Synthesis, Characterization, and Crystal Structures of Tin(IV) 1-Pyrrolethiocarboxylates†

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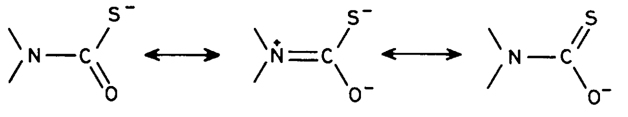
Tin 1-pyrrolecarbothioates (1-pyrrolethiocarboxylates) $SnR_{4-n}L_n$ (L = OSCNCH=CHCH=CH, *n* = 1—4) have been synthesized and characterized by i.r., n.m.r. (^1H, ^{13}C, and ^{119}Sn), and ^{119}Sn Mössbauer spectral studies. *X*-Ray crystal and molecular structure analyses were performed on the compounds $SnPh_3L$, $SnMe_2L_2$, $SnPhL_3$, and SnL_4. The triphenyltin complex is tetrahedral with a sulphur-bonded ligand. The bis complex can be considered to be essentially tetrahedral or as highly distorted octahedral if very weak Sn–O interactions (average bond length 2.65 Å) are taken into account. The phenyltin tris complex contains a seven-co-ordinated tin atom in a distorted pentagonal-bipyramidal environment with all the three ligands bound to the tin in an anisobidentate fashion (average Sn–O 2.506 Å). The complex SnL_4 shows a distorted-octahedral co-ordination geometry with two thiocarbamates functioning as bidentate chelates, the other two as monodentate ligands through the sulphur atom. In solution, these structures are essentially retained, as indicated by the n.m.r. spectral features.

Despite considerable information[1] on structural aspects of tin(IV) compounds, the factors influencing the co-ordination number, the co-ordination geometry, the co-ordination polyhedron, and the isomers formed are not well understood. Pursuing our interest in structural tin chemistry[2,3] and the ligational ability[4-8] of asymmetric sulphur ligands, we have synthesized and characterized the complete series $SnR_{4-n}L_n$ (L = OSCNCH=CHCH=CH, *n* = 1—4) and determined the *X*-ray structures of the compounds $SnPh_3L$ (**1a**), $SnMe_2L_2$ (**2c**), $SnPhL_3$ (**3a**), and SnL_4 (**4**). This series was chosen with the object of determining whether the successive incorporation of the ligand L results in changes of co-ordination at tin(IV) and subsequently in changes of the geometry at the tin atom.

The choice of asymmetric sulphur ligands[9] provides a viable method to assess some of the features of the derived metal complexes not observed with symmetrical bidentate oxygen or sulphur analogues. While the co-ordination chemistry of metal β-diketonates[10] and dithiocarbamates[11] has developed considerably, the monothiocarbamates have scarcely been examined so far. A few structural reports[12] on transition-metal monothiocarbamates reveal considerable structural deviations from the corresponding complexes of symmetrical ligands,[11,13] *e.g.* dithiocarbamates.

Monothiocarbamate R_2NCOS^-, as an ambidentate ligand, can bind through oxygen or sulphur to a metal centre. Usually these anions behave as bidentate ligands,[14,15] either chelating or bridging. The properties of *N,N*-dialkylmonothiocarbamates have been attributed to the enhanced mercaptide character with respect to dithiocarbamates[16] due to a larger contribution of the two resonance forms (**A**) and (**B**). The peripheral change of incorporating the nitrogen as a part of an aromatic ring in thiocarbamate ligands would diminish the contribution of the CN double-bonded form. The only structurally established example of this class is an octahedral compound of nickel,[17] $[NiL_2]\cdot 2py$ (py = pyridine).


(A) (B) (C)

Experimental

All experimental manipulations were carried out under strictly anhydrous conditions. Potassium 1-pyrrolecarbothioate was synthesized by the literature procedure.[18] The compounds $SnMe_3Cl$ (b.p. 152—154 °C, 760 mmHg), $SnBu_3Cl$ (b.p. 97 °C, 0.4 mmHg), $SnPh_3Cl$ (b.p. 249 °C, 13 mmHg), $SnMe_2Cl_2$ (b.p. 185—190 °C, 760 mmHg), $SnBu_2Cl_2$ (b.p. 50 °C, 1.0 mmHg), $SnPh_2Cl_2$ (b.p. 100 °C, 0.5 mmHg), $SnBuCl_3$ (b.p. 93 °C, 10 mmHg), $SnPhCl_3$ (b.p. 75 °C, 1.0 mmHg), and $SnCl_4$ (b.p. 114 °C) were distilled prior to use.

