Inorganic Compounds Containing the Trifluoroacetate Group. Part III.[1] Reactions of Bis(trifluoroacetato)divinyltin with *N*-, *O*-, or *N*- and *O*-Donor Ligands, and the Crystal Structure of (2,2'-Bipyridyl)bis(trifluoroacetato)divinyltin

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The addition complexes $[(H_2C{:}CH)_2Sn(O_2C{\cdot}CF_3)_2L_n]$ [$n = 1$, L = 2,2'-bipyridyl, 1,10-phenanthroline, NN'-ethylenebis(salicylidineimine) or ethylene-1,2-diamine; $n = 2$, L = triphenylphosphine oxide or hexamethyl-phosphoramide] have been prepared and characterised. These compounds (II)—(VII) all contain octahedrally co-ordinated tin(IV), with two unidentate trifluoroacetato-groups. This geometry has been confirmed by X-ray crystallography for the 2,2'-bipyridyl addition complex (II) which crystallises in the monoclinic space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 8{\cdot}04$, $b = 15{\cdot}39$, $c = 17{\cdot}37$ Å, and $\beta = 106{\cdot}6°$. The structure has been determined from three-dimensional X-ray diffraction data by Patterson and Fourier methods, and refined by least-squares to a final R of $0{\cdot}070$ (for 2194 diffractometer intensities). (II) Exists as discrete molecules in the crystal; some mean distances are: Sn–O 2·21(4), Sn–C 2·10(2) (two mutually *trans* σ-bonded vinyl groups), and Sn–N 2·34 ± 0·01 Å. $[(H_2C{:}CH)_2Sn(O_2C{\cdot}CF_3)_2]$ reacts with 8-hydroxyquinoline or sodium acetylacetonate to afford $[(H_2C{:}CH)_2Sn(ONC_9H_7)(O_2C{\cdot}CF_3)]$ or $[(H_2C{:}CH)_2Sn(O_2C_5H_7)_2]$ respectively, and with carboxylic acids to produce the corresponding $[Sn(O_2CR)_4]$ derivatives.

BIS(TRIFLUOROACETATO)DIVINYLTIN, $[(H_2C{:}CH)_2Sn(O_2C{\cdot}CF_3)_2]$ (I), prepared by the reaction between $[(H_2C{:}CH)_4Sn]$ and CF_3CO_2H under mild conditions, has been shown to be a useful synthetic intermediate for the preparation of divinyltin compounds.[1] As part of a study to characterise further the chemical behaviour of this compound, we have examined the reactions between (I) and a variety of *N*-, *O*-, or *N*- and *O*-donor ligands and now report the preparation and characterisation of several new divinyltin compounds.

EXPERIMENTAL

Molecular weights were determined by vapour-phase osmometry on a Mechrolab 310 osmometer. Mass spectra were recorded on an A.E.I. MS 12 (70 eV). I.r. spectra for Nujol and hexachlorobutadiene mulls were recorded on Perkin-Elmer 225 and 457 spectrometers

ated at room temperature under reduced pressure until crystallisation commenced and the solution cooled to -10 °C for 2 h, when the product (II) (90%) was obtained as white needles. Analytical data for (II) are in Table 1; M determined for 0·1, 0·05, and 0·01M-acetone solutions, 541 ± 25 (calc. 555). (II) behaves as a non-electrolyte in acetone; $\Lambda_m = 15{\cdot}2$ ohm^{-1} cm^{-1} (0·1M-solution). Mass spectrum (100 °C): intense peak at 156 mass units corresponding to $[N_2C_{10}H_8]^+$ and peaks corresponding to fragmentation of (I);[1] i.r. spectra (cm^{-1}, with assignments [2] in parentheses): 3110w, 3095w, 3065w, 2995w, 2948w (CH str), 1713vs (OCO asym str), 1184vs, b, 1142vs, b (CF$_3$ str), 989m, 961m, (CH$_2$ bend), 849w (CC str), 779s (OCO def), and 729m (CF$_3$ bend); also bands characteristic of 2,2'-bipyridyl. ^{1}H N.m.r. spectrum: τ_O, τ_G, and τ_T and coupling constants J_{CT}, J_{GT}, and J_{CG} for the vinyl groups calculated as τ 4·2, 3·2, and 3·9, and 2·3, 12·4, and 18·6 ($\pm 0{\cdot}5$) Hz respectively, similar to corresponding values [1]

TABLE 1

Analyses (%) and m.p. (°C) of addition complexes of (I) of formula $[(CH_2{:}CH)_2Sn(O_2C{\cdot}CF_3)_2L_n]$

