Preparation and Partial Oxidation of Tin(II) Trifluoroacetate: Spectroscopic Properties and *X*-Ray Crystal Structure of Di-μ_3-oxo-octakis-μ-trifluoroacetato-tetratin(II)tin(IV) †

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Pure $Sn(O_2CCF_3)_2$ has been prepared and characterized by ^{119}Sn Mössbauer and vibrational spectroscopy. A novel mixed-valence compound, $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$, has been prepared by the partial oxidation of $Sn(O_2CCF_3)_2$ and characterized spectroscopically and by single-crystal *X*-ray diffraction (to $R' = 0.0722$). The crystals are tetragonal, space group $I\bar{4}2d$, with $a = b = 12.448(3)$, $c = 33.300(4)$ Å, and $Z = 4$. The structure consists of discrete non-centrosymmetric units with point group S_4, the central feature of which is a $Sn^{II}_4Sn^{IV}O_2$ unit containing two μ_3-oxygen atoms each of which bridge between a tin(IV) atom and two symmetry-related tin(II) atoms. The tin(IV) co-ordination is completed by trifluoroacetate groups which bridge to the tin(II) atoms. The tin(IV) and the two μ_3-oxygen atoms lie on the S_4 axis and the two $Sn^{II}_2Sn^{IV}O$ planar units are at 90° to one another. Each pair of tin(II) atoms is bridged by two trifluoroacetates.

The synthesis and spectroscopic properties of carboxylic esters of tin(II) compounds are well documented.[1] It has been inferred from both tin-119 Mössbauer and i.r. data that the tin atom is in a distorted pyramidal environment with bridging and/or chelating carboxylates.[1,2] Although the preparation of tin(II) carboxylates was reported, only a few have been isolated as pure compounds. The only *X*-ray crystal structure so far known for a simple tin(II) carboxylate is that of tin(II) formate.[3] In this compound the tin atom has a 'local' stereochemistry of a distorted trigonal bipyramid with the non-bonding pair of electrons of the tin(II) atom occupying one of the equatorial sites.

It was our intention to isolate pure tin(II) carboxylates and to investigate the crystal structure of at least one of these simple salts. In this paper we report the isolation of pure tin(II) trifluoroacetate and its ^{119}Sn Mössbauer and vibrational spectra. In addition we have discovered a new mixed-valence tin trifluoroacetate and report its spectroscopic properties and *X*-ray crystal structure. Only a few mixed-valence derivatives of tin have been characterized to date and the i.r. spectra and *X*-ray crystal structures of two carboxylates have been described.[4,5] Tin-119 Mössbauer spectroscopy was instrumental in demonstrating the presence of both valence states in these and the compound reported in this paper.

Experimental

Preparation of Tin(II) *Trifluoroacetate.*—Freshly prepared blue-black tin(II) oxide (3.4 g, 0.025 mol) was placed in one side of a Dean-type[6] two-bulb reaction vessel fitted with a glass frit, and a mixture of CF_3CO_2H (15.5 g, 0.14 mol) and $(CF_3CO)_2O$ (5.2 g, 0.025 mol) was distilled onto it. The solid and the acid–anhydride mixture was stirred at room temperature for 18 h. The resulting solution was filtered to the other side of the vessel to give a clear colourless solution. The remaining acid was slowly removed by distillation to give a white crystalline material. This was dried overnight on the vacuum line [Found: C, 14.2; H, 0.45; F, 33.75; Sn, 34.2. $Sn(O_2CCF_3)_2$ requires C, 13.9; H, 0.00; F, 33.05; Sn, 34.45%].

Crystallography.—Tin(II) trifluoroacetate, prepared by the above method, was dissolved in a mixture of CF_3CO_2H and $(CF_3CO)_2O$ (0.6 mol l^{-1}) under a dry-N_2 atmosphere and placed in a tube capped with a valve *via* a 0.25-in Swagelock fitting and its ^{119}Sn n.m.r. spectrum recorded. After 1 month, pyramidal-shaped crystals had formed in the tube which we assumed would be tin(II) trifluoroacetate. However, the elemental analysis was incorrect for $Sn(O_2CCF_3)_2$ (Found: C, 14.0, 12.55; H, 0.20, 0.00; F, 20.6, 19.9; Sn, 38.85%) and furthermore ^{119}Sn Mössbauer spectroscopy showed the presence of a tin(IV) as well as a tin(II) signal.

A colourless bipyramidal crystal of dimensions 0.35 × 0.35 × 0.45 mm was selected and mounted under a dry nitrogen atmosphere in a Lindemann capillary and used for both initial precession *X*-ray photography and subsequent intensity-data collection. The unit-cell parameters were obtained from a least-squares fit of χ, φ, and 2θ for 15 reflections in the range $18.3 < 2\theta < 27.6°$ recorded on a Nicolet P3 diffractometer with the use of Mo-K_α radiation ($\lambda = 0.710\,69$ Å). No density was obtained because the material dissolved in halogenated hydrocarbons and reacted with aqueous solutions. Intensities were also recorded on the Nicolet P3 diffractometer with a θ(crystal)—2θ(counter) scan.

Crystal data. $C_{16}F_{24}O_{18}Sn_5$, $M = 1\,529.19$, systematic absences $hk0$ ($h + k = 2n + 1$), $h00$ ($h = 2n + 1$), hhl ($2h + l \neq 4n$), $0kl$ ($k + l = 2n + 1$), $0k0$ ($k = 2n + 1$), $h0l$ ($h + l = 2n + 1$), $00l$ ($l \neq 4n$), tetragonal, space group $I\bar{4}2d$, $a = b = 12.448(3)$, $c = 33.300(4)$ Å, $U = 5\,159.93$ Å^3, $Z = 4$, $D_c = 1.97$ g cm^{-3}, $F(000) = 2\,038.7$, μ(Mo-K_α) = 25.4 cm^{-1}, standard reflections 4,4,0 (estimated standard deviation 1.09%), -2,3,9 (1.05%), 22 °C, 7 126 reflections collected, 2 999 independent reflections (R_{int} 0.0289), 2 793 with $I > 0$, R 0.1445, R' 0.0722, final shift/error 0.030 (maximum), 0.005 (average), x (secondary extinction) 0.000 15, weighting scheme, $w = [\sigma^2(F_o) + (0.0001\sigma)^2 F_o]^{-1}$.

