Crystal Structure of Di-μ_3-oxo-octakis-μ-(trifluoroacetato)-ditin(II)ditin(IV)–Benzene (1/1)

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The crystal and molecular structure of $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2{\cdot}C_6H_6$ has been determined by single-crystal *X*-ray crystallography to R' = 0.058. Crystals are monoclinic, space group $C_{2/c}$, with a = 24.182(10), b = 9.828(3), c = 17.882(6) Å, β = 104.77(3)°, and Z = 4. The molecular structure consists of independent centrosymmetric $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2$ units. The two symmetry-related tin(IV) atoms are bridged by two μ_3-oxygen atoms to form a $Sn^{IV}{}_2O_2$ ring. Octahedral co-ordination at Sn^{IV} is completed by trifluoroacetates which bridge the Sn^{IV} and Sn^{II}. The tin(II) atoms have a distorted square-based-pyramidal geometry with the apical site occupied by a μ_3-oxygen, and the basal positions by oxygens from bridging trifluoroacetates. The O(basal)–Sn^{II}–O(basal) angles range from 74.40(26) to 118.40(27)°. The remaining apical site is presumably occupied by a non-bonding electron pair. One lattice benzene molecule is present per unit.

WHEN solid hexaphenylditin(IV) reacts with acetic acid '$Sn(O_2CCH_3)_3$' is produced. This has been formulated as the dimer $Sn_2(O_2CCH_3)_6$, containing a tin–tin bond stabilised by bridging acetato-ligands.[1] The reaction appears to be quite general for carboxylic acids and a series of '$Sn(O_2CR)_3$' compounds has been prepared.[2] However, spectroscopic evidence does not substantiate the presence of a tin–tin bond and indeed ^{119}Sn Mössbauer spectroscopy clearly indicates that these compounds contain both Sn^{II} and Sn^{IV}. The similarity of the Mössbauer parameters with those of $[Sn^{II}Sn^{IV}O(O_2CC_6H_4NO_2\text{-}o)_4{\cdot}C_4H_8O]_2$ prepared by Harrison and co-workers[3] suggested that the $Sn_2(O_2CR)_6$ compounds might have a similar structure. Attempts to produce crystals suitable for *X*-ray analysis by sublimation under vacuum failed. However, crystals were obtained by carrying out the solvolysis of $Sn_2(C_6H_5)_6$ in benzene solution with trifluoroacetic acid followed by slow crystallisation. These crystals had Mössbauer parameters very close to those for the original '$Sn(O_2CCF_3)_3$'. Characterisation by single-crystal *X*-ray diffraction shows that these crystals were in fact $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2{\cdot}C_6H_6$.

EXPERIMENTAL

Doubly recrystallised hexaphenylditin (0.5 g) was added to one side of a dry reaction vessel, and dry benzene (5 cm³) was condensed onto it. Trifluoroacetic acid (4 cm³) was added to the other side of the vessel, separated by a glass frit. All additions were made in a dry-atmosphere glovebox. The benzene solution was then filtered to the acid side of the vessel after the solvents had been degassed. After 1 d, the solvent was slowly condensed to the empty side of the vessel by immersing that side in cold running water overnight. In this way 90% of the solvent was removed from the solution leaving a pale yellow liquid and clear crystals. The remaining liquid was removed by filtration, and the solvent side of the vessel sealed off and removed. The crystals were then pumped dry on a vacuum line. The density of the hygroscopic material was not measured.

Crystal Data.—$C_{22}H_6F_{24}O_{18}Sn_4$, Monoclinic, M = 1 488.02, a = 24.182(10), b = 9.828(3), c = 17.882(6) Å, β = 104.77(3)°, U = 4 109.40 Å³, Z = 4, D_c = 2.28 g cm^{-3}, $F(000)$ = 2 792, λ(Mo-K_α) = 0.710 69 Å, and μ(Mo-K_α) = 26 cm^{-1}.

The unit-cell parameters were obtained from a least-squares refinement of 15 well centred reflections with $8.6 < 2\theta < 23.9°$. The diffractometer data indicated that reflections were absent for hkl when $h + k = 2n + 1$, for $h0l$ when $l = 2n + 1$ or $h = 2n + 1$, and for $0k0$ when $k = 2n + 1$, characteristic of the space groups C_c and $C_{2/c}$. The structure was successfully refined in $C_{2/c}$. The equivalent positions for $C_{2/c}$ are x,y,z and $\bar{x},y,\frac{1}{2} - z$.

