Spin–Spin Coupling between $^{119}Sn^{II}$–^{19}F and $^{119}Sn^{II}$–F–$^{119}Sn^{IV}$ in $Sn^{II}{}_2Sn^{IV}{}_2F_4(O_2CR)_8\cdot 2RCOOH$ and the *X*-Ray Crystal Structure of the Trifluoroacetate Analogue

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Spin–spin coupling is observed between $^{119}Sn^{II}$ and ^{19}F (1128—635 Hz), and $^{119}Sn^{II}$ and $^{119}Sn^{IV}$ (265—326 Hz) in compounds produced by the reaction of SnF_2 with $Sn(O_2CR)_4$; the *X*-ray crystal structure of $Sn^{II}{}_2Sn^{IV}{}_2F_4(O_2CCF_3)_8\cdot 2CF_3COOH$ has been determined.

There are few reports of spin–spin coupling to $^{117,119}Sn$ for the tin(II) valence state,[1,2] and no examples of coupling between a tin(II) nucleus with one in the tin(IV) oxidation state. We report the first examples of $^1J(^{119}Sn^{II}–F)$ and $^2J(^{119}Sn^{II}–F–^{119}Sn^{IV})$ in the molecules formed by reacting SnF_2 with $Sn(O_2CR)_4$. The *X*-ray crystal structure of $Sn^{II}{}_2Sn^{IV}{}_2F_4(O_2CCF_3)_8\cdot 2CF_3COOH$ has been determined.

The ^{119}Sn n.m.r. spectra of the solutions obtained by the reaction between equimolar mixtures of SnF_2 and $Sn(O_2CR)_4$ (R = CF_3, C_3F_7, and $CHCl_2$) yielded the parameters

Table 1. N.m.r. data for solutions of SnF_2 and $Sn(O_2CR)_4$.

	Temp. (°C)	$\delta(^{119}Sn)$ (p.p.m.)	$w_{1/2}$[a] (Hz)	$^1J(^{119}Sn–F)$ (Hz)	$^2J(^{119}Sn–F–^{117,119}Sn)$ (Hz)
1. $SnF_2/Sn(O_2CCF_3)_4$ in CF_3CO_2H/SO_2	Ambient	−805(t)	75	2106	
		−1374(br.)	930		
	−48	−800(t)	90	2118	262
		−1428(t)	90	1128	265
2. $SnF_2/Sn(O_2CC_3F_7)_4$ in C_3F_7COOH	Ambient	−811(t)	138	2160	
		−1453(br.)	2150		
	−23	−809(t)	71	2170	331
		−1461(t)	195	635	326
3. $SnF_2/Sn(O_2CCHCl_2)_4$ (a) in $CHCl_2COOH$	Ambient	−808(t)	430	2155	—
		—	v.br.		
(b) in $CHCl_2COOH/SO_2$	−30	−801(t)	67	2158	—
		−1363(br.)	2950		

[a] Width measured at half height of signals recorded at a field strength of 5.872 T.

summarized in Table 1. The low temperature ^{119}Sn n.m.r. spectra of these solutions consist of two sets of triplets, one at *ca.* −800 p.p.m. which does not change significantly when the acid system is varied, the other in the range −1300 to −1460 p.p.m. The position of this latter signal varies with the acid system as well as with temperature. Previous n.m.r. data on tin(II) and tin(IV) carboxylates show that tin(IV) compounds appear in a narrow range −800 to −850 p.p.m., whereas tin(II) compounds cover a wide range and mostly appear in the lower frequency region.[3] The triplet at *ca.* −800 p.p.m. is assigned to a tin(IV) species and the lower frequency signals are due to a tin(II) species.

That both signals appear as triplets indicates that each tin is coupled to two fluorines. This was confirmed by observation of the ^{19}F spectrum. The coupling constants to the tin(IV) fall in the range 2100—2300 Hz and indicate that they arise from direct Sn^{IV}–F coupling. The magnitudes of the Sn^{II}–F couplings appear to depend on the nature of the R group (1128 Hz for R = CF_3; 635 Hz for R = C_3F_7). There are only a few reports available on ^{119}Sn n.m.r. studies of tin(II) fluoro compounds,[4,5] but no Sn^{II}–F coupling constants have been reported until now.

The low temperature ^{119}Sn n.m.r. spectra of the $SnF_2/Sn(O_2CR)_4$ solutions (where R = CF_3, C_3F_7) show satellite peaks in the tin(II) and tin(IV) resonances. These arise from Sn^{II}–Sn^{IV} coupling. Direct tin–tin couplings, $^1J(^{119}Sn–^{119}Sn)$, range from *ca.* 4 000 Hz[6] to *ca.* 15 000 Hz,[7] while $^2J(^{119}Sn–X–^{119}Sn)$ are an order of magnitude smaller.[8—10] The couplings reported here are consistent with these latter values and the satellite intensities suggest that each tin is bound to two tin atoms of the other oxidation state.