Structure determination. The methods of selection of scan rates and initial data treatment have been described.[7,8] Corrections were made for Lorentz-polarization and absorption by a psi-scan and Bond correction.[9] The calculations were carried out on a Cyber 170/730 computer. Programs used for initial data treatment were from the *X*-RAY 76 package.[10] The structure was solved using SHELX 76.[11] Diagrams were prepared using ORTEP II.[12]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Final fractional atomic co-ordinates, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn(1)	0.0	0.0	0.0
Sn(2)	0.105 8(2)	0.110 2(1)	0.089 8(1)
O(1)	0.0	0.0	0.062 0(4)
O(2)	0.064 4(9)	0.157 3(9)	0.004 9(3)
O(3)	0.237 6(10)	0.002 5(11)	0.048 6(3)
O(4)	−0.024 8(9)	0.128 0(10)	0.139 7(3)
O(5)	0.163 3(10)	−0.019 6(12)	0.130 7(3)
C(1)	0.232 1(15)	−0.048 1(14)	0.017 2(5)
C(2)	0.336 0(8)	−0.103 9(10)	0.003 4(4)
C(3)	0.112 4(4)	−0.099 2(16)	0.146 0(5)
C(4)	0.186 3(19)	−0.167 2(16)	0.181 1(4)
F(1)	0.104 1(10)	0.402 6(8)	−0.031 3(3)
F(2)	0.059 8(10)	0.388 9(8)	0.027 7(3)
F(3)	0.197 0(10)	0.314 2(8)	0.007 5(3)
F(4)	0.120 0(4)	0.345 6(16)	0.033 6(5)
F(5)	0.036 0(14)	0.429 0(16)	−0.009 5(5)
F(6)	0.181 9(14)	0.360 7(16)	−0.023 4(5)
F(7)	−0.155 4(10)	0.258 0(9)	0.184 9(4)
F(8)	−0.168 9(10)	0.096 1(9)	0.210 5(4)
F(9)	−0.288 2(10)	0.173 1(9)	0.165 7(4)
F(10)	−0.243 8(19)	0.267 7(16)	0.151 8(4)
F(11)	−0.113 9(19)	0.210 4(16)	0.183 5(4)
F(12)	−0.249 9(19)	0.116 3(16)	0.177 6(4)
O(H)*	0.437(1)	0.330(1)	0.110 9(4)

* Disordered water molecule.

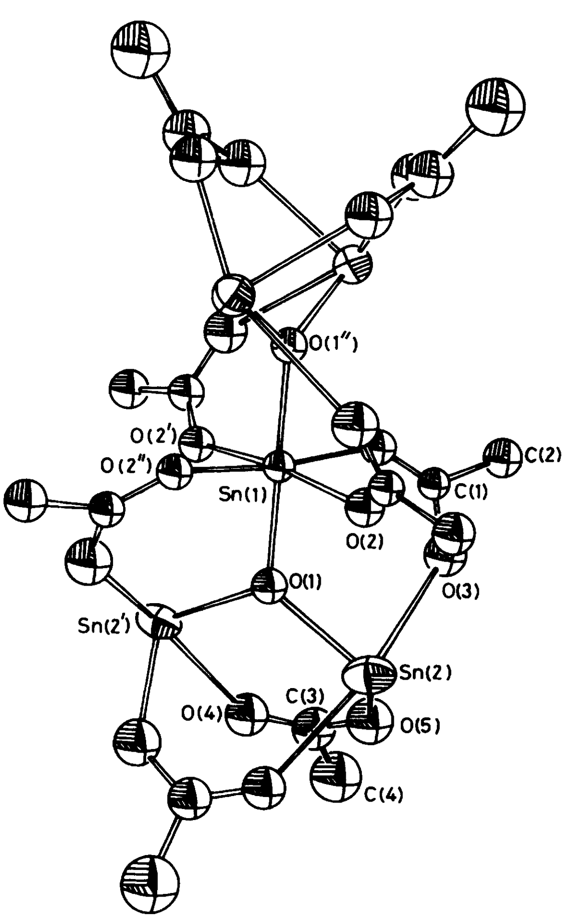

Figure 1. Molecular structure of $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$ viewed down the *b* axis, with 10% probability vibration ellipsoids. Fluorine atoms have been omitted for clarity

The co-ordinates of the two types of tin atoms were obtained from a three-dimensional Patterson synthesis, and a series of full-matrix least-squares refinements, followed by three-dimensional electron-density difference syntheses, revealed all of the atoms. Anisotropic thermal parameters were assigned to the tin atoms and further refinement with full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error was <0.02. Some difficulties were encountered in the refinement because the CF_3 groups were disordered. A number of solutions were attempted with very little success. The final solution, reported here, replaces each CF_3 group with two partially occupied CF_3 groups, and only the fluorine atoms are disordered. Corrections were made for secondary extinction by use of the method of SHELX.[11] Throughout the refinement, scattering factors were taken from ref. 13 and anomalous dispersion corrections for Sn from ref. 14. The space group $I\bar{4}2d$ is non-centrosymmetric and the tin atom has an appreciable anomalous scattering factor. The structure has been refined in both absolute configurations and that whose positional parameters are given in Table 1 gave a better agreement factor (*R* and *R*′). Bond lengths and angles are given in Table 2.

Results and Discussion

Simple tin(II) carboxylates have proven rather difficult to isolate in a pure form. Tin-119 Mössbauer spectra have been recorded for a number of such carboxylates, though not all spectra were obtained from the pure compound.[2] In those instances where the pure solid could be isolated, Donaldson and Jelen[2] found that the Mössbauer parameters of the pure solid at 77 K and those recorded for the compound dissolved in the parent acid, and frozen to 77 K, were the same. They inferred that the co-ordination at Sn^{II} did not change on dissolution and was of the three-co-ordinated pyramidal type.

During our investigations of some related compounds we were able to isolate pure tin(II) trifluoroacetate, whose properties are reported below. Moreover, a solution of $Sn(O_2CCF_3)_2$, in a mixture of trifluoroacetic acid and trifluoroacetic anhydride, produced small bipyramidal crystals which we initially assumed to be $Sn(O_2CCF_3)_2$. Subsequent Mössbauer analysis showed that these crystals could not be tin(II) trifluoroacetate but were a new mixed-oxidation-state compound of tin.

