Trifluoroacetate as a Bridging Ligand for Antimony(v): *X*-Ray Molecular Structure of μ-Oxo-μ-bis(trifluoroacetato)bis[trifluoroantimony(v)]

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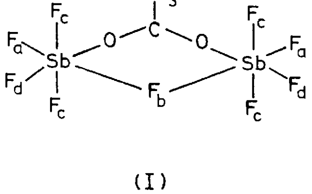
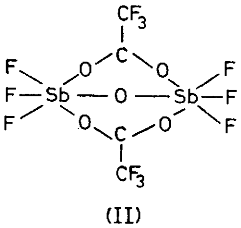
Summary $Sb_2(CF_3CO_2)F_9$ (I) and $Sb_2O(CF_3CO_2)_2F_6$ (II) have been obtained from the reaction of trifluoroacetic anhydride and antimony(v) fluoride and characterised by ^{19}F n.m.r. spectroscopy and *X*-ray crystallography, respectively.

Stable fluoride trifluoroacetate derivatives of antimony(v) have not been reported previously. The anion, $F_5Sb_2O_2CCF_3^-$, for example, which has been characterised in solution by ^{19}F n.m.r. spectroscopy[1] and in which the trifluoroacetate group presumably functions as a monodentate ligand, could not be isolated in the solid phase.



(I)



(II)

In an attempt to isolate a trifluoroacetate derivative of antimony(v) we have investigated the reaction between trifluoroacetic acid anhydride and SbF_5; mass balance studies and ^{19}F n.m.r. spectroscopy have shown that the reaction yields a binuclear antimony complex according to equation (1).

$$(CF_3CO)_2O + 2SbF_5 \rightarrow CF_3COF + Sb_2(CF_3CO_2)F_9 \qquad (1)$$

The ^{19}F n.m.r. spectrum of the products in SO_2ClF at temperatures in the range 30 to − 100 °C showed that CF_3COF [ϕ − 15·6 (q) and + 74·4 (d, J_{F-F} 6 Hz) p.p.m.†] does not generate the trifluoroacetylium ion[2] under these conditions. Five more solute resonances were observed at − 100 °C (ϕ 53·3, 72·2, 98·2, 125·0, and 131·3 p.p.m.; relative intensities 1 : 3 : 4 : 2 : 2), only one of which (ϕ 72·2 p.p.m.) appeared at temperatures above − 70 °C. The latter is assigned to fluorine atoms bonded to the carbon atom of a trifluoroacetate group and the four multiplets [Figure 1(i)] are attributable to those bonded to Sb^V. These five resonances are consistent with the presence, in solution, of the novel antimony compound (I) which could be readily isolated as a white crystalline solid which sublimes at room temperature *in vacuo* and fumes in moist air. The ^{19}F n.m.r. spectrum of a sample of the sublimate, however, showed that some decomposition was occurring on sublimation and the presence of more than one phase in the sublimate was confirmed by single crystal *X*-ray crystallography. The nature of the decomposition process, which

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† Chemical shifts upfield from $CFCl_3$, ϕ (SO_2ClF) = − 99·9 p.p.m.

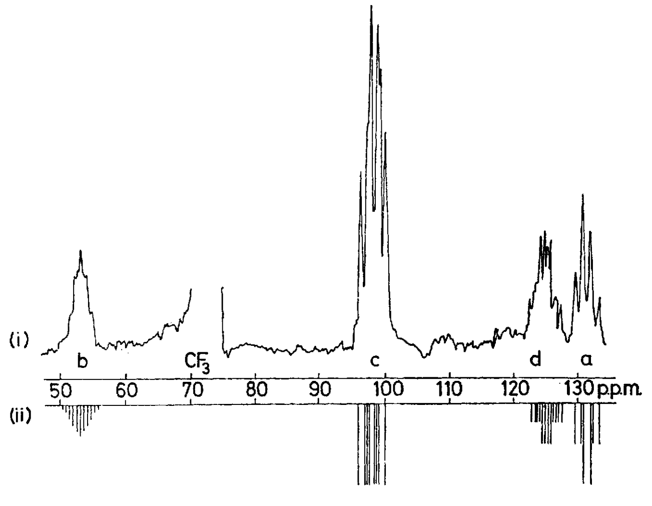

FIGURE 1. (i) ^{19}F N.m.r. spectrum of a solution of (I) containing $(CF_3CO)_2O$–SbF_5–SO_2ClF (1:2:7·3) at 94·1 MHz and − 100 °C; (ii) the calculated line spectrum of (I) with coupling constants: F_a–F_c, 130; F_c–F_d, 150; F_b–F_c, 101; F_a–F_d, 85; F_b–F_d, 50 Hz.