X-Ray Intensity Measurement.—A cylindrically shaped crystal 0.20 mm in diameter and 0.30 mm long was sealed in a quartz capillary under dry air and mounted on a Syntex $P2_1$ diffractometer. Intensities were measured with graphite-monochromated radiation, using a θ—2θ scan, for

TABLE 1

Atomic co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Sn(1)	2 691(2)	985(7)	−67(3)
Sn(2)	3 637(3)	3 005(8)	1 524(4)
O(1)	2 858(2)	2 599(6)	673(3)
O(2)	2 916(3)	5 124(7)	4 583(3)
O(3)	3 668(3)	4 766(8)	603(4)
C(1)	1 576(4)	78(11)	5 066(6)
C(2)	1 219(6)	821(14)	5 517(7)
F(1)	3 679(4)	2 865(10)	4 482(6)
F(2)	3 655(4)	4 507(11)	3 769(5)
F(3)	4 316(3)	4 313(12)	4 765(6)
O(4)	2 984(3)	4 563(8)	1 938(4)
O(5)	2 554(3)	537(7)	4 125(4)
C(3)	2 327(4)	447(10)	3 389(6)
C(4)	2 469(6)	1 623(14)	2 942(7)
F(4)	2 168(5)	1 670(11)	2 246(5)
F(5)	3 001(4)	1 583(9)	2 922(5)
F(6)	2 416(3)	2 817(7)	3 258(5)
O(6)	3 542(3)	545(8)	1 732(4)
O(7)	1 756(3)	4 574(7)	4 426(4)
C(5)	3 538(4)	349(11)	6 258(6)
C(6)	1 053(6)	3 466(14)	3 493(7)
F(7)	1 293(4)	2 348(9)	3 591(8)
F(8)	679(4)	3 461(12)	3 876(7)
F(9)	9 238(6)	3 547(12)	2 201(5)
O(8)	1 659(3)	3 519(7)	579(4)
O(9)	9 026(3)	3 105(8)	5 502(4)
C(7)	3 855(4)	1 674(11)	9 822(6)
C(8)	4 489(7)	1 606(17)	9 348(9)
F(10)	4 786(4)	1 848(17)	9 722(6)
F(11)	4 184(5)	2 456(15)	8 790(8)
F(12)	712(5)	4 506(14)	980(8)
C(9)	5 064(7)	4 481(18)	2 143(10)
C(10)	5 111(6)	3 256(26)	1 797(8)
C(11)	5 062(5)	2 056(18)	2 162(8)

a total of 3 718 reflections with $0 \leqslant h \leqslant 30$, $0 \leqslant k \leqslant 12$, $-23 \leqslant l \leqslant 22$, and $0 \leqslant 2\theta \leqslant 55$, after equivalent reflections were averaged and the systematically absent reflections along with those whose intensities were less than 1 σ (standard counting error) had been removed from the data set. Of these 3 718 reflections, 2 550 had intensities three times greater than the standard counting error. Two standard reflections were measured every 48 reflections and these showed no significant variation during data collection. No correction for absorption was necessary since $\mu(\text{Mo-}K_{\alpha}) = 26$ cm^{-1}.

TABLE 2

Bond lengths (Å) and bond angles (°) for $[\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{O}(\text{O}_2\text{CCF}_3)_4]_2\cdot\text{C}_6\text{H}_6$ with estimated standard deviations in parentheses

(*i*) Tin co-ordination

(*a*) Lengths

Sn(1)–O(1)	2.040(6)	Sn(2)–O(1)	2.136(5)
Sn(1)–O(1′)	2.035(5)	Sn(2)–O(3)	2.403(8)
Sn(1)–O(2)	2.065(7)	Sn(2)–O(4)	2.446(8)
Sn(1)–O(5)	2.047(6)	Sn(2)–O(6)	2.466(8)
Sn(1)–O(7)	2.060(6)	Sn(2)–O(9)	2.509(8)
Sn(1)–O(8)	2.070(7)	Sn(2)–C(9′)	3.720(12)
Sn(2)–C(9)	3.645(17)	Sn(2)–C(10′)	3.689(12)
Sn(2)–C(10)	3.481(14)	Sn(2)–C(11′)	3.538(12)
Sn(2)–C(11)	3.470(12)		