Structure of $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$.—The structure of the molecule is shown in Figure 1. It consists of independent non-centrosymmetric $[Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8]$ units. The central feature of the cluster is a $Sn^{II}_4Sn^{IV}O_2$ unit containing two μ_3-oxygen atoms which each form a bridge between a tin(IV) atom and two symmetry-related tin(II) atoms and lie in the plane containing these atoms. This type of planar unit is a common feature in oxo-organotin compounds.[4,5,15–18] The tin(IV) atom lies on the symmetry element $\bar{4}$, the two μ_3-oxygen atoms on an associated two-fold axis. The two $Sn^{II}_2Sn^{IV}O$ planar units are at 90° to each other. Each of the pairs of tin(II) atoms is bridged by two trifluoroacetate groups. In addition, four trifluoroacetate groups bridge the central tin(IV) atom to each of the tin(II) atoms.

The atom Sn(1) is in a slightly distorted octahedral environment with the axial Sn–O distance [2.07(1) Å] being shorter than the equatorial Sn–O distance [2.12(1) Å]. Similar six-co-ordination is shown by tin(IV) atoms in the other two mixed-valence tin compounds whose structures have been reported, although in these cases the bond lengths were not very different.[4,5] One pair of opposite O(2) atoms [O(2),O(2′)] are

0.90 Å below the plane which goes through Sn(1) and is perpendicular to the S_4 axis. The other pair of O(2) atoms are 0.90 Å above this plane. The Sn(1)–O distances are at the lower end of the range usually shown by tin(IV) carboxylates (1.88—2.46 Å).

The Sn(2) atoms show a range of Sn–O bond distances. The shortest Sn(2)–O bond [2.118(6) Å] is that to the oxygen O(1) which bridges the three tin atoms. There are two others of intermediate length [Sn(2)–O(4) 2.23(1), Sn(2)–O(5) 2.33(1) Å], formed by the trifluoroacetates bridging the two Sn(2) atoms. Another slightly longer bond [Sn(2)–O(3) 2.53(1) Å] is formed by those trifluoroacetates bridging the Sn(1) and Sn(2) atoms. In addition, the presence of a long interaction between Sn(2) and O(2) [2.94(1) Å] is considered significant since this is well within the sum of the van der Waals radii of tin and oxygen (3.70 Å). Furthermore such an interaction accounts for the distortions of the Sn(1)–$[O(2)]_4$ unit from planarity. This results in a five-co-ordinated environment for the Sn(2) atoms. In structures containing tin(II) the effect of the non-bonding electron pair is manifested in a vacant space in the structure, and a distortion of the tin–ligand bonds occurs. This effect is clearly seen around the tin(II) atoms, and their environments may be described as pseudo-six-co-ordinate (SnX_5E), with the non-bonding pair (E) pointing along the axial direction of this distorted octahedron. It is interesting that few five-co-ordinate (pseudo-six-co-ordinate) examples of tin(II) have been reported, these being one of the tin sites in α-SnF_2,[19] the tin(II) in $BaSnF_4$,[20] and the tin(II) site in the tin mixed-oxidation-state trifluoroacetate.[5]

The assignment of the co-ordination number to an atom is however often extremely difficult, involving the question as to whether an adjacent, potentially co-ordinating atom is in fact a part of the co-ordination sphere. Consider the case of Sn(2) atoms in our structure. If the long interaction [Sn(2)–O(2), 2.94(1) Å] is left out, then the co-ordination can best be described as a distorted trigonal bipyramid with the non-bonding pair presumably occupying an equatorial position. Similar tin(II) environments are observed in tin(II) formate[3] and in the tin(II) oxalate anion.[21] The tin(II) environment in the mixed-valence tin trifluoroacetate prepared by Birchall and Johnson[5] is a distorted square pyramid, whereas in the mixed-valence tin *o*-nitrobenzoate made by Ewings *et al.*[4] the tin(II) atom has a pentagonal pyramidal co-ordination. In the latter complex the longest tin(II)–oxygen distance is 2.661(9) Å. The tin(II) atom in our compound has different Sn–O_{eq} bond distances. The O_{eq}–Sn–O_{eq} and O_{ax}–Sn–O_{ax} angles exhibit the usual reduction from the values expected for an ideal trigonal bipyramidal or octahedral geometry due to lone pair–bond pair repulsions and the unequal Sn^{II}–O distances.

The trifluoroacetic O–C–O units bridging the tin(II) atoms are asymmetric [C(3)–O(4) 1.17(2), C(3)–O(5) 1.28(2) Å], whereas those bridging the tin(II) and tin(IV) atoms are symmetric [C(1)–O(3) 1.22(2), C(1)–O(2) 1.20(2) Å]. The Sn–O bond distances arising from the trifluoroacetates bridging between the Sn^{II} and the Sn^{IV} are very different however [Sn(2)–O(3) 2.53(1), Sn(1)–O(2) 2.12(1) Å], whilst those arising from the trifluoroacetates bridging the two tin(II) atoms are quite similar [Sn(2)–O(4) 2.23(1), Sn(2)–O(5) 2.33(1) Å]. The shortness of the tin(IV)–oxygen bond compared to the tin(II)–oxygen bonds is a consequence of the greater degree of covalent character in the former.