Complex	Empirical formula	L [a]	n	Analyses [b]					M.p.
				C	H	N	Other		
(II)	$C_{18}H_{14}N_2SnO_4F_6$	bipy	1	39·0 (39·0)	2·6 (2·5)	4·8 (5·0)			161—162
(III)	$C_{20}H_{14}N_2SnO_4F_6$	phen	1	41·5 (41·5)	2·4 (2·4)	4·9 (4·8)			189—191
(IV)	$C_{24}H_{24}N_2SnO_6F_6$	H$_2$salen	1	42·8 (43·1)	3·2 (3·6)	4·4 (4·2)			174—175
(V)	$C_{10}H_{14}N_2SnO_4F_6$	en	1	26·0 (26·2)	3·2 (3·1)		26·1 [c] (25·9 [c])		112—114
(VI)	$C_{44}H_{36}P_2SnO_6F_6$	tppo	2	55·0 (55·3)	3·2 (3·8)		6·4 [d] (6·5 [d])		152—153
(VII)	$C_{20}H_{42}N_6P_2SnO_6F_6$	hmpa	2	31·5 (31·7)	5·5 (5·8)	11·1 (11·1)			135—136

[a] bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline, H$_2$salen = NN'-ethylenebis(salicylideneimine), en = ethylene-1,2-diamine, tppo = triphenylphosphine oxide, hmpa = hexamethylphosphoramide. [b] Calc. value in parentheses. [c] Sn. [d] P.

calibrated with polystyrene film. ^{1}H N.m.r. spectra were recorded on a Varian HA 100 instrument at 60 MHz in CDCl$_3$ with tetramethylsilane as internal reference. (I) Was prepared and purified as described previously.[1] Chloroform was reagent grade.

Preparation of (II) *2,2'-Bipyridylbis(trifluoroacetato)divinyltin.*—$[(H_2C{:}CH)_2Sn(O_2C{\cdot}CF_3)_2]$ (1·0 g, 2·5 mmol) and 2,2'-bipyridyl (0·39 g, 2·5 mmol) were separately dissolved in CHCl$_3$ (10 ml), and the solutions mixed and stirred for 15 min at room temperature. Solvent was then evapor-

for (I); spectrum to lower τ values similar to that for pure 2,2'-bipyridyl.

Needles of (II) obtained as described were suitable for X-ray diffraction analysis.

Crystal Data.—$C_{18}H_{14}N_2O_4F_6Sn$, $M = 554{\cdot}9$, Monoclinic, $a = 8{\cdot}04 \pm 0{\cdot}01$, $b = 15{\cdot}39 \pm 0{\cdot}02$, $c = 17{\cdot}37 \pm 0{\cdot}02$ Å, $\beta = 106{\cdot}6 \pm 0{\cdot}1°$, $U = 2058$ Å^3, $Z = 4$, $D_c = 1{\cdot}80$ g cm^{-3}, $F(000) = 1088$, Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 1·34 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ for $l \neq 2n$ and $0k0$ for $k \neq 2n$.

[1] Part II, C. D. Garner and B. Hughes, *J.C.S. Dalton*, 1974, 1306.

[2] R. L. Redington and K. C. Lin, *Spectrochim. Acta*, 1971, **27A**, 2445; P. J. Miller, R. A. Butler, and E. R. Lippincott, *J. Chem. Phys.*, 1972, **57**, 5451.

Preliminary unit-cell dimensions and space-group data were obtained from Weissenberg and oscillation photographs, and refined on a Hilger and Watts four-circle diffractometer. The layers 0—9kl were explored and 2194 reflections with $I > 3\sigma(I)$ were considered observed. No account was taken of anomalous dispersion and no corrections were made for absorption or secondary extinction. Data reduction and crystallographic calculations were carried out on the Nottingham University English Electric KDF 9 computer by use of the National Research Council (Ottawa) programs.[3] Atomic scattering factors were taken from ref. 4. The positions of the tin atoms were located from a three-dimensional Patterson synthesis and a three-dimensional Fourier synthesis phased by these atoms revealed the positions of the carbon, nitrogen, oxygen, and fluorine atoms. Block-diagonal least-squares refinement, finally, by use of anisotropic temperature factors for all atoms, converged at R 0·070.* Atomic co-ordinates are listed in Table 2 and the thermal parameters in Table 3.

TABLE 2

Atomic positions with standard deviations in parentheses of (II)