(*b*) Angles

O(1)–Sn(1)–O(1′)	78.93(21)	O(1)–Sn(2)–O(3)	79.77(22)
O(1)–Sn(1)–O(2)	95.20(25)	O(1)–Sn(2)–O(4)	79.17(22)
O(1)–Sn(1)–O(5)	174.92(26)	O(1)–Sn(2)–O(6)	79.93(21)
O(1)–Sn(1)–O(7)	99.72(23)	O(1)–Sn(2)–O(9)	80.00(23)
O(1)–Sn(1)–O(8)	93.22(25)	O(3)–Sn(2)–O(4)	83.80(27)
O(1′)–Sn(1)–O(2)	93.81(24)	O(3)–Sn(2)–O(6)	146.10(25)
O(1′)–Sn(1)–O(5)	99.10(23)	O(3)–Sn(2)–O(9)	74.40(26)
O(1′)–Sn(1)–O(7)	178.42(25)	O(4)–Sn(2)–O(6)	118.40(27)
O(1′)–Sn(1)–O(8)	93.99(24)	O(4)–Sn(2)–O(9)	152.11(23)
O(2)–Sn(1)–O(5)	89.58(26)	O(6)–Sn(2)–O(9)	75.54(26)
O(2)–Sn(1)–O(7)	85.48(26)		
O(2)–Sn(1)–O(8)	169.49(26)		
O(5)–Sn(1)–O(7)	82.32(24)	C(9)–Sn(2)–C(10)	22.0(5)
O(5)–Sn(1)–O(8)	82.23(26)	C(10)–Sn(2)–C(11)	22.1(5)
O(7)–Sn(1)–O(8)	86.90(26)	C(11)–Sn(2)–C(11′)	21.6(4)
		C(11′)–Sn(2)–C(10′)	21.7(5)
		C(10′)–Sn(2)–C(9′)	21.3(5)
Sn(1)–O(1)–Sn(1)	101.07(21)	C(9′)–Sn(2)–C(9)	21.7(5)
Sn(1)–O(1)–Sn(2)	126.94(28)	C(9′)–Sn(2)–C(11)	44.9(4)
Sn(1)–O(1)–Sn(2)	126.04(27)	C(9)–Sn(2)–C(11′)	44.8(4)
		C(10–Sn(2)–C(10)	44.2(3)
Sn(1)–O(2)–C(1)	124.7(6)		
Sn(2)–O(3)–C(1)	139.0(7)	O(1)–Sn(2)–C(9)	152.3(3)
Sn(1)–O(5)–C(3)	128.2(6)	O(1)–Sn(2)–C(10)	143.0(3)
Sn(2)–O(4)–C(3)	132.8(7)	O(1)–Sn(2)–C(11)	143.7(3)
Sn(1)–O(7)–C(5)	129.1(7)	O(1)–Sn(2)–C(9′)	167.6(4)
Sn(2)–O(6)–C(5)	125.8(7)	O(1)–Sn(2)–C(10′)	169.7(4)
Sn(1)–O(8)–C(7)	121.7(6)	O(1)–Sn(2)–C(11′)	153.8(3)
Sn(2)–O(9)–C(7)	135.9(7)		

(*ii*) Trifluoroacetate

(*a*) Lengths

C(1)–O(2)	1.245(11)	C(5)–O(7)	1.250(13)
C(1)–O(3)	1.229(11)	C(5)–O(6)	1.219(13)
C(1)–O(3)	1.510(18)	C(5)–C(6)	1.520(16)
C(2)–F(1)	1.315(17)	C(6)–F(7)	1.244(16)
C(2)–F(2)	1.278(15)	C(6)–F(8)	1.267(19)
C(2)–F(3)	1.272(14)	C(6)–F(9)	1.262(15)
C(3)–O(5)	1.293(11)	C(7)–O(8)	1.279(11)
C(3)–O(4)	1.199(12)	C(7)–O(9)	1.200(12)
C(3)–C(4)	1.494(18)	C(7)–C(8)	1.510(21)
C(4)–F(4)	1.271(14)	C(8)–F(10)	1.240(16)
C(4)–F(5)	1.298(18)	C(8)–F(11)	1.277(21)
C(4)–F(6)	1.323(16)	C(8)–F(12)	1.241(22)

TABLE 2 (*continued*)

(*ii*) Trifluoroacetate (*continued*)