Tin was estimated as SnO_2 and sulphur by Messenger's method. Nitrogen analyses were carried out by microelemental analysis. Molecular weights were determined cryoscopically in benzene or nitrobenzene. Conductance was measured on a conductivity bridge (model no. L-370873 from Cambridge Instrument Co.) in an acetonitrile or a nitrobenzene solution. Infrared spectra were recorded on a Perkin-Elmer 621 model instrument in the 4 000—200 cm^{-1} range as neat liquids or as Nujol mulls using CsI plates or solutions in chloroform. N.m.r. spectra (^1H, ^{13}C, and ^{119}Sn) were recorded at approximately 25 °C on a JEOL-FX 90Q spectrometer in $CDCl_3$ ($SiMe_4$ as internal standard for ^1H, ^{13}C; $SnMe_4$ for ^{119}Sn; sealed capillaries). Tin-119 Mössbauer spectral data in the solid state were obtained with a Texas Instruments cryoflask model CLF3; $^{119}SnO_2$ in a lucite matrix at room temperature was used as the source whereas absorbers were examined at 80 K (liquid-nitrogen temperature).

General Procedure for the Preparation of Tin(IV) *1-Pyrrolecarbothioates.*—The compounds were synthesized by adding a stoicheiometric amount of the appropriate tin tetrachloride or organotin(IV) chloride in dichloromethane (*ca.* 20 cm^3) to a suspension of potassium 1-pyrrolecarbothioate in dichloromethane (*ca.* 30 cm^3) with constant stirring at ambient

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† IUPAC recommended name is tin(IV) 1-pyrrolecarbothioate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Physical properties and analytical data

	Complex[a]	Nature	M.p./b.p. (°C)	Analysis[b] (%) Sn	S	N	$M^{b,c}$
(1a)	$SnPh_3L$	Yellow solid	140	23.6	6.85	3.10	513
				(24.9)	(6.70)	(2.45)	(476)
(1b)	$SnBu_3L$	Yellow liquid	—	28.9	6.95	3.95	394
				(28.5)	(7.70)	(3.35)	(416)
(1c)	$SnMe_3L$	Yellow liquid	73 °C/0.7 mmHg	39.2	10.6	4.15	256
				(40.9)	(11.0)	(4.80)	(290)
(2a)	$SnPh_2L_2$	Yellow solid	93	21.7	11.5	6.10	521
				(22.6)	(12.2)	(5.35)	(525)
(2b)	$SnBu_2L_2$	Yellow liquid	—	23.8	12.9	5.10	464
				(24.4)	(13.2)	(5.75)	(485)
(2c)	$SnMe_2L_2$	Yellow solid	133	29.0	16.8	7.20	366
				(29.6)	(15.7)	(7.00)	(401)
(3a)	$SnPhL_3$	Yellow solid	132—134	20.5	16.4	7.10	558
				(20.7)	(16.7)	(7.30)	(573)
(3b)	$SnBuL_3$	Yellow solid	142—144[d]	21.5	14.7	7.30	538
				(21.7)	(15.5)	(7.60)	(554)
(4)	SnL_4	Yellow solid	146	19.8	20.3	9.10	598
				(19.1)	(20.5)	(9.00)	(622)

[a] Yields 85—90%. [b] Calculated values in parentheses. [c] Cryoscopically in benzene [(1)—(3)] or in nitrobenzene [(4)]. [d] Decomposed.