Atom	x/a	y/b	z/c
Sn	0·0951(2)	0·2163(1)	0·1900(1)
O(1)	0·1930(19)	0·1355(9)	0·2962(8)
O(2)	0·1655(23)	0·2185(11)	0·3966(8)
O(3)	0·1527(15)	0·3595(9)	0·1912(7)
O(4)	0·3757(25)	0·3321(10)	0·2902(10)
N(1)	−0·0734(20)	0·2441(10)	0·0583(9)
N(2)	−0·0241(21)	0·0861(10)	0·1292(10)
C(1)	−0·1718(24)	0·1785(12)	0·0212(9)
C(2)	−0·0921(30)	0·3250(13)	0·0286(10)
C(3)	−0·2089(28)	0·3463(15)	−0·0427(13)
C(4)	−0·3223(32)	0·2811(18)	−0·0836(12)
C(5)	−0·2992(28)	0·1943(14)	−0·0527(12)
C(6)	−0·1411(26)	0·0919(13)	0·0546(11)
C(7)	0·0247(28)	0·0080(12)	0·1684(11)
C(8)	−0·0529(34)	−0·0688(14)	0·1286(15)
C(9)	−0·1749(36)	−0·0648(14)	0·0517(14)
C(10)	−0·2197(31)	0·0160(14)	0·0186(11)
C(11)	0·2031(27)	0·1528(13)	0·3718(11)
C(12)	0·2645(39)	0·0772(15)	0·4230(13)
C(13)	0·2858(28)	0·3784(11)	0·2425(12)
C(14)	0·3491(40)	0·4677(16)	0·2381(20)
C(15)	−0·1250(26)	0·2399(15)	0·2300(14)
C(16)	−0·2211(33)	0·3085(18)	0·2137(17)
C(17)	0·3240(29)	0·1873(14)	0·1615(12)
C(18)	0·3684(33)	0·2202(19)	0·0979(15)
F(1)	0·1390(37)	0·0326(19)	0·4298(26)
F(2)	0·3125(57)	0·0920(16)	0·4896(11)
F(3)	0·3356(40)	0·0187(15)	0·4043(11)
F(4)	0·4559(45)	0·4800(14)	0·2085(26)
F(5)	0·2006(34)	0·5232(15)	0·1998(13)
F(6)	0·3746(70)	0·5120(20)	0·2888(33)

Preparation of Addition Complexes of (I) *with* 1,10-*Phenanthroline,* NN'-*Ethylenebis(salicylidineimine), Ethylene-1,2-diamine, Triphenylphosphine Oxide, and Hexamethylphosphoramide.*—Complexes $[(H_2C\text{:}CH)_2Sn(O_2C\cdot CF_3)_2L_n]$ [$n = 1$, L = phen (III), H_2salen (IV), or en (V); $n = 2$, L = tppo (VI) or hmpa (VII)] were prepared analogously to the 2,2'-bipyridyl complex (II). The preparation of (V) (L = en) was carried out under anhydrous conditions since (V) is readily hydrolysed to $(H_2en)(CF_3CO_2)_2$ and $[(H_2C\text{:}CH)_2SnO]_n$.[5] Analytical data are in Table 1; i.r. and mass spectral data were also obtained.

* Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21208 (19 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

TABLE 3

Final anisotropic thermal parameters * ($\times 10^3$) with estimated standard deviations in parentheses of (II)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	49·2(0·6)	39·5(0·5)	34·2(0·5)	3·3(0·8)	1·9(0·4)	−0·9(0·7)
O(1)	79(10)	45(8)	52(8)	10(7)	−10(7)	6(7)
O(2)	136(15)	57(9)	48(8)	26(11)	23(9)	−2(8)
O(3)	48(7)	68(9)	38(7)	−7(7)	−14(6)	−9(7)
O(4)	128(15)	54(10)	97(13)	9(10)	−2(11)	8(9)
N(1)	58(10)	46(8)	35(7)	−3(7)	−3(7)	2(6)
N(2)	64(11)	34(9)	58(10)	−8(8)	18(8)	0(8)
C(1)	53(12)	56(11)	20(8)	1(9)	−1(8)	−8(8)
C(2)	91(17)	48(12)	30(9)	11(11)	4(10)	13(9)
C(3)	73(14)	61(14)	61(13)	0(12)	−1(11)	0(12)
C(4)	84(18)	92(17)	48(12)	−24(17)	−4(12)	−14(14)
C(5)	64(13)	65(15)	45(12)	−2(11)	−9(10)	1(10)
C(6)	52(13)	49(11)	41(11)	3(10)	5(9)	2(9)
C(7)	70(14)	42(11)	44(11)	8(10)	12(10)	−2(9)
C(8)	113(20)	43(13)	87(17)	6(13)	52(15)	7(12)
C(9)	102(22)	50(13)	60(15)	20(14)	17(15)	7(11)
C(10)	95(18)	67(14)	33(10)	−25(13)	15(11)	−16(10)
C(11)	69(14)	50(12)	36(10)	1(11)	17(9)	−5(9)
C(12)	127(23)	47(13)	43(12)	7(14)	27(13)	6(10)
C(13)	70(14)	32(10)	62(12)	11(9)	21(11)	7(9)
C(14)	111(21)	49(13)	123(23)	−29(14)	54(18)	0(15)
C(15)	45(12)	70(16)	79(15)	0(11)	5(11)	−16(12)
C(16)	56(16)	91(20)	108(20)	20(14)	−18(15)	−12(15)
C(17)	62(15)	66(14)	41(11)	0(11)	−1(10)	−13(10)
C(18)	85(18)	84(17)	84(17)	−11(17)	31(14)	−21(17)
F(1)	185(27)	175(26)	448(54)	19(20)	105(30)	199(33)
F(2)	562(63)	132(21)	57(11)	99(30)	−8(20)	25(12)
F(3)	403(40)	220(23)	120(14)	237(27)	162(20)	108(15)
F(4)	383(39)	92(15)	609(69)	−61(20)	437(49)	−24(25)
F(5)	236(24)	113(16)	142(17)	−17(17)	32(16)	−27(14)
F(6)	645(78)	126(23)	616(83)	257(39)	391(69)	182(40)

* In the form: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{31} + 2hka^*b^*U_{12})]$.