The asymmetry of the C–O distances observed for the trifluoroacetates bridging the two Sn(2) atoms indicates bonding of the type  $Sn^{II}-O-\overset{|}{C}=O\rightarrow Sn^{II}$. This pattern has also been observed for the carboxylates which bridge two tin(IV) atoms[17,18] or tin(II) and tin(IV) atoms.[4,5] The C–O bond lengths of the trifluoroacetate group which bridges Sn(2) and

Table 2. Bond distances (Å) and angles (°) for $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$ with e.s.d.s in parentheses

(*a*) Tin co-ordination

Sn(1)–O(1)	2.07(1)	Sn(2)–O(1)	2.118(6)
Sn(1)–O(2)	2.12(1)	Sn(2)–O(2)	2.94(1)
		Sn(2)–O(3)	2.53(1)
		Sn(2)–O(4)	2.23(1)
		Sn(2)–O(5)	2.33(1)

O(1)–Sn(1)–O(2)	85.6(3)	O(1)–Sn(2)–O(2)	66.1(4)
O(1)–Sn(1)–O(2″)	94.4(3)	O(1)–Sn(2)–O(3)	79.6(3)
O(2′)–Sn(1)–O(2″)	90.3(4)	O(1)–Sn(2)–O(4)	86.5(4)
O(2)–Sn(1)–O(2′)	171.3(4)	O(1)–Sn(2)–O(5)	89.9(4)
		O(2)–Sn(2)–O(3)	72.1(3)
		O(2)–Sn(2)–O(4)	122.9(3)
		O(2)–Sn(2)–O(5)	142.0(4)
		O(3)–Sn(2)–O(4)	153.0(4)
Sn(2)–O(1)–Sn(2′)	127.8(6)	O(3)–Sn(2)–O(5)	74.9(4)
Sn(2)–O(1)–Sn(1)	116.1(3)	O(4)–Sn(1)–O(5)	82.0(4)

(*b*) Trifluoroacetate: F atoms are disordered with the F(1),F(2),F(3) site having occupancy 0.65, F(4),F(5),F(6) 0.35, F(7),F(8),F(9) 0.555, and F(10),F(11), F(12) 0.445 of an atom

C(1)–O(2)	1.20(2)	C(3)–O(4)	1.17(2)
C(1)–O(3)	1.22(2)	C(3)–O(5)	1.28(2)
C(1)–C(2)	1.54(2)	C(3)–C(4)	1.71(3)
C(2)–F(1)	1.25(2)	C(4)–F(7)	1.20(2)
C(2)–F(2)	1.34(2)	C(4)–F(8)	1.34(2)
C(2)–F(3)	1.25(2)	C(4)–F(9)	1.37(2)
C(2)–F(4)	1.25(2)	C(4)–F(10)	1.74(3)
C(2)–F(5)	1.45(2)	C(4)–F(11)	1.05(3)
C(2)–F(6)	1.22(2)	C(4)–F(12)	1.02(3)
O(H) · · · O(H)	2.21(2)		

O(2)–C(1)–O(3)	131(2)	O(4)–C(3)–O(5)	129(2)
O(2)–C(1)–C(2)	113(1)	O(4)–C(3)–C(4)	118(2)
O(3)–C(1)–C(2)	116(2)	O(5)–C(3)–C(4)	113(1)
C(1)–C(2)–F(1)	109(2)	C(3)–C(4)–F(7)	111(2)
C(1)–C(2)–F(2)	117(1)	C(3)–C(4)–F(8)	95(1)
C(1)–C(2)–F(3)	109(1)	C(3)–C(4)–F(9)	106(1)
C(1)–C(2)–F(4)	116(1)	C(3)–C(4)–F(10)	101(1)
C(1)–C(2)–F(5)	112(1)	C(3)–C(4)–F(11)	81(2)
C(1)–C(2)–F(6)	114(1)	C(3)–C(4)–F(12)	92(2)
F(1)–C(2)–F(2)	104(1)	F(7)–C(4)–F(8)	120(2)
F(1)–C(2)–F(3)	111(1)	F(7)–C(4)–F(9)	107(2)
F(1)–C(2)–F(4)	132(1)	F(7)–C(4)–F(10)	61(1)
F(1)–C(2)–F(5)	51(1)	F(7)–C(4)–F(11)	40(1)
F(1)–C(2)–F(6)	55(1)	F(7)–C(4)–F(12)	148(3)
F(2)–C(2)–F(3)	105(1)	F(8)–C(4)–F(9)	117(2)
F(2)–C(2)–F(4)	43(1)	F(8)–C(4)–F(10)	162(2)
F(2)–C(2)–F(5)	58(1)	F(8)–C(4)–F(11)	98(2)
F(2)–C(2)–F(6)	129(1)	F(8)–C(4)–F(12)	78(2)
F(3)–C(2)–F(4)	66(1)	F(9)–C(4)–F(10)	51(1)
F(3)–C(2)–F(5)	139(1)	F(9)–C(4)–F(11)	143(2)
F(3)–C(2)–F(6)	58(1)	F(9)–C(4)–F(12)	43(2)
F(4)–C(2)–F(5)	99(1)	F(10)–C(4)–F(11)	92(2)
F(4)–C(2)–F(6)	113(1)	F(10)–C(4)–F(12)	94(2)
F(5)–C(2)–F(6)	101(1)	F(11)–C(4)–F(12)	172(3)

(*c*) Intermolecular interactions

F(2) · · · F(8)	2.88(2)	F(2) · · · F(8)	2.94(2)
F(2) · · · F(11)	2.81(2)	F(3) · · · F(7)	3.17(2)
F(4) · · · F(8)	3.18(2)	F(4) · · · F(11)	3.19(2)
F(5) · · · F(8)	3.05(2)	F(5) · · · F(8)	3.12(2)
F(6) · · · F(7)	3.00(2)	F(6) · · · F(9)	2.86(2)
F(6) · · · F(10)	2.95(2)	F(10) · · · F(10′)	2.84(2) *
F(10) · · · F(12′)	3.01(2)	F(10) · · · F(7′)	3.11(2)
F(9) · · · F(10′)	2.43(2) *		

* Considered short enough to be significant. Van der Waals radii: F, 1.50—1.60; Sn, 2.20 Å.