Table 2. Details of crystallographic data collection and structure solutions

Crystal data	(1a)[a]	(2c)[b]	(3a)[c]	(4)[a]
Formula	$C_{23}H_{19}NOSSn$	$C_{12}H_{14}N_2O_2S_2Sn$	$C_{21}H_{17}N_3O_3S_3Sn$	$C_{20}H_{16}N_4O_4S_4Sn$
M	476.16	401.07	574.26	623.30
a/Å	7.744(3)	22.560(8)	8.675(2)	20.154(13)
b/Å	16.996(7)	10.597(6)	10.527(2)	10.091(6)
c/Å	31.102(12)	13.628(6)	13.080(3)	12.157(6)
α/°	90	90	80.79(2)	90
β/°	90	104.59(3)	82.34(2)	102.02(5)
γ/°	90	90	81.16(2)	90
U/Å^3	4 093.5	3 152.9	1 157.8	2 418.2
D_c/g cm^{-3}	1.545	1.679	1.636	1.701
Z	8	8	2	4
Space group	*Pbca*	*C2/m*	$P\bar{1}$	*C2/m*
μ(Mo-K_α)/cm^{-1}	13.61	18.79	13.93	14.25
F(000)	1 903.87	1 583.8	571.92	1 239.82
Size of crystal (mm)	0.35 × 0.35 × 0.7	0.4 × 0.3 × 0.2	0.1 × 0.7 × 0.35	0.6 × 0.4 × 0.6
Data collection[d]				
2θ range/°	2—50	2—50	2—50	2—50
hkl	$h, k, \pm l$	$h, k, \pm l$	$h, \pm k, \pm l$	$h, k, \pm l$
Scan speed (° min^{-1}) for 150—$\geqslant$2 500 counts	2—29.3	2—29.3	2—29.3	2—29.3
Measured reflections	7 700	2 233	4 575	2 424
Unique (averaged) reflections for $F \geqslant 3\sigma(F)$	3 541	2 078	3 701	2 250
Maximum/minimum transmission	0.443/0.422	0.674/0.580	—	—
Structure solution	Heavy-atom method	Direct method	Direct method	Direct method
Variables	301	203	348	400
R[e]	0.0339	0.0380	0.0277	0.0345
R'[f]	0.0340	0.0407	0.0297	0.0386
g	0.000 14	0.000 73	0.000 38	0.0003
Largest residual electron density/e Å^{-3}	0.78[g]	0.50[h]	0.39[i]	0.28[j]

[a] Crystals obtained from dichloromethane–hexane. [b] Crystals obtained from dichloromethane–methanol. [c] Crystals obtained from dichloromethane–light petroleum (b.p. 40—60 °C). [d] Two check reflections were measured after every 48 intensity measurements (ω—2θ scans). Intensities were corrected for Lorentz and polarization as well as for absorption effects (empirical, ψ scan). Peak-profile fitting was employed. [e] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [f] $R' = \Sigma w^{\frac{1}{2}}|\Delta F|/\Sigma w^{\frac{1}{2}}|F_o|$ with $w^{-1} = \sigma^2 F_o + gF_o^2$. [g] Next to the Sn atom. [h] Next to Sn and S(1). [i] Near the Sn atom. [j] Near Sn and S(2).

temperature under a nitrogen atmosphere. Stirring was continued for 8—12 h, and then the insoluble material was filtered from the solution. The volatiles were removed from the filtrate and the non-volatile products obtained were dried at 28 °C (0.1 mmHg) for *ca.* 6 h. Finally, the solid products were crystallized from dichloromethane–n-hexane (2:1) or dichloro-

