms are known to be bridged symmetrically by trifluoroacetato-ligands.[2,11]

Assignments of the i.r. and Raman spectra of solid $Sb(O_2CCF_3)_3$ are presented in Table 3. The carboxylato-stretching modes also appear in the Raman whereas the C–F stretch appears only weakly. The remaining assignments are less obvious and, indeed, differ in a number of respects from those adopted by Baillie *et al.*[12] We prefer the interpretations of Miller *et al.*[13a] and Agambar and Orrell [13b] for bands below 1 000 cm^{-1}. Moreover there are several close similarities between our spectra of the covalent $Sb(O_2CCF_3)_3$ and those of ionic alkali-metal salts.

It is evident from the crystal-structure determination that each Sb atom lies on a three-fold axis with its lone pair orientated along the axis. The three equivalent trifluoroacetato-groups lie in a propeller arrangement around the axis at an angle of pitch of 45.9°; the molecular symmetry is C_3 and presumably the compound crystallises as a mixture of the two enantiomorphs. The O(1)–Sb(1)–O(1′) angle (84.9°) is very close to the value [87.3 (1.6)°] for the mean F–Sb–F angle in SbF_3,[14] a structure in which the Sb is surrounded by three F atoms at 1.92 and three F′ atoms at 2.61 Å. Such longer range interactions influence the rigidity of the SbF_3 lattice (m.p. 292 °C), and, together with the repulsion of the lone pair on Sb, act to close up the F–Sb–F angle. The O(1)–Sb(1)–O(1) angle in the trifluoroacetate is similarly influenced by the lone pair but also by two other contacts, Sb(1) · · · O(2) 2.87 and Sb(1) · · · O(2*) 3.04 Å (Figure 2). Although these are both weak interactions the stronger of them must be classed as an intramolecular interaction. Hence the title compound exhibits a moderate (114—117 °C) melting point and may be sublimed at 80 °C *in vacuo*. On the other hand the intermolecular interactions in $Sb(O_2CCF_3)_3$ are sufficiently strong to make this compound significantly less volatile than the arsenic analogue.

TABLE 4

Average bond lengths and angles of some co-ordinated trifluoroacetato-groups

	Bond length/Å				Angle/°					
Compound	C–F	C–C	C–O	C=O	F–C–F	F–C–C	C–C–O	C–C=O	O–C=O	M(H)–O–C
$KH(O_2CCF_3)_2$[16]	1.325(6)	1.541(2)	1.268(3)	1.215(2)	107.7(6)	111.3(7)	111.3(1)	119.6(1)	129.2(2)	114.6(2)
$Sb(O_2CCF_3)_3$	1 304(8)	1.539(9)	1.282(7)	1.192(7)	108.3(7)	110.6(6)	113.0(6)	120.6(6)	126.3(6)	110.5(4)
$[Cr_3(C_5H_5)_2(O_2CCF_3)_6]$[17] unidentate	1.316(9)	1.531(10)	1.287(7)	1.193(7)	107.1(7)	111.8(8)	112.3(6)	120.0(7)	127.6(6)	119.8(4)
bridging bidentate	1.261(9)	1.530(7)	1.236(7)		105.9(8)	112.6(6)	115.1(6)		129.9(5)	135.0(4)

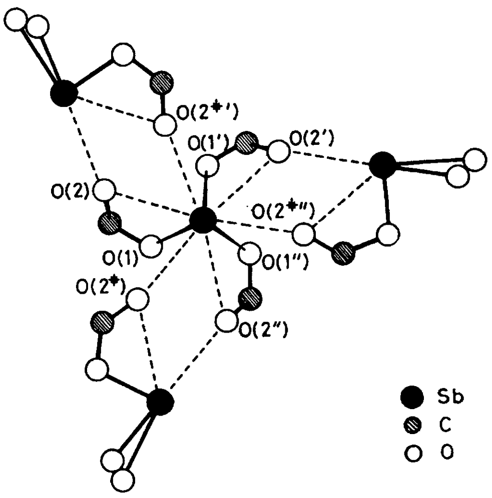

FIGURE 2 View of the molecule (CF_3 groups omitted) showing nine-fold co-ordination of Sb by O

A useful approach is to examine the ratios of the Sb(1) · · · O(2) and Sb(1) · · · O(2*) distances to the single bond length; these ratios are 1.40 and 1.49 : 1, corresponding to bond orders of 0.05 and 0.03, respectively.[15] In polymeric SbF_3 the mean ratio of the M · · · F to M–F distance, 1.36 : 1, is smaller than the value (1.49 : 1) we find for the intermolecular interaction in $Sb(O_2CCF_3)_3$, thus confirming our view that this trifluoroacetato-group is essentially molecular.