(*b*) Angles

O(2)–C(1)–O(3)	128.1(10)	O(6)–C(5)–O(7)	128.8(9)
O(2)–C(1)–C(2)	115.6(9)	O(6)–C(5)–C(6)	117.3(8)
O(3)–C(1)–C(2)	116.2(9)	O(7)–C(5)–C(6)	114.0(9)
C(1)–C(2)–F(1)	110.1(12)	C(5)–C(6)–F(7)	113.3(10)
C(1)–C(2)–F(2)	113.0(11)	C(5)–C(6)–F(8)	110.3(11)
C(1)–C(2)–F(3)	113.4(11)	C(5)–C(6)–F(9)	113.5(12)
F(1)–C(2)–F(2)	104.4(11)	F(7)–C(6)–F(8)	107.0(13)
F(1)–C(2)–F(3)	105.9(12)	F(7)–C(6)–F(9)	108.5(13)
F(2)–C(2)–F(3)	109.5(12)	F(8)–C(6)–F(9)	103.7(12)
O(4)–C(3)–O(5)	126.6(10)	O(8)–C(7)–O(9)	129.1(10)
O(4)–C(3)–C(4)	120.0(9)	O(8)–C(7)–C(8)	113.2(9)
O(5)–C(3)–C(4)	113.4(9)	O(9)–C(7)–C(8)	117.7(9)
C(3)–C(4)–F(4)	113.6(11)	C(7)–C(8)–F(10)	114.0(13)
C(3)–C(4)–F(5)	110.8(10)	C(7)–C(8)–F(11)	112.4(13)
C(3)–C(4)–F(6)	113.4(11)	C(7)–C(8)–F(12)	112.8(14)
F(4)–C(4)–F(5)	107.4(13)	F(10)–C(8)–F(11)	105.5(15)
F(4)–C(4)–F(6)	107.0(11)	F(10)–C(8)–F(12)	108.0(15)
F(5)–C(4)–F(6)	104.0(11)	F(11)–C(8)–F(12)	103.3(15)

(*iii*) Benzene

(*a*) Lengths		(*b*) Angles	
C(9)–C(9′)	1.389(27)	C(9′)–C(9)–C(10)	118.6(17)
C(9)–C(10)	1.372(30)	C(9)–C(10)–C(11)	120.9(15)
C(10)–C(11)	1.368(29)	C(11′)–C(11)–C(10)	120.4(17)
C(11)–C(11′)	1.317(22)		

Primes denote symmetry-related atoms.

Structure Determination and Refinement.—The positional parameters of the two tin atoms in the asymmetric unit were obtained from a three-dimensional Patterson synthesis, and were used to phase the initial structure-factor calculations. Least-squares refinement, using the locally written program CUDLS, of positional and isotropic thermal parameters of the tin atoms gave a R index of 0.34. The positional parameters of the remaining atoms were located by a difference-Fourier synthesis. All positions refined successfully, except the fluorines which would not converge. The fluorines were assumed to be disordered, and the positions of a second set of fluorines were calculated and given 25% weight. The R factor dropped significantly with convergence of the fluorine positional and temperature factors. The second set of fluorines was then removed and anisotropic temperature factors were imposed on the first set. The R index dropped further, and at that point a molecule of benzene was added to the structure. A weighting scheme was imposed on the data set along with a secondary extinction correction, $F^* = F[1 + 0.36 \times 10^{-8} \times \beta(2\theta)F^2]^{\frac{1}{2}}$ given by Larson.[4] The refinement converged at $R = 0.054$ and $R' = \{[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\} = 0.058$ where $w = |\sigma^2 + (0.025F_o)^2|^{-1}$, σ being the standard error in F_o derived from counting statistics. The maximum value of shift over error for $U(1,1)$ or C(10) was 0.053, and the average shift over error for all variables was 0.009 6. The final value of $[\Sigma w(|F_o| - |F_c|)^2/(N_F - N_p)]^{\frac{1}{2}} = 1.29$, where N_F = number of reflections and N_p = number of refined parameters (223). This indicates that the model accounts for all structurally significant information in the observed structure factors. A final electron-difference map did not reveal the positions of the hydrogen atoms of the benzene ring. The largest feature was a peak of 0.5 e Å^{-3} in the region of the tin atoms. Atomic scattering factors corrected for anomalous dispersion were taken from ref. 5.

The final positional co-ordinates of the atoms in the asymmetric unit are given in Table 1, bond lengths and angles in Table 2. Temperature and structure factors have been deposited as Supplementary Publication No. SUP 22913 (20 pp.).*

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

DISCUSSION

The molecular structure consists of independent centrosymmetric $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2 \cdot C_6H_6$ units (Figure 1). The central feature of the cluster is a $Sn^{IV}_2O_2$ ring in which two μ_3-oxygen atoms form a bridge to two symmetry-related tin(IV) atoms. This type of ring is a common feature in oxo-organotin compounds.[3,4,6-8] The remaining co-ordination site of the three-co-ordinate oxygen atom is occupied by a tin(II) atom of the cluster to yield an almost planar $Sn^{II}O(\mu\text{-}Sn^{IV})_2OSn^{II}$ unit. The co-ordination spheres about both Sn^{IV} and Sn^{II} are completed by four independent trifluoroacetate groups each of which bridges a Sn^{II} and a Sn^{IV}.