The ^{119}Sn Mössbauer spectrum of the crystalline material isolated from the $SnF_2/Sn(O_2CCF_3)_4$ reaction mixture consists of a single line for the tin(IV) absorption (δ = −0.16, Γ = 1.03 mm s^{-1}) and a quadrupole doublet for the tin(II) resonance (δ = 4.13, Δ = 0.84, Γ = 1.00 mm s^{-1}). The parameters of the tin(IV) and tin(II) sites are different from those of the starting $Sn(O_2CCF_3)_4$ and SnF_2. The absence of a quadrupole splitting for the tin(IV) resonance indicates that this tin nucleus is in a cubic, or near cubic, environment, while the doublet observed for the tin(II) indicates that this tin atom is in a distorted environment.

A structure of the crystals obtained from the reaction of SnF_2 and $Sn(O_2CCF_3)_4$ showed the compound to be $Sn^{II}_2Sn^{IV}_2F_4(O_2CCF_3)_8·2CF_3CO_2H$.† This structure consists of two independent centrosymmetric molecules (Figure 1a and 1b). Each molecule consists of an eight membered ring with a $-Sn^{II}-F-Sn^{IV}-F-$ arrangement. Adjacent tin(II) and tin(IV) atoms in molecule I and molecule II are also bridged by either one or two trifluoroacetate groups. There are also unidentate trifluoroacetate groups and acid molecules co-ordinated to the tin atoms. There are eight trifluoroacetate groups associated with each tetramer and the two trifluoroacetic acid molecules, C(7)C(8)O(10)O(6) and C(7′)C(8′)O(10′)O(6′) associated only with molecule I, are co-ordinated to the two tin(II) atoms