Preparation of Quinolin-8-olato(trifluoroacetato)divinyltin (VIII).—(I) (1·0 g, 2·5 mmol) Was dissolved in $CHCl_3$ (10 ml) and 8-hydroxyquinoline (0·37 g, 2·55 mmol) in $CHCl_3$ (10 ml) added. Evaporation of solvent at room temperature under reduced pressure from the resultant bright yellow solution, followed by cooling to −10 °C, yielded a bright yellow microcrystalline solid (85%), m.p. 122—123 °C (Found: C, 41·7; H, 2·8; F 13·1; N, 3·0; Sn, 27·8. $C_{15}H_{12}NSnO_3F_3$ requires C, 41·8; H, 2·8; F, 13·3; N, 3·3; Sn, 27·6%). Mass spectrum: (100 °C) peaks for [120]Sn (relative intensity) corresponding to ions at 431 (25) $[(H_2C\text{:}CH)_2Sn(ONC_9H_7)(O_2C\cdot CF_3)]^+$, 404 (100) $[(H_2C\text{:}CH)Sn(ONC_9H_7)(O_2C\cdot CF_3)]^+$, 377 (15) $[Sn(ONC_9H_7)(O_2C\cdot CF_3)]^+$, 318 (30) $[(H_2C\text{:}CH)_2Sn(ONC_9H_7)]^+$, 310 (85) $[(H_2C\text{:}CH)Sn(ONC_9H_7)F]^+$, 283 (60) $[Sn(ONC_9H_7)F]^+$, and 264 (90) $[Sn(ONC_9H_7)]^+$, in addition to peaks at lower mass numbers corresponding to further fragmentation of these ions. M Determined for 0·1, 0·05, and 0·01M-acetone solutions was 423 ± 20 (calc. 430). I.r. spectrum (cm^{-1}, assignments[2] in parentheses): 3102w, 3080w, 3058w, 3037w, 2995w (C–H str), 1725m, 1690s (OCO asym str), 1202vs, b, 1133s (CF$_3$ str), 995m, 950m (CH$_2$ bend), 850m, 833s (C–C str), 801m (OCO def), and 726s (CF$_3$ bend); also bands characteristic of 8-quinolinolato-groups.

Preparation of Bis(acetylacetonato)divinyltin (IX).—Solid $Na(O_2C_5H_7)$ (0·91 g, 7·5 mmol) was added to a solution of (I) (1·0 g, 2·5 mmol) in pure dry tetrahydrofuran (40 ml)

3 F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson, Natural Research Council, Ottawa, Crystallographic Programs.

4 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

5 S. D. Rosenberg and A. J. Gibbons, *J. Amer. Chem. Soc.*, 1955, **79**, 2138.

under dry nitrogen, and the resultant suspension stirred for 2 h at room temperature. The filtrate was then evaporated at room temperature under reduced pressure. The residue was extracted with dried CH_2Cl_2 (15 ml), and solvent evaporated from the filtrate under reduced pressure at room temperature until crystallisation commenced. Cooling to -10 °C afforded a white microcrystalline solid (50%), m.p. 121—122 °C (Found: C, 45·4; H, 5·6; $C_{14}H_{20}$-SnO_4 requires C, 45·3; H, 5·4%). Mass spectrum: peaks for ^{120}Sn (relative intensity) corresponding to ions at 372 (5) $[(H_2C:CH)_2Sn(O_2C_5H_7)_2]^+$, 345 (65) $[(H_2C:CH)Sn$-$(O_2C_5H_7)_2]^+$, 318 (10) $[Sn(O_2C_5H_7)_2]^+$, 273 (100) $[(H_2C:CH)_2$-$Sn(O_2C_5H_7)]^+$, 219 (90) $[Sn(O_2C_5H_7)]^+$ in addition to peaks at lower mass numbers corresponding to further fragmentation of these ions. I.r. spectrum (cm^{-1}, with assignments [6] in parentheses): 3054w, 2998m, 2951m, 2932w, 2913m (C–H str), 1583vs, 1532vs (C=C, C=O str), 1420w, 1373s (CH$_3$ def), 1024m (CH$_3$ rock), 997m, 955m (vinyl C–H bend), 937w (C–CH$_3$ def), 845m (C–C str), 798m, and 739m (C–H out-of-plane bend).