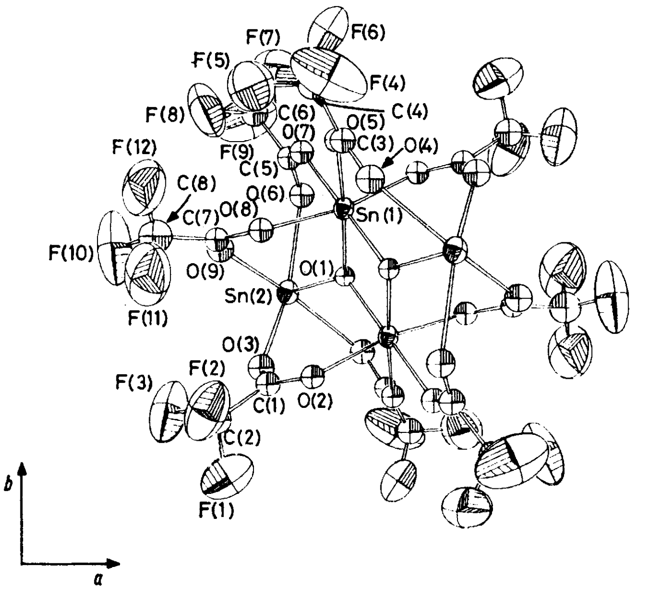

FIGURE 1 Molecular structure of the $[Sn^{II}Sn^{IV}O(OOCCF_3)_4]_2$ dimer viewed down the *c* axis, with 10% probability vibration ellipsoids for the atoms. The labelling of the atoms is as in Table 1. Benzene molecules have been omitted for clarity

Two of the four trifluoroacetate groups are approximately coplanar with the $Sn^{IV}_2O_2$ ring while the other two are almost perpendicular to this ring. The oxygen atoms of the coplanar trifluoroacetate groups are *trans* with respect to the μ_3-oxygen atoms attached to the tin(IV) atoms. One of each type of trifluoroacetate group is quite asymmetric: the C–O group bonded to Sn^{II} is 0.09 Å shorter than that bonded to Sn^{IV}. This shortening is a consequence of the greater degree of covalent character in the tin(IV)–oxygen bonds (Sn^{IV}–O 2.06 Å) compared to the tin(II)–oxygen bonds (Sn^{II}–O 2.45 Å). This difference in C–O bond lengths also causes a distortion of the C–C–O angles. The short C–O bond, that is the one bonded to Sn^{II}, has more double-bond character, and this results in an increase in one C–C–O angle at the expense of the other [O(4)–C(3)–C(4) 120.0(9), O(5)–C(3)–C(4) 113.4(9)°] because of the difference in bond–bond repulsions.

The tin(IV) atom has a distorted-octahedral co-ordination [O–Sn–O 78.93(21)—99.72(23)°] with quite short Sn–O distances, which range from 2.040(6) to 2.070(7) Å. The tin–oxo-bridge distances are at the lower end of this range. These are virtually identical to the values reported by Harrison and co-workers[3] for the closely related *o*-nitrobenzoato-mixed-oxidation-state compound of tin. The tin(IV)–carboxylate-oxygen distances are at the short end of the range of such distances (1.88—2.46 Å) found for tin(IV)–carboxylate compounds.[8-14] The tin(IV)–oxo-bridge distances are only marginally smaller than those of the tin–carboxylate oxygens.

Each tin(II) is bonded to five oxygens in a distorted square-pyramidal arrangement, the Sn^{II}–O(apical) distance being 2.136(5) Å with the Sn^{II}–O basal distances ranging from 2.403(8) to 2.509(8) Å, these values being typical Sn^{II}–O distances.[3] A similar arrangement has been observed for the compound $(C_6H_5)_3Sn^{IV}Sn^{II}(NO_3)$ [15] in which the Sn^{IV} occupies the apical position of a pyramid about the Sn^{II}, with oxygens of the nitrate groups forming the square base: these oxygens are bent away from the apical triphenyltin moiety. Unfortunately details about the O–Sn^{II}–O angles in the basal plane were not given. In the *o*-nitrobenzoato-complexes prepared by Harrison and co-workers[3] the geometry at the Sn^{II} is quite different, being that of a pentagonal bipyramid with an electron pair presumably occupying one of the axial positions. In such an arrangement the O–Sn^{II}–O angles in the equatorial plane would ideally be 72° but in fact they range from 68.9(3) to 76.1(3)°. The tin(II) atom in this pentagonal-bipyramidal arrangement lies 0.32 Å below the basal plane of these five oxygens and the O(apical)–Sn^{II}–O(basal) angle is 83°.