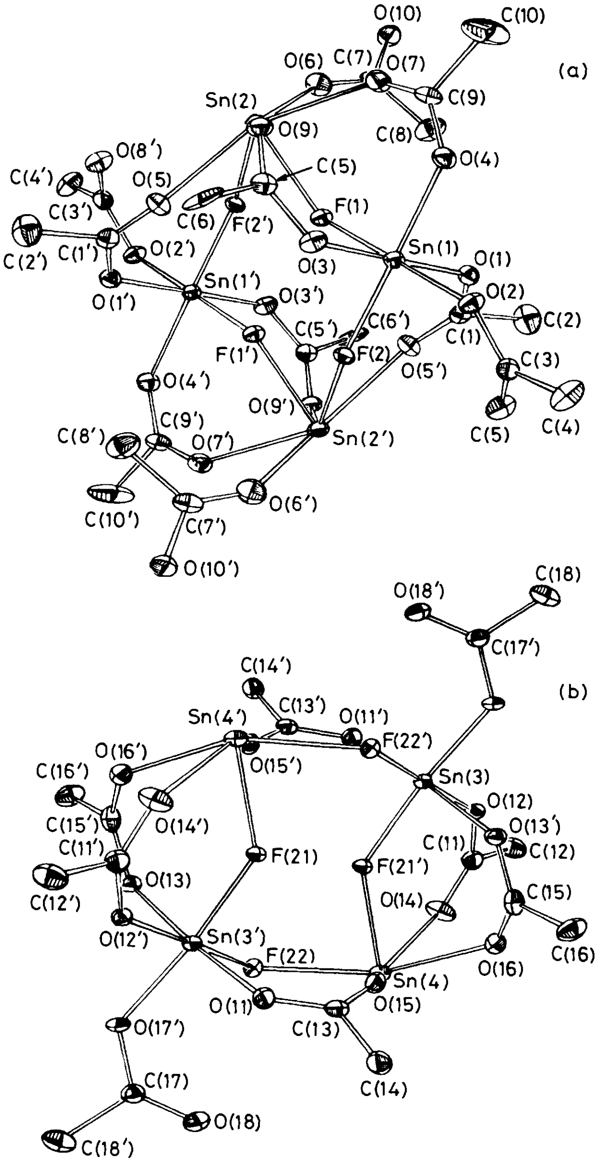

Figure 1. (a) Structure of molecule I. Fluorine atoms of the CF_3 groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sn(1)–F(1), 2.000(5); Sn(1)–F(2), 1.975(5); Sn(1)–O(1), 2.027(8); Sn(1)–O(2), 2.020(6); Sn(1)–O(3), 2.033(8); Sn(1)–O(4), 2.038(7); Sn(2)–F(1), 2.186(5); Sn(2)–F(2′), 2.296(4); Sn(2)–O(5), 2.501(9); Sn(2)–O(6), 2.567(9); Sn(2)–O(7), 2.466(8); Sn(2)–O(9), 2.675(6); Sn(2)–O(19), 3.309(9); F(1)–Sn(1)–F(2), 87.6(2); F(1)–Sn(1)–O(1), 90.3(2); F(1)–Sn(1)–O(2), 177.6(2); F(1)–Sn(2)–F(2′), 72.7(2); F(1)–Sn(2)–O(5), 78.9(2); F(1)–Sn(2)–O(6), 100.4(2).

(b) Structure of molecule II. Fluorine atoms of the CF_3 groups are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Sn(3)–F(21), 2.014(6); Sn(3)–F(22′), 1.951(6); Sn(3)–O(11′), 2.039(6); Sn(3)–O(12), 2.043(7); Sn(3)–O(13′), 2.053(6); Sn(3)–O(17), 2.010(8); Sn(4)–F(21), 2.162(5); Sn(4)–F(22), 2.469(2); Sn(4)–O(14), 2.473(9); Sn(4)–O(15), 2.435(6); Sn(4)–O(16), 2.357(7); Sn(4)–O(19), 3.144(5); Sn(4)–F(37′), 3.164(7); F(21)–Sn(3)–F(22′), 91.0(2); F(21)–Sn(3)–O(11′), 89.9(3); F(21)–Sn(3)–O(12), 90.1(3); F(21)–Sn(3)–O(17), 173.4(3); F(21)–Sn(4)–F(22), 75.6(2); F(21)–Sn(4)–O(9), 147.4(2); F(21)–Sn(4)–O(14), 75.9(2); F(21)–Sn(4)–O(15), 78.8(2); F(21)–Sn(4)–O(16), 78.1(2).

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† *Crystal data:* $Sn_4F_4(O_2CCF_3)_8·2CF_3CO_2H$, M = 1682.9, triclinic, space group $P\bar{1}$ (No. 2), a = 11.586(3), b = 19.182(3), c = 12.491(3) Å, α = 110.44(1), β = 119.50(2), γ = 92.77(2)°, U = 2180.1(8) Å^3, Z = 2, D_{calcd} = 2.56 g cm^{-3}, T = 198 K, $F(000)$ = 1572, μ(Mo-K_α) = 25.13 cm^{-1}. The structure solution and refinement were based on 7091 observed ($I > 0$) reflections (from 8164 measured intensities, 2θ < 50°) obtained from a Syntex P2$_1$ diffractometer. Absorption corrections were not applied (estimated conceivable errors in F are *ca.* 7% min., *ca.* 25% max.). Full matrix refinement with anisotropic thermal parameters (SHELX 76)[11] converged at R = 0.071, R_w = 0.051. The weighting scheme was of the form $w = 1/[\sigma^2(F) + gF^2]$, where g = 0.0001. A final difference map was featureless.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

i.e. Sn(2) and Sn(2′), respectively. There are no other contacts closer than 3.144(5) Å to the tin(II) atoms Sn(2)(2′) or Sn(4)(4′). The oxygen atoms O(10)(10′) are the OH oxygens of the CF_3COOH groups bonded to tin(II), Sn(2)(2′), and there are two other CF_3COOH molecules in the unit cell which have weak interaction with the tin(II) atoms, [Sn(2)–O(19), 3.309(9); Sn(4)–O(19), 3.144(5) Å].

The low temperature ^{119}Sn n.m.r. data of the $SnF_2/Sn(O_2CR)_4$ (R = CF_3, C_3F_7) solutions are consistent with this structure provided that the fluorine atoms bonded to each of the tin atoms are equivalent. In the above structure the fluorines bonded to the tin atoms are crystallographically different, but in solution they are not distinguishable by n.m.r. This is probably because of the exchange process that is clearly occurring. For R = $CHCl_2$ it was not possible to stop this exchange process and no $^2J(Sn^{II}–F–Sn^{IV})$ was observed for this system.

The structure of $Sn^{II}_2Sn^{IV}_2F_4(O_2CCF_3)_8{\cdot}2CF_3CO_2H$ contains two slightly different, nearly octahedral, *cis* fluorine bridged tin(IV) environments which is consistent with the single line observed in the Mössbauer spectrum. The two tin(IV) sites are so similar that they could not be differentiated by Mössbauer spectroscopy. Similarly the two tin(II) environments in this structure are also Mössbauer indistinguishable.

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