Reactions between (I) *and Acetic and Propionic Acids and Isolation of the Tetracarboxylates* $[Sn(O_2CR)_4]$ (R = Me or Et).—All manipulations were carried out under dry nitrogen. (I) (2·0 g, 5·0 mmol) Was added to a mixture (10 ml) of acetic acid and acetic anhydride and the resulting solution heated under reflux. After 1 h, when gas evolution had ceased, the mixture was allowed to cool to room temperature, when fine white needles crystallised. The product was washed with dried pentane (2 × 20 ml) and traces of solvent removed at room temperature under reduced pressure: crystals (95%), m.p. 227—228° (lit. m.p.[5] 225—226 °C) are hygroscopic; (Found: C, 27·1; H, 3·3; Sn, 34·0. Calc. for $C_8H_{12}SnO_8$: C, 27·1; H, 3·4; Sn, 33·4%). Mass spectrum: (80 °C) peaks for ^{120}Sn (relative intensity) corresponding to ions at 297 (100) $[Sn(O_2CMe)_3]^+$, 255 (40) $[Sn(O_2CMe)_2OH]^+$, 238 (25) $[Sn(O_2CMe)_2]^+$, 179 (50) $[Sn(O_2CMe)]^+$, together with other peaks corresponding to fragmentation of these ions. I.r. spectrum (cm^{-1}, with assignments [7] in parentheses): 3004w, 2947w, 2855w (C–H str), 1568s, b (OCO sym str), 1056m 1022m (CH$_3$ rock), 942m (C–C str), 718vs (OCO def), and 615s (OCO out-of-plane bend).

The hygroscopic compound $[Sn(O_2CEt)_4]$ was prepared analogously from propionic acid–propionic anhydride (10 : 1) and isolated (90%) as fine white needles, m.p. 146—147 (lit. m.p.[8] 146 °C) (Found: C, 34·8; H, 5·0; Sn, 29·0. Calc. for $C_{12}H_{20}SnO_8$: C, 35·1; H, 4·9; Sn, 28·9%). Mass spectrum (80 °C): ^{120}Sn peaks (relative intensity) corresponding to ions at 339 (85) $[Sn(O_2CEt)_3]^+$, 283 (55) $[Sn(O_2CEt)_2OH]^+$, 266 (10) $[Sn(O_2CEt)_2]^+$, 227 (15) $[Sn(O_2CEt)(OH)_2]^+$, 193 (100) $[Sn(O_2CEt)]^+$, and peaks corresponding to fragments of these ions. The i.r. spectrum closely resembled that previously reported.[8]

RESULTS AND DISCUSSION

Crystal and Molecular Structure.—The quality of the refinement of the crystal structure of (II) is somewhat less than desired because of disorder in the position of the fluorine atoms which appear to be almost anywhere

in the volume swept out by rotating the CF$_3$ groups about the C–C axis of each trifluoroacetato-group. No special significance therefore should be attached to the positions given for the fluorine atoms (Table 2). This lack of definition has resulted in the estimated standard deviations in the atomic positions and several of the temperature factors being larger than usually found, these effects being more pronounced for atoms furthest from the metal in each molecule.

Crystals of (II) are composed of discrete monomeric molecules (Figure 1) in which the tin(IV) atom has a
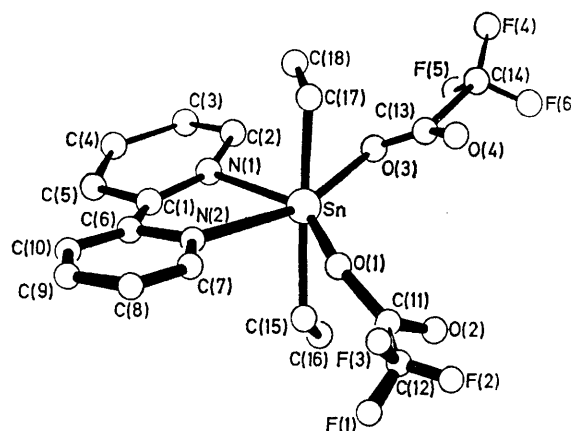

FIGURE 1   The structure of (II)

distorted octahedral environment, being co-ordinated to a bidentate 2,2'-bipyridyl group, two σ-bonded vinyl groups, mutually *trans*, and two unidentate trifluoroacetato-groups, mutually *cis*. Selected bond lengths and interbond angles are listed in Table 4 and some least-squares data in Table 5. The 2,2'-bipyridyl group is essentially planar [maximum displacement of an atom from the plane, C(2) 0·15 Å]. Each six-membered aromatic ring is co-planar to within ±0·027 Å with a dihedral angle between these planes of 8·3°, the Sn being 0·42 Å from the plane of the ring containing N(1) and 0·03 Å from the plane of that containing N(2). The carbon atoms of the vinyl groups and the tin atom lie in a plane [maximum displacement of an atom from the plane, C(17) 0·12 Å], and the tin and the two oxygen and carbon atoms of each trifluoroacetato-group are coplanar to within ±0·09 Å.

The arrangement of the molecules of (II) within the unit cell is shown in Figure 2. There are no abnormally close intermolecular approaches.