The geometry about the Sn^{II} in the structure discussed here is quite different. There are only four oxygens in the basal plane in our trifluoroacetato-complex, which are displaced towards the apical oxygen so that the Sn^{II} lies 0.440(8) Å below the mean plane of these oxygen atoms (Table 3). The O(basal)–Sn^{II}–O(apical) angles are substantially reduced from 90° [79.17(22)—80.00(23)°]. Such behaviour is strong evidence that the non-bonding electron pair of the Sn^{II} occupies the second apical position of an octahedron with the lone-pair–bond-pair repulsions accounting for the observed distortions. A more interesting aspect of the structure concerns the distortion of the O(basal)–Sn^{II}–O(basal) angles from the idealised value of 90°. These angles are not all equal but vary from 74.40(26) to 118.40(27)°, the larger of these being between O(4) and O(6). It is not possible to locate the non-bonded electron pair in this space, rather than the position discussed above, and still rationalise the arrangement of atoms about the Sn^{II}. Clearly there must be a reason for the angles in the basal plane being so disparate. The observed arrangement is a compromise between the O(basal)–Sn^{II} bonds being at 90° to one another, in order to minimise bond-pair–bond-pair repulsions, and the desire for the CO_2 group to be coplanar with the Sn^{II} and Sn^{IV}. In order to preserve the coplanarity of the $Sn^{IV}_2O_2$ ring and at the same

TABLE 3

Deviations (Å) of atoms from least-squares planes [a]

Plane			
(*a*) $Sn^{II}Sn^{IV}$ μ_3-oxo			
Sn(1)	−0.001(6)	Sn(1′)	0.001(5)
Sn(2)	−0.095(5)	Sn(2′)	0.095(5)
O(1)	0.253(5)	O(1′)	−0.253(5)
(*b*) Sn^{II}–O(basal)			
Sn(2) [b]	0.440(8)	O(6)	0.007(8)
O(3)	0.009(8)	O(9)	−0.010(8)
O(4)	−0.006(8)		
(*c*) Benzene ring			
C(9)	−0.01(3)	C(9′)	−0.01(3)
C(10)	−0.01(3)	C(10′)	0.01(3)
C(11)	0.01(3)	C(11′)	−0.01(3)
Sn(2) [b]	−3.30(1)	Sn(2′) [b]	3.30(1)
(*d*) Sn^{IV}–O			
Sn(1)	−0.056(6)	O(7)	−0.040(6)
O(1)	0.056(6)	O(5)	0.055(6)
O(1′)	−0.043(5)		
Sn(1)	0.032(7)	O(1)	0.061(6)
O(8)	−0.086(7)	O(5)	0.073(6)
O(2)	−0.081(7)		
Sn(1)	0.042(7)	O(7)	0.071(6)
O(1′)	0.060(5)	O(8)	−0.086(7)
O(2)	−0.087(7)		
(*e*) Trifluoroacetate			
O(2)	0.00(1)	F(1) [b]	−1.22(2)
O(3)	0.00(1)	F(2) [b]	0.69(2)
C(1)	0.01(2)	F(3) [b]	0.37(1)
C(2)	0.00(2)		
O(4)	0.00(1)	F(4) [b]	0.23(1)
O(5)	0.00(1)	F(5) [b]	−1.13(2)
C(3)	−0.01(2)	F(6) [b]	0.89(2)
O(6)	0.00(1)	F(7) [b]	−0.93(2)
O(7)	0.00(1)	F(8) [b]	1.08(2)
C(5)	−0.01(2)	F(9) [b]	−0.02(2)
C(6)	0.00(2)		
O(8)	0.00(1)	F(10) [b]	0.06(2)
O(9)	0.00(1)	F(11) [b]	0.99(2)
C(7)	0.00(2)	F(12) [b]	−0.98(2)
C(8)	0.00(2)		

[a] Calculated by the local program P.A.L.S. written by P. G. Ashmore according to V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600. [b] Not used in the calculation of the least-squares plane.