gave the oxo-bridged product whose structure is described below, is still being investigated. The specimen of the crystalline phase chosen for *X*-ray diffractometry was found to be twinned. A Hilger and Watts four-circle diffractometer was used to determine the cell dimensions and the diffraction data could be indexed in terms of the monoclinic space groups *C*2/*c* or *Cc*.‡

Crystal data: $Sb_2O(CF_3CO_2)_2F_6$, *M* 599·5, monoclinic, space group *Cc*, $a = 12·322(6)$, $b = 13·867(8)$, $c = 9·443(5)$ Å, $\beta = 122·57(5)°$, $Z = 4$, $D_c = 2·93$ g cm^{-3}. 1760 independent, observed intensities were measured using the diffractometer (θ_{max} 27·5°) with graphite-monochromated Mo-K_α radiation (λ 0·7107 Å). A Patterson synthesis suggested the position of a single antimony atom per asymmetric unit but this failed to refine in the space group *C*2/*c*. Two antimony atomic positions with almost identical *y* co-ordinates resulted by direct methods with space group *Cc* and these refined successfully enabling the structure to be completed by difference Fourier syntheses. Weighted, full-matrix, anisotropic refinement for all atoms gave an *R*, at convergence, of 4·3%.

Although the antimony atoms are crystallographically independent, the triply-bridged binuclear molecule (II) approximates closely to C_{2v} symmetry if the CF_3 groups are neglected (Figure 2). The angles around the Sb atoms are all close to 90°. The geometry of the trifluoroacetato-bridges is in good agreement with those found in other structures;[3] thus, there is no sign of strain in this molecule. This is confirmed by the similarity between the angle at the oxygen, O′ [131·1(3)°] and those in the anions $Sb_2OF_{10}^{2-}$ [4] and $Sb_3O_3F_{12}^{3-}$ [5] where the SbOSb angles are 133·2(7) and 133·5(10)°, respectively.

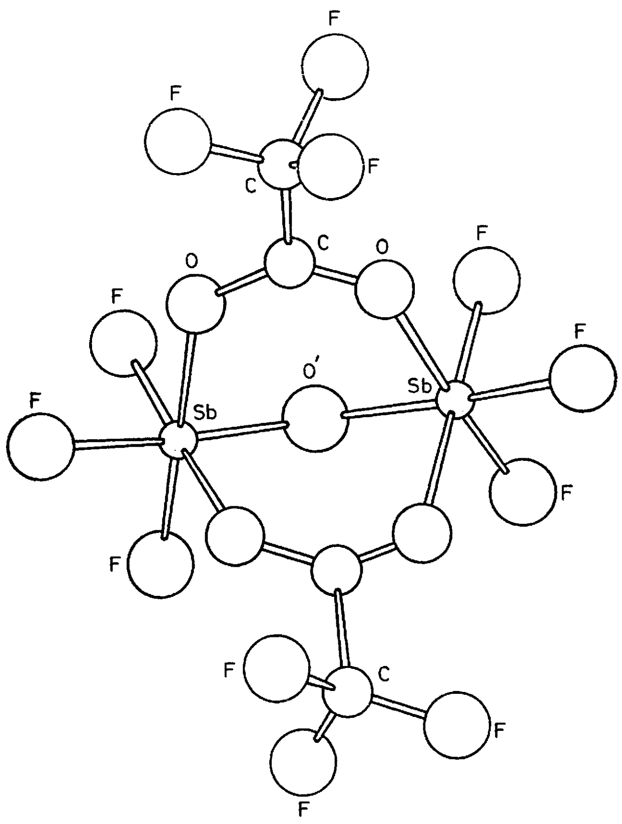

FIGURE 2. Structure of $Sb_2O(CF_3CO_2)_2F_6$ (II) projected along the *y* axis. Some average bond lengths are: Sb–F, 1·840(17); Sb–O′, 1·888(21); Sb–O, 2·079(16) Å.

The ^{19}F n.m.r. spectrum of (I) shows no coupling between fluorines on the carbon atom and those on Sb^V; the nine fluorine atoms bonded to Sb are exchanging rapidly between sites at temperatures above − 70 °C. The four F_c fluorine atoms appear to be chemically equivalent presumably because the ring is either planar or, as is more likely, averages to a planar geometry on the n.m.r. time-scale. The chemical shift of F_b is at lower field than for bridging fluorine atoms in $F_5SbFSbF_4{\cdot}L$ (L = F^-, $MeSO_2F$, and SO_2ClF)[6] owing to the presence of the bridging trifluoroacetate group. The other chemical shifts due to F atoms bonded to Sb and the coupling constants [Figure 1(ii)] are, however, comparable with those reported for SbF_5 adducts.[6]

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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