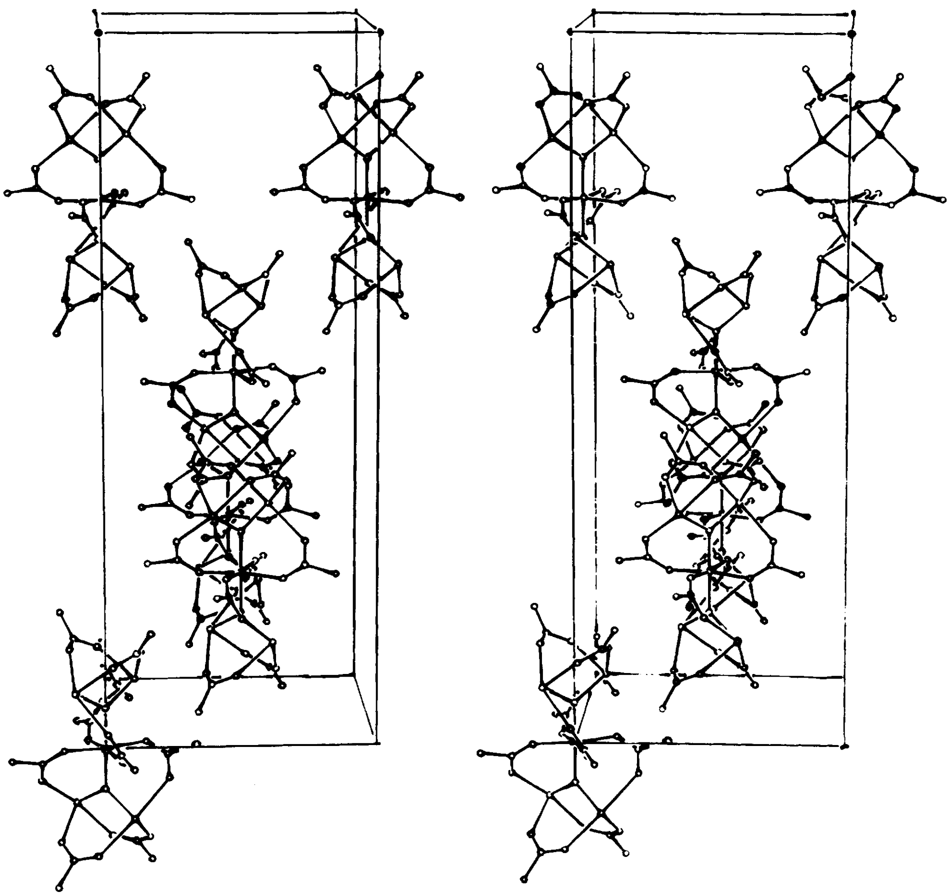

Figure 2. Stereoscopic view down the *b* axis of the molecular packing with 2% probability vibration spheres. Of the molecules having their centres at the corners of the cell only one is shown

Sn(1) in the structure described here have similar values [1.20(2), 1.22(2) Å] and this is rather unexpected.

The differences in the C–O bond lengths may also cause a distortion in the C–C–O angles. The short C–O bond presumably 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) 118(2), O(5)–C(3)–C(4) 113(1)°] because of bond repulsion. In the case of symmetrically bridging carboxylate groups, one would expect the angles to be the same, as is observed [O(2)–C(1)–C(2) 113(1), O(3)–C(1)–C(2) 116(2)°]. The packing of these molecular units is shown in Figure 2. There are no strong interactions between molecules but some distances between CF_3 fluorines are less than the sum of two fluorine van der Waals radii. The relevant intermolecular F $\cdots$ F interactions are listed in Table 2 and a few of these are sufficiently short to suggest that the CF_3 groups are correlated from cell to cell such that in one cell the CF_3 group has the F(i = 7—9) position and in the next the F(i = 10—12) position. In addition to the tin-containing molecule there is a highly disordered water molecule in the lattice.

Mössbauer Spectroscopy.—Tin trifluroacetate had not been isolated as a pure solid until now. The original attempted preparation resulted in a yellow syrup whose Mössbauer parameters were reported[1,2] as δ = 3.16 mm s^{-1} and Δ = 1.76 mm s^{-1}. We have been able to isolate this compound as a pure white crystalline material, the Mössbauer parameters of which are given in Table 3. We also include the parameters obtained upon dissolution of tin(II) trifluoroacetate in a trifluoroacetic acid–trifluoroacetic anhydride mixture and then freezing to 77 K, at which temperature the spectrum was recorded. The spectra of the pure solid and of the frozen solution are shown in Figure 3. It is clear that they are quite different, indicating that the tin environment in the solid state is not the same as that in the frozen solution. Furthermore our frozen-solution results are quite different from those of Donaldson and Jelen.[2] In order to compare our results further with those of the earlier workers[2] we have included data for $Sn^{II}(O_2CCHCl_2)_2$ in Table 3. In this case our results are in good agreement with those of Donaldson and Jelen[2] after allowing for the different references used. We attempted to record frozen-solution spectra of the dichloroacetate in the acid–anhydride mixture and obtained essentially the same spectrum as for the solid. However, close examination of this 'frozen solution' revealed that small crystallites were present, presumably due to precipitated $Sn^{II}(O_2CCHCl_2)_2$. We feel therefore that we were not examining a true frozen solution in this instance, unlike the case with tin(II) trifluoroacetate discussed above where the solubility is quite high and a true frozen solution was obtained. It seems likely that the differences in Mössbauer parameters between our 'frozen solution' tin(II) trifluoroacetate and the earlier results[2] lie in the method of preparation of the two solutions. In our experiment there is no possibility that water could be present, whereas the earlier solution was prepared by evaporation of an aqueous acid

Table 3. Mössbauer data (mm s^{-1})

Compound	T/K	Sn^{IV}			Sn^{II}			A (high-velocity line) / A (low-velocity line)
		δ[a]	Δ	Γ	δ[a]	Δ	Γ	
$Sn(O_2CCF_3)_2$	77				3.53	2.29	1.01, 1.03	1.09
$Sn(O_2CCF_3)_2$[b]	77				3.64	1.59	0.94	
$Sn(O_2CCF_3)_2$[c,d]	77				3.16	1.76		
$Sn(O_2CH)_2$[e]	77				3.33	1.70	1.02, 1.11	1.28
$Sn(O_2CCHCl_2)_2$	77				3.60	1.66	1.17, 1.19	1.24
$Sn(O_2CCHCl_2)_2$[d]	77				3.48	1.64		
								$A(Sn^{II})$/ $A(Sn^{IV})$
$Sn_5O_2(O_2CCF_3)_8$	4	0.10	1.11	1.01	3.66	1.85	1.09	2.75
	4[f]	0.17	0.97	1.15	3.36	1.86	1.12	2.98
	20	0.10	1.07	1.07	3.65	1.84	1.08	2.77
	34	0.09	1.04	1.25	3.60	1.82	1.11	2.73
	55	0.09	1.03	1.19	3.52	1.78	1.08	2.77
	77	0.09	1.12	1.84	3.59	1.78	0.92	2.82
	125[g]	0.06	1.14	1.00	3.58	1.78	1.00	2.58
	150[g]	0.12	1.13	1.00	3.57	1.76	1.00	2.32
$[Sn_2O(O_2CC_6H_4NO_2\text{-}o)_4\text{-}(thf)]_2$[h]	77	0.068	0.00	1.18	3.597	1.823	0.829	
$[Sn_2O(O_2CCF_3)_4{\cdot}O(OCCF_3)_2]_2$[i]	77	−0.03	0.52	0.81	3.94	1.11	0.85	0.86