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Complex						
(1a)	Sn–S	2.453(1)	C–S	1.762(3)	N–C(4)	1.391(4)
	Sn–C(10)	2.140(3)	C–O	1.207(4)	C(1)–C(2)	1.338(4)
	Sn–C(20)	2.123(3)	C–N	1.402(4)	C(2)–C(3)	1.413(5)
	Sn–C(30)	2.123(3)	N–C(1)	1.389(4)	C(3)–C(4)	1.333(5)
(2c)	Sn–S(1)	2.505(2)	S(1a)–C(1a)	1.750(6)	N(1)–C(2)	1.392(8)
	Sn–S(1a)	2.501(2)	C(1)–O(1)	1.214(7)	N(1)–C(5)	1.388(8)
	Sn–C(a)	2.108(5)	C(1a)–O(1a)	1.224(7)	C(2)–C(3)	1.335(9)
	Sn–C(b)	2.111(6)	C(1)–N(1)	1.390(7)	C(3)–C(4)	1.400(12)
	S(1)–C(1)	1.757(6)	C(1a)–N(1a)	1.382(7)	C(4)–C(5)	1.353(10)
(3a)	Sn–S(1)	2.448(1)	C(1)–S(1)	1.750(3)	C(2)–N(2)	1.380(4)
	Sn–S(2)	2.529(1)	C(2)–S(2)	1.742(3)	C(3)–N(3)	1.380(4)
	Sn–S(3)	2.538(1)	C(3)–S(3)	1.741(4)	N(1)–C(11)	1.394(4)
	Sn–O(1)	2.523(2)	C(1)–O(1)	1.224(3)	N(1)–C(14)	1.403(4)
	Sn–O(2)	2.517(2)	C(2)–O(2)	1.227(4)	C(11)–C(12)	1.332(5)
	Sn–O(3)	2.480(2)	C(3)–O(3)	1.237(3)	C(12)–C(13)	1.421(5)
	Sn–C(40)	2.123(3)	C(1)–N(1)	1.375(4)	C(13)–C(14)	1.336(5)
(4)	Sn–S(1)	2.463(1)	N(1)–C(1)	1.402(5)	N(1)–C(5)	1.373(6)
	Sn–S(2)	2.446(1)	N(2)–C(6)	1.366(5)	N(2)–C(7)	1.396(7)
	Sn–O(2)	2.424(3)	N(1)–C(2)	1.392(7)	C(7)–C(8)	1.345(8)
	S(2)–C(6)	1.739(4)	C(2)–C(3)	1.333(7)	C(8)–C(9)	1.385(11)
	S(1)–C(1)	1.771(5)	C(3)–C(4)	1.418(10)	C(9)–C(10)	1.329(9)
	O(2)–C(6)	1.241(5)	C(4)–C(5)	1.349(8)	N(2)–C(10)	1.424(6)
	O(1)–C(1)	1.192(5)				
(1a)	C(10)–Sn–C(20)	110.0(1)	Sn–S–C	94.5(1)	N–C(1)–C(2)	108.0(3)
	C(20)–Sn–C(30)	114.3(1)	S–C–O	124.2(2)	C(1)–C(2)–C(3)	107.6(3)
	C(10)–Sn–C(30)	113.9(1)	O–C–N	121.0(3)	C(2)–C(3)–C(4)	109.0(3)
	S–Sn–C(10)	98.2(1)	S–C–N	114.8(2)	C(3)–C(4)–N	107.3(5)
	S–Sn–C(20)	112.2(1)	C–N–C(1)	128.4(2)	C(1)–N–C(4)	108.2(2)
	S–Sn–C(30)	107.2(1)	C–N–C(4)	123.4(2)		
(2c)	C(1a)–Sn–C(b)	132.9(3)	Sn–S(1)–C(1)	85.2(2)	S(1)–C(1)–N(1)	117.1(4)
	S(1)–Sn–S(1a)	92.6(1)	Sn–S(1a)–C(1a)	86.5(2)	S(1a)–C(1a)–N(1a)	118.1(4)
	S(1)–Sn–C(a)	106.8(2)	S(1)–C(1)–O(1)	122.0(4)	O(1)–C(1)–N(1)	120.9(5)
	S(1a)–Sn–C(b)	106.5(2)	S(1a)–C(1a)–O(1a)	121.5(4)	O(1a)–C(1a)–N(1a)	120.3(5)
	S(1a)–Sn–C(a)	105.5(1)				
(3a)	S(1)–Sn–S(2)	100.0(0)	S(1)–Sn–O(2)	85.4(1)	C(40)–Sn–O(3)	87.1(1)
	S(1)–Sn–S(3)	97.0(0)	O(1)–Sn–S(2)	133.1(1)	Sn–O(1)–C(1)	92.7(2)
	S(2)–Sn–S(3)	89.6(0)	O(1)–Sn–S(3)	133.4(1)	Sn–O(2)–C(2)	94.7(2)
	O(1)–Sn–O(2)	73.1(1)	O(2)–Sn–S(3)	151.1(1)	Sn–O(3)–C(3)	95.3(2)
	O(1)–Sn–O(3)	73.4(1)	O(3)–Sn–S(2)	151.9(0)	Sn–S(1)–C(1)	83.9(1)
	O(3)–Sn–O(2)	146.2(1)	C(40)–Sn–S(1)	150.7(1)	Sn–S(2)–C(2)	82.9(1)
	O(1)–Sn–S(1)	62.9(0)	C(40)–Sn–S(2)	101.2(1)	Sn–S(3)–C(3)	82.0(1)
	O(2)–Sn–S(2)	61.7(1)	C(40)–Sn–S(3)	103.2(1)	O(1)–C(1)–S(1)	120.5(2)
	O(3)–Sn–S(3)	62.3(1)	C(40)–Sn–O(1)	87.7(1)	O(2)–C(2)–S(2)	120.4(2)
	S(1)–Sn–O(3)	83.6(1)	C(40)–Sn–O(2)	87.0(1)	O(3)–C(3)–S(3)	120.4(2)
(4)	S(1)–Sn–S(2)	96.1(0)	S(2)–Sn–O(2)	64.4(1)	C(6)–N(2)–C(7)	128.1(4)
	S(1)–Sn–O(2)	87.7(1)	Sn–S(2)–C(6)	81.9(1)	C(6)–N(2)–C(10)	123.7(4)
	S(1)–Sn–S(1a)	103.2(1)	Sn–O(2)–C(6)	93.7(2)	S(1)–C(1)–O(1)	125.3(3)
	S(1a)–Sn–S(2)	108.8(0)	Sn–S(1)–C(1)	100.3(1)	S(1)–C(1)–N(1)	112.6(3)
	S(1)–Sn–O(2a)	168.0(1)	S(2)–C(6)–O(2)	120.0(3)	O(1)–C(1)–N(1)	122.1(4)
	S(2)–Sn–O(2)	84.9(1)	S(2)–C(6)–N(2)	119.2(3)	C(1)–N(1)–C(2)	122.4(4)
	S(2)–Sn–S(2a)	139.6(1)	O(2)–C(6)–N(2)	120.7(4)	C(1)–N(1)–C(5)	130.0(4)
	O(2)–Sn–O(2)	82.0(1)				