time retain the octahedral arrangement at Sn^{IV}, the bridging trifluoroacetato-ligand cannot remain coplanar with the Sn^{II} and the Sn^{IV}. A coplanar arrangement of, for example, Sn(1)–O(7)–C(5)–O(6)–Sn(2), would result in the O(6)–Sn(2)–O(4′) angle being 180° and coincidence of O(3) and O(9); clearly an impossible situation. The trifluoroacetato-ligand therefore undergoes a twist destroying the potential coplanar arrangement and the O(6)–Sn(2)–O(4′) angle does open up from the ideal 90 to 118.40(27)°, while the O(3)–Sn(2)–O(9) angle closes down to 74.40(26)°. As a result the Sn^{II} is no longer coplanar with the $Sn^{IV}_2O_2$ ring. This arrangement then creates a large open space above O(6)–Sn(2)–O(4′) which could accommodate another ligand. In the case of the *o*-nitrobenzoato-complex reported earlier [3] this vacant space is used to accommodate a molecule of tetrahydrofuran (thf) which results in five oxygen atoms being in the basal plane of the Sn^{II} and the O(basal)–Sn^{II}–O(basal) angles are *ca.* 72°. This site is unoccupied in our structure.

There are further large open spaces in the unit all of which accommodate molecules of benzene. These are located between the regions presumably occupied by the non-bonded electron pair of the tin(II) atoms of adjacent units. Each benzene molecule is shared by two tin(II) atoms on opposite faces of the ring. This arrangement is illustrated in Figure 2, the trifluoroacetato-ligands being omitted for clarity. The tin(II)–carbon (benzene) distances, although quite long at 3.5 Å, are still shorter than the sum of the van der Waals radii for Sn^{II} and C (*i.e.* 4 Å).[16] These distances are slightly longer than those found in $Sn(C_6H_6)(AlCl_4)_2{\cdot}C_6H_6$ where the tin–carbon distance is 3.08 A.[16] However, in the latter compound each benzene is co-ordinated to only one tin, whereas in the title compound each benzene is shared by two tin atoms. It can be seen that the Sn^{II}–O(apical) bond does not lie on the six-fold axis of the benzene ring. The tin(II) atom lies closer to C(10), (C11), and C(11′) of the benzene ring, at distances ranging from 3.470(12) to 3.538(12) Å, than to the other three carbons C(9), C(9′), and C(10′), these latter distances ranging from 3.645(17) to 3.720(12) Å (Table 4). The projection of

TABLE 4

Miscellaneous parameters

	x/*a*	*y*/*b*	*z*/*c*
(*a*) Calculated positions of hydrogen atoms of benzene ring			
H(9)	0.506	0.544	0.187
H(10)	0.511	0.326	0.119
H(11)	0.506	0.106	0.187

(*b*) Bond lengths (Å) and angles (°) of benzene ring

C(9)–H(9)	1.06
C(10)–H(10)	1.09
C(11)–H(11)	1.11

H(9)–C(9)–C(10)	125	H(10)–C(10)–C(11)	120
H(9)–C(9)–C(9′)	116	H(11)–C(11)–C(10)	121
H(10)–C(10)–C(9)	118	H(11)–C(11)–C(11′)	118

(*c*) Interactions (Å)

H(10) ··· F(3)	2.67
H(10) ··· F(10)	2.89 *
H(11) ··· F(12)	2.99

* Intramolecular.

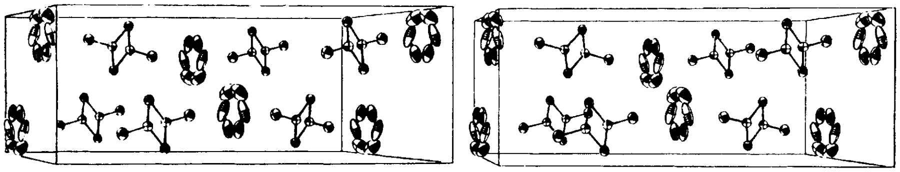

FIGURE 2 Stereoscopic view of the molecular packing of benzene rings and Sn_4O_2 units, with 50% probability vibration ellipsoids for the atoms. The contents of one unit cell are shown plus other atoms outside the unit cell to show the packing with trifluoroacetates omitted for clarity. The crystallographic *a* axis lies along the horizontal direction, the *b* axis on the vertical direction, and the *c* axis completes the right-handed co-ordinate system

the Sn(2)–O(1) bond vector intersects the plane of the benzene ring at an angle of 76°. This results in a zigzag arrangement of $(Sn^{II}Sn^{IV}O)_2$ cluster units and benzene molecules as shown in Figure 2. If this arrangement were the result of some interaction between the π-electron cloud of the benzene ring with the empty *d* orbitals on tin(II) one might have expected a rather more symmetrical location of the benzene molecule. Since this is not the case we must look elsewhere for an explanation.