[a] Mössbauer spectra were recorded on equipment described (T. Birchall, R. C. Burns, L. A. Devereaux, and G. J. Schrobilgen, *Inorg. Chem.*, 1985, **24**, 890), and were fitted using the program of R. Ruenbauer and T. Birchall (*Hyperfine Interact.*, 1978, **7**, 125). All isomer shifts are relative to $CaSnO_3$ at room temperature. [b] Frozen solution in CF_3CO_2H. [c] Syrup. [d] Ref. 2. [e] Ref. 3. [f] Amount of tin used was 2 mg cm^{-2} and both source and absorber were at 4 K; in all other measurements the amount of tin used was 15 mg cm^{-2}. [g] Linewidths fixed at 1.00 mm s^{-1} in order to obtain realistic fits because of the poor statistics. [h] Ref. 4, thf = tetrahydrofuran. [i] T. Birchall and J. P. Johnson, *Inorg. Chem.*, 1982, **21**, 3724.

solution. Pure tin(II) trifluoroacetate obviously has the tin(II) in a very distorted environment with the non-bonding electron pair being stereochemically active.

On the basis of these data it is not possible to infer the geometry about the tin. It has been generally assumed[22] that this will be pyramidal, but the only structure of a simple tin(II) carboxylate so far published, $Sn^{II}(O_2CH)_2$,[3] has four oxygens in close proximity, which together with the non-bonding electron pair form a trigonal bipyramidal arrangement about the tin(II). From the magnitude of the quadrupole splitting in $Sn^{II}(O_2CCF_3)_2$ it would appear that the Sn^{II} is in a more asymmetric environment that that found in the tin(II) oxalate complexes which have distorted square pyramidal environments. It is also clear that in the frozen solution the environment is much less distorted, since the isomer shift has increased (3.53 to 3.64 mm s^{-1}) and the quadrupole splitting has decreased (2.29 to 1.59 mm s^{-1}). In all of the spectra of tin(II) carboxylates that we have recorded we note an asymmetry to the quadrupole doublets. This is characteristic of a rather asymmetrically bonded tin. We have checked that this is not the result of preferred crystal orientation.

The Mössbauer parameters of the crystals whose structure is described above are summarized in Table 3 and the spectrum obtained at 77 K is shown in Figure 4. There are clearly two non-cubic tin environments, one due to Sn^{IV} and the other, more intense, to Sn^{II}. The data are consistent with the *X*-ray crystallographic results discussed above. The spectrum arising from the tin(IV) is a well resolved quadrupole doublet, Δ = 1.12 mm s^{-1}, in agreement with the distorted environment found, *i.e.* Sn^{IV}–O(1) 2.07(1), Sn^{IV}–O(2) 2.12(1) Å, with the plane of the four Sn^{IV}–O(2) being buckled as described earlier. This distortion is more severe than was reported in either of the two previous *X*-ray crystal structure reports on mixed-oxidation-state tin carboxylates.[4,5] In both of the previous cases no quadrupole splitting was observed from the tin(IV) atom.

The doublet arising from the tin(II) nuclei is typical for tin(II) carboxylates with an isomer shift of 3.59 mm s^{-1} and a quadrupole splitting of 1.78 mm s^{-1}. *X*-Ray crystallography shows the Sn^{II} to be in a distorted SnX_5E environment, the short Sn^{II}–O(1) bond being opposite the space that the non-bonding electron pair presumably occupies. The electron pair has a considerable influence on the equatorial Sn^{II}–O bonds so that the Sn^{II} is out of the plane of these atoms. Furthermore the bond lengths range from 2.23 to 2.33 Å for the short bonds, to 2.94 Å for the longest. The isomer shift and quadrupole splitting observed for these tin(II) atoms are similar to the values obtained for the simple $Sn^{II}(O_2CCF_3)_2$ and it might be tempting to infer therefore that the tin(II) trifluoroacetate has a similar environment, rather than the generally assumed pyramidal environment.[2] This latter co-ordination for $Sn^{II}(O_2CCF_3)_2$ cannot be ruled out however from the Mössbauer data alone.

Variable-temperature Mössbauer data provide additional information about the lattice structure. The recoil-free fraction (f) is related to the mean-square vibrational amplitude of the Mössbauer atom. Since the vibrational amplitude is temperature dependent, the recoil-free fraction, $f(T)$, itself is temperature dependent and, through this, chemical information can be extracted. Since, for a thin absorber, $f(T)$ is directly related to the area [$A(T)$] under the resonance curve of a Mössbauer spectrum, the temperature variation of $f(T)$ may be followed by experimentally evaluating the parameter $A(T)$. Semilogarithmic plots of resonance areas (normalized to 77 K) against temperature for the tin(II) and tin(IV) sites of the above mixed-valence tin compound are shown in Figure 5. These are found to be linear in the temperature range $4 \leqslant T \leqslant 150$ K with correlation coefficients 0.9939 (Sn^{II}) and 0.9855 (Sn^{IV}).