The crystallographic data in this paper represent only the third set of high quality data on structures containing unidentate trifluoroacetato-groups. The first such structure was that of the potassium acid salt; [16] very recently Cotton and Rice [17] have published the structure of centrosymmetric $[Cr_3(\eta\text{-}C_5H_5)_2(O_2CCF_3)_6]$ which contains four conventional bridging trifluoroacetato-groups as well as two others, each of which is bonded strongly to one Cr atom (Cr–O 1.995 Å) and weakly to another (Cr–O 2.584 Å). The bond lengths and angles of the unidentate trifluoroacetato-groups in these three compounds are collected in Table 4; they show that the unidentate ligands in the antimony and chromium compounds are nearly isodimensional, whereas the groups in the acid salt have the C–O bond shorter and the C=O longer, which is consistent with partial delocalisation and, therefore, partial ionic character. The Sb(Cr)–O–C angles differ widely and in our view reflect the less crowded environment of the antimony atom compared with the Cr. Data for the bidentate tri-

TABLE 5

Least-squares planes for $Sb(O_2CCF_3)_3$. Displacements (Å) of atoms from the planes are given in square brackets. A plane is defined, in direct space, by the equation $PX + QY + RZ = S$

Plane	P	Q	R	S	Displacements
Plane (1): O(1), O(2), C(1), C(2), Sb(1)	10.393	8.898	−2.082	−1.153	[O(1) 0.053, C(1) 0.024, O(2) 0.015, C(2) −0.048, Sb(1) −0.043]
Plane (2): O(1), O(2), C(1), C(2)	10.743	8.551	−1.736	−1.042	[O(1) −0.003, C(1) 0.009, C(2) −0.002, O(2) −0.004, Sb(1) −0.178]
Plane (3): O(1), O(1′), O(1″)	−7.990	−7.990	−7.990	0.386	[Sb(1) 1.280]
Plane (4): O(2), O(2′), O(2″)	−7.990	−7.990	−7.990	1.332	[Sb(1) 0.334]
Plane (5): O(2*), O(2*′), O(2*″)	7.990	7.990	7.990	−2.979	[Sb(1) 1.313]

fluoroacetato-groups in the trinuclear chromium compound represent some of the best bonding parameters known at present for such ligands [2] and have been included in Table 4 by way of contrast.

The trifluoroacetato-groups of the antimony(III) compound are closely planar. The planes analysis shows that the Sb atom is 0.18 Å away from the best plane [Table 5, plane (2)] through the C_2O_2 skeleton. This could be to allow O(2) to take up a more favourable position to bridge the Sb to an adjacent Sb atom.

The overall co-ordination number of Sb in the tris(trifluoroacetate) is nine in what can best be described as a distorted tricapped trigonal prism. The three bonded O(1) atoms form the base of the prism, 1.280 Å below the Sb atom, while the three intermolecular O(2*) atoms form the upper face. This face, 1.313 Å above the Sb atom, is greatly enlarged, presumably by the lone pair pointing away from the base and through the upper face, which is twisted 25.88° relative to the base. The three intramolecular O(2) atoms project from the prism faces and are 0.334 Å below the level of the Sb atom. This co-ordination is reminiscent of the structures of $Bi(O_2CH)_3$[18] and YF_3.[19]

We thank Professor T. J. King for assistance with the diffractometry, and the S.R.C. and I.S.C. Chemicals Ltd. for support (to D.P.B.).

[9/275 *Received, 20th February,* 1979]

REFERENCES

[1] C. D. Garner and B. Hughes, *Inorg. Chem.*, 1975, **14**, 1722.

[2] D. P. Bullivant, M. F. A. Dove, and M. J. Haley, following paper.

[3] MULTAN 77, P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J.-P. Declercq, University of York.

[4] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[5] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 3, pp. 73, 85.

[6] J. R. Carruthers, ' The Oxford Crystallographic Package—CRYSTALS.'

[7] C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.

[8] J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, 1966, **5**, 1420.

[9] C. D. Garner and B. Hughes, *J.C.S. Dalton*, 1974, 735.

[10] D. I. Nichols and A. S. Charleston, *J. Chem. Soc.* (*A*), 1969, 2581.

[11] D. P. Bullivant, M. F. A. Dove, and M. J. Haley, unpublished work.

[12] M. J. Baillie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc.* (*A*), 1968, 3110.

[13] (*a*) P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, 1972, **57**, 5451; (*b*) C. A. Agambar and K. G. Orrell, *J. Chem. Soc.* (*A*), 1969, 897.

[14] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751.

[15] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1960, p. 239.

[16] A. L. Macdonald, J. C. Speakman, and D. Hadži, *J.C.S. Perkin II*, 1972, 825.

[17] F. A. Cotton and G. W. Rice, *Inorg. Chim. Acta*, 1978, **27**, 75.

[18] C.-I. Stalhandske, *Acta Chem. Scand.*, 1969, **23**, 1525.

[19] A. Zalkin and D. H. Templeton, *J. Amer. Chem. Soc.*, 1953, **75**, 2453.