The length of the Sn–O and Sn–C bonds obtained are in the ranges typical for such bonds.[9] The Sn–N bonds are, however, some 0·16 Å longer than those (2·182 Å) found [10] for $[SnF_4(N_2C_{10}H_8)]$ which would appear to be more representative of tin(IV)–nitrogen

[6] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, 1960, **32**, 588.

[7] K. Nakamoto, 'Infrared Spectra of Co-ordination Compounds,' Wiley, New York, 1963, pp. 198—199; C. Oldham, *Progr. Inorg. Chem.*, 1968, **10**, 233; B. F. G. Johnson, R. D. Johnston, J. Lewis, and I. G. Williams, *J. Chem. Soc. (A)*, 1971, 689, and refs. therein.

[8] A. Henderson and A. K. Holliday, *J. Organometallic Chem.*, 1965, **4**, 377.

[9] G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677, and refs. therein.

[10] A. D. Adley, P. H. Bird, A. R. Fraser, and M. Onyszchuk, *Inorg. Chem.*, 1972, **11**, 1402.

bonds involving related systems.[11] The reason for the longer Sn–N bonds in (II) is not obvious. Steric crowding is not apparent either about each tin(IV) centre or between individual molecules. One possible explanation is that the trifluoroacetato-groups effect a static *trans*-effect; however, structural data for other

TABLE 4

Selected distances (Å) and angles (°) with estimated standard deviations in parentheses for (II)

(a) Co-ordination geometry about the tin(IV) atom

(i) Bonds

Sn–O(1)	2·178(13)	Sn–N(1)	2·340(14)
Sn–O(2)	3·471(14)	Sn–N(2)	2·339(15)
Sn–O(3)	2·250(14)	Sn–C(15)	2·106(24)
Sn–O(4)	3·008(14)	Sn–C(17)	2·086(24)

(ii) Angles

O(1)–Sn–O(3)	121·9(0·5)	N(1)–Sn–N(2)	70·6(0·5)
O(1)–Sn–N(1)	154·1(0·5)	N(1)–Sn–C(15)	89·1(0·7)
O(1)–Sn–N(2)	83·9(0·5)	N(1)–Sn–C(17)	90·5(0·7)
O(1)–Sn–C(15)	87·4(0·7)	N(2)–Sn–C(15)	91·2(0·7)
O(1)–Sn–C(17)	87·1(0·7)	N(2)–Sn–C(17)	89·1(0·7)
O(3)–Sn–N(1)	83·7(0·5)	C(15)–Sn–C(17)	174·4(0·8)
O(3)–Sn–N(2)	154·2(0·5)	O(1)–Sn–O(2)	38·4(0·6)
O(3)–Sn–C(15)	91·1(0·7)	O(3)–Sn–O(4)	45·2(0·6)
O(3)–Sn–C(17)	91·0(0·7)		

(b) Trifluoroacetato-groups

(i) Distances

O(1)–C(11)	1·319(24)	O(4)–C(13)	1·172(24)
O(2)–C(11)	1·172(27)	O(3) · · · O(4)	2·141(19)
O(1) · · · O(2)	2·224(21)	C(13)–C(14)	1·476(32)
C(11)–C(12)	1·462(29)	Mean C–F	1·27(16)
O(3)–C(13)	1·215(21)		

(ii) Angles

O(1)–C(11)–O(2)	126·3(1·8)	O(3)–C(13)–C(14)	115·4(1·8)
O(1)–C(11)–C(12)	111·1(1·8)	O(4)–C(13)–C(14)	116·8(2·0)
O(2)–C(11)–C(12)	122·6(1·9)	Mean F–C–F	100·3(10·3)
O(3)–C(13)–O(4)	127·5(1·9)	Mean F–C–C	116·6(6·2)

(c) Bipyridyl group

(i) Distances

C(1)–N(1)	1·329(23)	C(6)–N(2)	1·369(22)
N(1)–C(2)	1·341(25)	N(2)–C(7)	1·381(24)
C(2)–C(3)	1·363(26)	C(7)–C(8)	1·420(29)
C(3)–C(4)	1·404(33)	C(8)–C(9)	1·414(31)
C(4)–C(5)	1·432(34)	C(9)–C(10)	1·373(30)
C(5)–C(1)	1·416(23)	C(10)–C(6)	1·389(28)
C(1)–C(6)	1·446(29)	N(1) · · · N(2)	2·703(22)

(ii) Angles

C(1)–N(1)–C(2)	122·2(1·4)	N(2)–C(6)–C(1)	115·6(1·6)
N(1)–C(2)–C(3)	123·1(1·8)	C(10)–C(6)–C(1)	126·3(1·6)
C(2)–C(3)–C(4)	117·8(2·1)	C(10)–C(6)–N(2)	118·1(1·7)
C(3)–C(4)–C(5)	118·7(1·8)	C(6)–C(10)–C(9)	122·8(1·8)
C(4)–C(5)–C(1)	118·8(1·8)	C(10)–C(9)–C(8)	117·6(1·9)
C(5)–C(1)–N(1)	119·1(1·7)	C(9)–C(8)–C(7)	120·9(1·9)
C(5)–C(1)–C(6)	121·2(1·6)	C(8)–C(7)–N(2)	117·5(1·6)
N(1)–C(1)–C(6)	119·7(1·4)	C(7)–N(2)–C(6)	123·0(1·5)