The Debye model of solids can be expressed, in the high-temperature limit, as in equation (1) where $T > \theta_D/2$ and where E_γ = γ-ray energy, M = mass of system, and θ_D = Debye

$$\ln f = -\frac{3E_\gamma^2}{Mc^2k_B\theta_D^2} \cdot T \qquad (1)$$

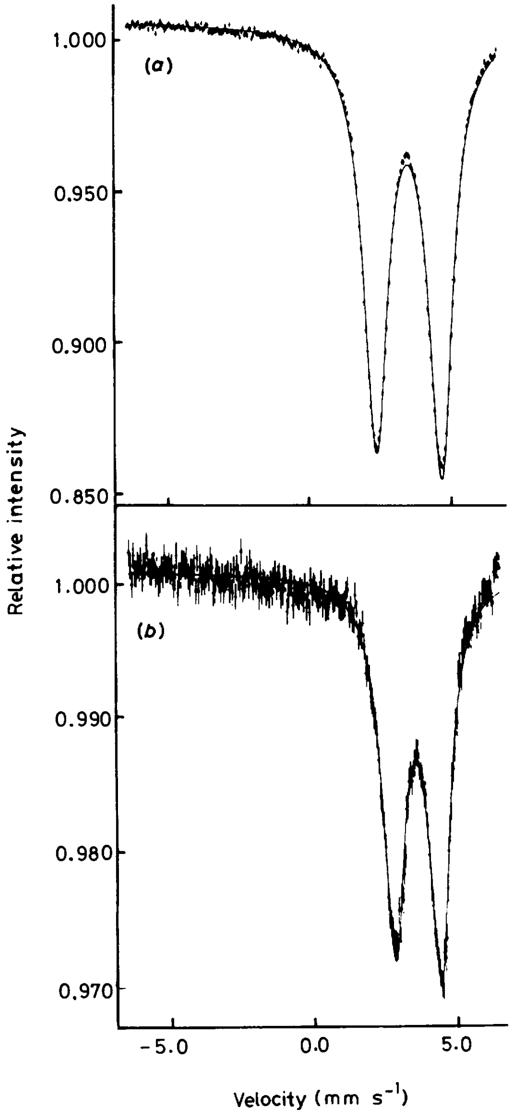

Figure 3. Tin-119 Mössbauer spectra of $Sn(O_2CCF_3)_2$: (*a*) solid, (*b*) a frozen solution of at 77 K

temperature. In the low-temperature limit ($T \to 0$) ln f becomes independent of temperature, with all atoms in the zeroth vibrational state. Under these conditions the recoil-free fraction is given by equation (2) and this reflects the zero-point motion of the atom in its potential-energy well.

$$\ln f = -3E_\gamma^2/Mk_B\theta_D \qquad (2)$$

Herber *et al.*[23] in their variable-temperature study ($4 \leqslant T \leqslant 175$ K) of cyclic dibutyl distannoxanes, observed a linear function in the high-temperature limit ($60 \leqslant T \leqslant 175$ K) and then departure from linearity at lower temperatures, which reflects the zero-point motion. The linear plot shown in Figure 5 is in accord with the Debye model of solids at high temperature. The gradient of this plot is a useful guide to the lattice structure. The more tightly bound are the tin atoms, the more gentle is the slope. The temperature coefficients $-\{d[\ln A(T)/A(77)]/dT\}$ of the tin(II) and tin(IV) atoms are 1.76×10^{-2} and 1.66×10^{-2} K^{-1} respectively. These values can be compared with those reported for a number of organotin compounds of known structure.[24] Compounds which have lattices consisting of non-interacting monomeric molecules have temperature coefficients of *ca.* 1.8×10^{-2} K^{-1}, irrespective of co-ordination number. Strongly hydrogen-bonded lattices exhibit temperature coefficients of *ca.* 1.0×10^{-2} K^{-1} and tightly packed ionic lattices, such as tin(II) oxide, exhibit values as low as 0.23×10^{-2} K^{-1}. The values for the two types of tin atoms in the mixed-valence *o*-nitrobenzoate prepared by Harrison and co-workers[4] are 1.71×10^{-2} K^{-1} for the tin(II) atoms and 1.30×10^{-2} K^{-1} for the tin(IV) atoms. The values obtained for our compound are consistent with the monomeric nature of the structure with the tin(IV) atoms being slightly more tightly bound than the tin(II) atoms in the lattice.

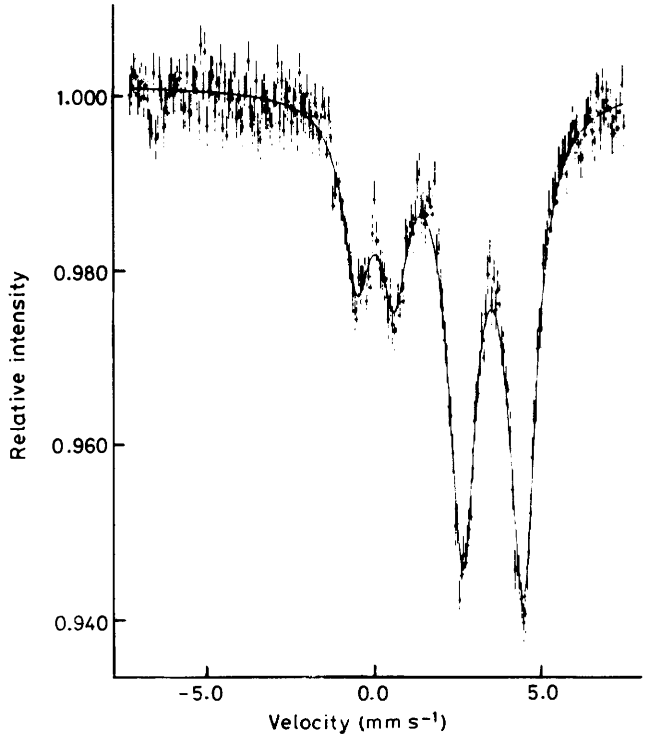

Figure 4. Tin-119 Mössbauer spectrum of $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$ at 77 K

The relative areas of the tin(II) and tin(IV) resonances should reflect the relative numbers of such nuclei. It is clear that the relative areas are not in the 4:1 ratio expected from the crystallographic and analytical results. The temperature-dependent study shows that this ratio varies from 2.32 at 150 K to 2.98 at 4 K (Table 3), never reaching the expected value of 4 even by 4 K, indicating that even at this temperature the tin sites are still 'rather soft.' This is clear from Figure 5, which demonstrates that the tin(II) and tin(IV) atoms are far from their zero-point vibrational state even at 4 K.