One possibility is that there are hydrogen-bonding interactions between the hydrogens of the benzene and the fluorine atoms of the trifluoroacetato-ligands. Estimation of the hydrogen-atom positions of the benzene ring then allows one to calculate the distance between these hydrogens and neighbouring fluorine atoms. After such a procedure there are found to be three significant (*i.e.* <3 Å) hydrogen–fluorine interactions (Table 4). One of these is between a hydrogen and a fluorine in the same zigzag chain while the other two hydrogen bonds are to fluorines in adjacent chains. These interactions are probably one reason for the unusual orientation of the benzene in this compound. Hydrogen–fluorine interactions of this kind may account for the fact that none of the CF_3 groups lies in its lowest-energy configuration. One might have expected that within each $F_3C–CO_2$ unit one fluorine would lie above the $C–CO_2$ plane while the other two would lie below this plane. This is not the case (see Table 3), and suggests that there are other interactions present. In addition to the hydrogen-bonded interactions discussed above there are also seven long-range $F \cdots F$ interactions [2.95(3)–3.27(3) Å], *i.e.* between CF_3 groups, which are of a repulsive kind. A balance between $H \cdots F$ attractions and $F \cdots F$ repulsions then, presumably, determines the orientations of the CF_3 groups. There are large anisotropic temperature factors associated with the fluorine atoms indicating that their positions within the lattice are not rigid.

Both $[Sn^{II}Sn^{IV}O(O_2CC_6H_4NO_2\text{-}o)_4(thf)]_2$[3] and the title compound $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2\cdot C_6H_6$ are composed of the same basic centrosymmetric $[Sn^{II}Sn^{IV}O(O_2CR)_4]_2$ unit. The large angle between $O(4)–Sn^{II}–O(6)$ in the trifluoroacetato-complex could be used to accommodate other base molecules, tetrahydrofuran for example in the *o*-nitrobenzoato-complex, with only slight changes in bond angles at Sn^{II} being necessary. When $Sn_2(C_6H_5)_6$ is solvolysed by carboxylic acids, in the absence of benzene as a solvent, then the products isolated have the empirical formula $Sn(O_2CR)_3$ and spectroscopic evidence indicates that these are in fact $Sn_2(O_2CR)_6$.[2] The similarity of the spectroscopic data of these compounds to those of the title compound and Harrison's [3] *o*-nitrobenzoato-complex strongly suggests that these $Sn_2(O_2CR)_6$ species have the same basic oxo-bridged structure, but with the vacant position in the basal plane being taken up by an oxygen of an anhydride molecule. Their formulae would then be $[Sn^{II}Sn^{IV}O(O_2CR)_4]_2\cdot[O(OCR)_2]_2$.

The formation of the title compound, from the solvolysis of $Sn_2(C_6H_5)_6$ by trifluoroacetic acid, is thought to take place by initial attack on $Sn_2(C_6H_5)_6$ by trifluoroacetic acid which results in the cleavage of all tin–carbon bonds. An unstable hexakis(trifluoroacetato)ditin intermediate, (I), is formed [equation (1)] in which the tin–tin bond is

$$Sn_2(C_6H_5)_6 + 6CF_3CO_2H \longrightarrow \underset{(I)}{[Sn(O_2CCF_3)_3]_2} + 6C_6H_6 \quad (1)$$

still intact. Asymmetric cleavage of the tin–tin bond then occurs to produce tin(IV) trifluoroacetate and tin(II) trifluoroacetate which may be associated [equation (2)] *via* bridging trifluoroacetate ligands, (II). Elimination of trifluoroacetic anhydride then occurs [equation (3)] to

$$[Sn(O_2CCF_3)_3]_2 \longrightarrow \underset{(II)}{Sn^{IV}(O_2CCF_3)_4\cdot Sn^{II}(O_2CCF_3)_2} \quad (2)$$

produce (III), an oxo-bridged mixed-oxidation-state compound of tin. This of course has the overall composition $Sn_2(O_2CCF_3)_6$ and is the analogue of

$$2[Sn^{IV}(O_2CCF_3)_4\cdot Sn^{II}(O_2CCF_3)_2] \longrightarrow \underset{(III)}{[Sn^{II}Sn^{IV}O(O_2CCF_3)_4\cdot O(OCCF_3)_2]_2} \quad (3)$$

$Sn_2(O_2CCH_3)_6$ reported many years ago.[1] The molecule of anhydride is obviously rather easily displaced and in an excess of benzene the title compound is the preferred solid product. Incorporation of a benzene molecule into the crystal appears to be either the result of an interaction of the π cloud with empty tin *d* orbitals or, more likely, weak hydrogen-bonded interactions between the fluorines of the trifluoroacetates and the benzene hydrogens. Presumably when anhydride is present, instead of benzene, ordered crystalline material is difficult to obtain.

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