(d) Vinyl groups

(i) Distances

C(15)–C(16)	1·291(0·034)	C(17)–C(18)	1·352(0·037)

(ii) Angles

C(16)–C(15)–Sn	125·2(2·1)	C(18)–C(17)–Sn	124·8(1·7)

systems are required before such an effect can be confirmed. The 'bite' of the 2,2′-bipyridyl ligand [N · · · N 2·703(22) Å] is similar to that observed [12] in other complexes of this ligand with similar metal–nitrogen separations. The C–C [mean 1·401(24) Å]

TABLE 5

Equations of some least-squares and, in square brackets, distances (Å) of atoms from the planes. The equations are referred to the *a*, *b*, *c** crystal axes and *X*, *Y*, and *Z* are in Å

Plane (1): Sn, N(1), N(2),) C(1)—(10)

$$0.892X - 0.132Y - 0.432Z = -1.803$$

[Sn −0·160, N(1) 0·106, C(1) −0·036, C(2) 0·153, C(3) 0·101, C(4) −0·105, C(5) −0·123, N(2) −0·044, C(6) −0·028, C(7) 0·008, C(8) 0·070, C(9) 0·080, C(10) −0·020]

Plane (2): Sn, C(15)—(18)

$$0.380X + 0.594Y + 0.709Z = 4.183$$

[Sn −0·031, C(15) −0·095, C(16) 0·080, C(17) 0·120, C(18) −0·074]

Plane (3): Sn, O(1), O(2), C(11), C(12)

$$-0.936X - 0.327Y - 0.130Z = -1.358$$

[Sn 0·025, O(1) −0·040, O(2) −0·001, C(11) −0·015, C(12) 0·031]

Plane (4): Sn, O(3), O(4), C(13), C(14)

$$0.756X - 0.219Y - 0.616Z = -2.882$$

[Sn 0·068, O(3) −0·081, O(4) −0·022, C(13) −0·055, C(14) 0·091]

Dihedral angles (°) subtended between these least-squares planes

(1)–(2)	92·6	(2)–(3)	130·0
(1)–(3)	137·4	(2)–(4)	106·2
(1)–(4)	14·1	(3)–(4)	123·6

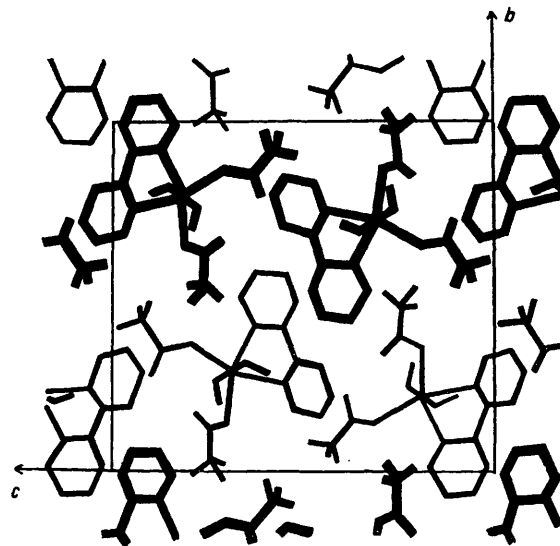

FIGURE 2 Packing of (II) in the crystal as viewed down the *a* axis (thinner lines represent molecules at *x*, *y*, *z* and *x*, ½ − *y*, ½ + *z*, and thicker lines those at *x̄*, *ȳ*, *z̄* and *x̄*, ½ + *y*, ½ − *z*)

and the C–N [mean 1·355(25) Å] bond lengths are not significantly different from the corresponding values reported for the free ligand [13] [1·39(2) and 1·36(2) Å] and for the [SnF₄(bipy)] complex [10] [1·384(10) and 1·346(8) Å].

The present *trans*-arrangement of the vinyl groups appears to be the rule for octahedral dialkyltin(IV) complexes.[9] However, the relatively large σ values

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involved here preclude any discussion of the dimensions of these vinyl groups.

Earlier crystallographic studies have confirmed that $[Ph_4As]_2[Co(O_2C\cdot CF_3)_4]$ [14] and $[Cu_2(OH)(quinoline)_2(O_2C\cdot CF_3)_3]_2$ [15] contain unidentate trifluoroacetato-groups. The anions of the salts $K[H(O_2C\cdot CF_3)_2]$ and $K[D(O_2C\cdot CF_3)_2]$ may also be considered to involve such groups since neutron-diffraction studies have shown that the hydrogen bonding is strong and specific to one oxygen atom of each carboxylate group.[16] This latter study has afforded the most accurate structural data presently available for trifluoroacetato-groups. The present dimensions do not differ significantly from those of these potassium salts. As expected,[17] the C–O bond involving the non-co-ordinated is shorter than that involving the co-ordinated oxygen for both unidentate trifluoroacetato-groups of (II), although in only one case in this difference significant.