Vibrational Spectroscopy.—Table 4 contains a summary of the i.r. and Raman data for both the tin(II) trifluoroacetate and $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$. No vibrational bands were detected at frequencies higher than *ca.* 1 780 cm^{-1} confirming that free trifluoroacetic acid is not present in either of these materials. There is little difference in the spectra of the two compounds in the range 1 780—1 100 cm^{-1} with the bands at *ca.* 1 700 cm^{-1} being associated with ν_{asym}(O–C–O) while bands arising from vibrations due to the CF_3 groups are found in the range 1 200—1 100 cm^{-1}. In the region below 1 100 cm^{-1} the spectrum of the mixed-oxidation-state compound is more complex than that of

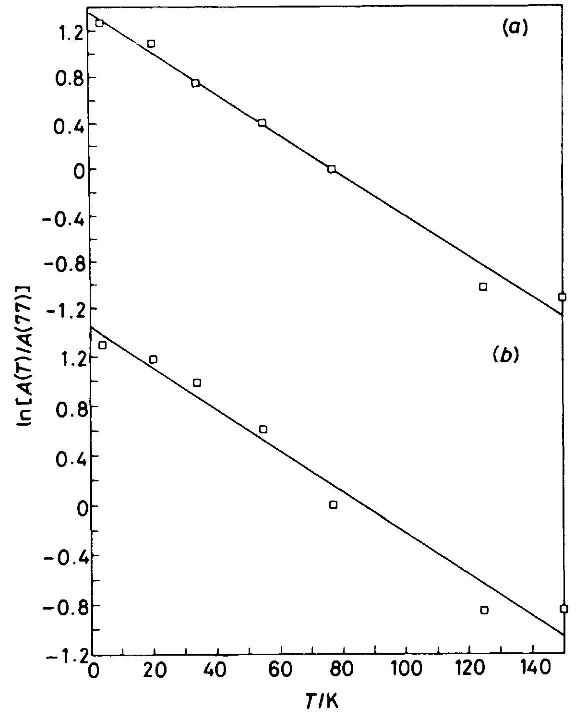

Figure 5. Plot of the natural logarithm of the area under the Mössbauer resonance curve (normalized to 77 K) against temperature for (*a*) the tin(II) site and (*b*) the tin(IV) site of $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$

Table 4. Vibrational spectroscopic data (cm^{-1}) for $Sn^{II}(O_2CCF_3)_2$ and $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$ [a]

$Sn^{II}(O_2CCF_3)_2$		$Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$		
I.r.	Raman [b]	I.r.	Raman [b]	Assignment
		1 776w		
1 710s	1 696(22)	1 700m		
1 690s		1 660m	1 660(43)	$\nu_{asym}(CO_2)$
1 645s		1 610s	1 625(55)	
1 465m	1 456(23)	1 450w	1 450(100)	$\nu_{sym}(CO_2)$
1 410m	1 418(43)	1 430m	1 430(29)	
1 225s,br		1 224m	1 200(12)	
1 200s,br		1 189s	1 182(15)	$\nu(CF_3,CF_2)$
1 170s,br		1 154m	1 118(3)	
1 039w				
970w				
850m	853(100)	854w	850(34)	$\delta(CO_2),\nu(C-C)$
	816(24)	794m	845(63)	
	814(18)			
780m				
720s	730(2)	724s	728(2)	$\nu(Sn-O-Sn)$
680m			718(2)	$\nu(CO_2)$
620 (sh)	636(13)		610(4)	
600m		604m	600(4)	$\pi(O-C-O)$
590 (sh)				
	236(19)		290(32)	
	204(76)		271(12)	$\nu(Sn-O)$
	170(2)		205(11)	
	160(5)		150(13)	$\delta(O-Sn-O)$

[a] s = Strong, sh = shoulder, m = medium, w = weak, and br = broad. For $Na(O_2CCF_3)$: $\nu_{sym}(CO_2)$ 1 680, $\nu_{asym}(CO_2)$ 1 457 cm^{-1}. For $K(O_2CCF_3)$, $\nu_{sym}(CO_2)$ 1 678, $\nu_{asym}(CO_2)$ 1 437 cm^{-1}. [b] Relative intensities are given in parentheses.

tin(II) trifluoroacetate. Tentative assignments have been made in Table 4.

Deacon and Phillips[25] have pointed out the difficulties in deciding between the presence of unidentate, bridging, or chelating carboxylates. They conclude that when $\nu_{asym}(CO_2)$ is at higher frequency and $\nu_{sym}(CO_2)$ at lower frequency than in the ionic carboxylate, one can infer the presence of a unidentate carboxylate. They demonstrated that correlations claimed to establish a variety of other modes of co-ordination are not valid.[26] In the case of our mixed-oxidation-state tin trifluoroacetate, more than one band is observed in the regions where one would expect both $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$. Since our structural analysis, Table 2 and Figure 1, shows that we do in fact have two kinds of carboxylate, these observations are reasonable. The values for $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ for $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$ in fact bracket the frequencies for the alkali-metal trifluoroacetates. All of the trifluoroacetates in $Sn^{II}_4Sn^{IV}O_2(O_2CCF_3)_8$ act as bridging ligands, one set symmetrical, the other very asymmetrical. For $Sn^{II}(O_2CCF_3)_2$ the two $\nu_{asym}(CO_2)$ bands are shifted to lower frequency than for ionic trifluoroacetate, while the $\nu_{sym}(CO_2)$ bands are relatively unshifted. Taking all of this evidence from the two compounds, we conclude that $Sn(O_2CCF_3)_2$ probably does not contain a unidentate trifluoroacetate ligand. We note that tin(II) formate which has symmetrical as well as asymmetrically bridging formate ligands also shows multiplicity in its $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ vibrational spectra.[3]

Conclusions

We have isolated pure $Sn^{II}(O_2CCF_3)_2$ and characterized it by analysis and spectroscopic techniques. We conclude that it probably has a polymeric structure similar to that found for $Sn^{II}(O_2CH)_2$ with only bridging trifluoroacetates. Tin(II) trifluoroacetate is easily oxidized to produce a novel mixed-oxidation-state compound in which there is a central tin(IV) μ-oxo-bridged to four tin(II) atoms. The co-ordination about the tin atoms involves two types of trifluoroacetate, one bridging Sn^{IV} and Sn^{II}, the other bridging only tin(II) atoms.

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