Synthetic and Spectral Studies.—Compound (I) readily forms 1 : 1 addition complexes with bidentate *N*-donor ligands such as 2,2-bipyridyl, 1,10-phenantholine, *NN'*-ethylenebis(salicylideneimine), and ethylene-1,2-diamine, although complexes with unidentate *N*-donor ligands have not yet been prepared. Unidentate *O*-donor ligands, which are reasonably strong Lewis bases, *e.g.* triphenylphosphine oxide and hexamethylphosphoramide, readily form 2 : 1 addition complexes with (I), but weaker Lewis bases, *e.g.* ethers, show no tendency to co-ordinate to the tin(IV) atom of the parent compound. Bidentate ligands containing *O*-donor atoms readily substitute for the trifluoroacetato-groups of (I); quinolin-8-olate or acetylacetonate replace one or two such groups, respectively, under the mild reaction conditions employed. Carboxylic acids RCO_2H (R = Me or Et) effect the conversion to the tetracarboxylato-complex $[Sn(O_2CR)_4]$. We suggest that this reaction proceeds *via* the formation of $[(H_2C\text{:}CH)_2Sn(O_2CR)_2]$ compounds which, unlike the corresponding trifluoro-acetate,[1] readily afford the tetracarboxylato-complex with the acid.[8] The *P*- and *S*-donor ligands triphenylphosphine, bis(diphenylphosphino)ethane, thiourea, and bis(diphenylthio)ethane, exhibit no tendency to react with (I). The R_2Sn^{2+} centre thus displays the expected 'hard' character.[18]

Molecular-weight and conductance data recorded for (II) in acetone solution suggest that the discrete monomeric molecules of the crystal state persist in solution. The position of the asymmetric carboxylato-stretching frequency at 1713 cm^{-1} is consistent with the unidentate co-ordination of the trifluoroacetato-groups.[17] Unfortunately, owing to the complexity of the i.r. spectrum (1200—1480 cm^{-1}) it is not possible unambiguously to assign the symmetric carboxylato-stretching frequency of the trifluoroacetato-groups.

The addition complexes (II)—(VII) (Table 1) seem to have molecular structures similar to that of (II). All exhibit an asymmetric carboxylato-stretching frequency in the 1680—1720 cm^{-1} region, strongly suggesting unidentate co-ordination of the trifluoroacetato-groups and the compounds appear to dissolve in acetone to give solutions containing the covalent monomer. In the case of (IV), all the data obtained indicate that the salen ligand remains neutral and, in view of the other reactions reported here, it seem likely that co-ordination to the tin(IV) is achieved *via* the imino-nitrogen atoms alone. In contrast to salen, quinolin-8-ol reacts with (I) under mild conditions with the elimination of one mole of trifluoroacetic acid to form (VIII) $[(H_2C\text{:}CH)_2Sn(ONC_9H_7)(O_2C\cdot CF_3)]$. Molecular-weight and mass spectral data are consistent with a composition of discrete molecular units. The asymmetric carboxylato-stretching frequency of the trifluoroacetato-groups exhibits a strong sharp absorption at 1690 cm^{-1} in the i.r. and which suggests unidentate co-ordination of this group.[17] We therefore suggest that this compound contains five-co-ordinate tin(IV) bonded to two vinyl-, one bidentate quinolin-8-olato-, and one unidentate trifluoroacetato-groups.

Compound (I) reacts with sodium acetylacetonate to afford (IX) $[(H_2C\text{:}CH)_2Sn(acac)_2]$. The mass spectrum and molecular weight data obtained for (IX), suggest a composition of discrete molecules, probably having a structure closely related to that determined for $[Me_2Sn(acac)_2]$.[9]

The compound isolated by us as $[Sn(O_2Me)_4]$ has an i.r. spectrum different from that reported previously,[8] the 1704 cm^{-1} absorption not being observed for mulls prepared under anhydrous conditions; however, an absorption at this frequency did appear after exposure of the mulls to the atmosphere. Since acetic acid was then also detected by smell and the 1704 cm^{-1} frequency is close to the symmetric carboxylato-stretching frequency observed [19] when acetic acid acts as a donor to tin(IV), it seems probable that the sample whose i.r. spectrum was recorded previously [8] contained some acetic acid as a result of hydrolysis. The i.r. spectrum of $[Sn(O_2CEt)_4]$ obtained in this study is, however, very similar to that previously reported.[7] These spectral results, with $[Sn(O_2CMe)_4]$ exhibiting carboxylato-stretching frequencies at 1568 and 1415 and $[Sn(O_2CEt)_4]$ at 1690 and 1565 (asym), and 1445 and 1301 cm^{-1} (sym), suggest that these two compounds have different structures, the latter but not the former containing unidentate carboxylato-groups.[7]

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