methane–methanol (2:1). Physical properties and analytical data for the vacuum-dried compounds are given in Table 1. Preparations were performed on a 10—20 mmol scale.

X-Ray Structure Analyses.—The *X*-ray structure determinations were performed using a Syntex R3 four-circle automated diffractometer operating with a graphite monochromator and Mo-K_α radiation, $\lambda = 0.710\,69$ Å, for data collection at 25 °C and the SHELXTL program package[19] for structure solution and refinement. A Data General NOVA 3 computer was used in all computational work. Crystallographic data and details of the data collection and *X*-ray crystal structure determinations are summarized in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

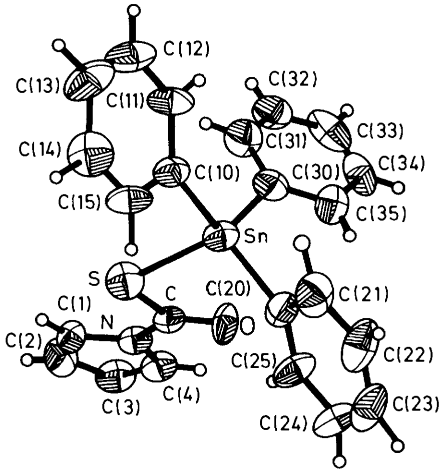


Figure 1. ORTEP plot of the molecular structure of $SnPh_3L$, (**1a**). Thermal ellipsoids are represented on a 30% probability level

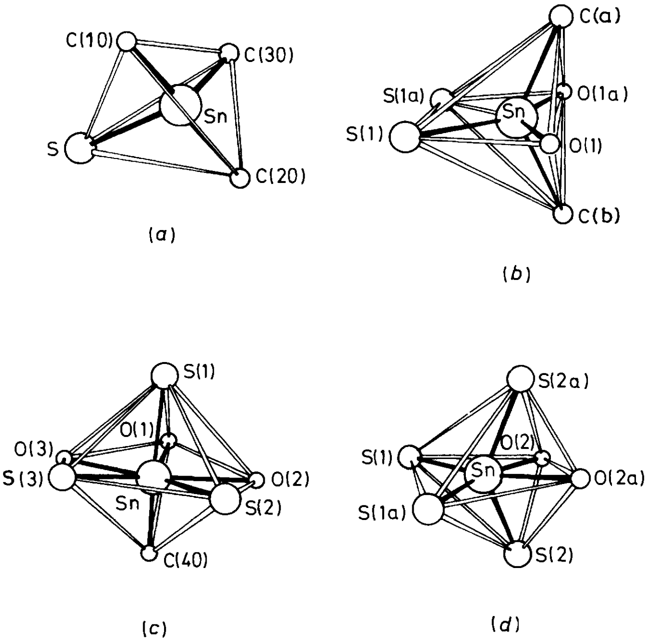


Figure 2. The co-ordination sphere of the tin atom in (*a*) $SnPh_3L$, (*b*) $SnMe_2L_2$, (*c*) $SnPhL_3$, and (*d*) SnL_4

Results and Discussion

Tin(IV) 1-pyrrolecarbothioates have been synthesized in good yields by route (1). All the complexes exist as unimolecular

$$SnR_{4-n}Cl_n + n\,KL \xrightarrow{n=1-4} SnR_{4-n}L_n + n\,KCl \quad (1)$$

species, as found by molecular weight determinations cryoscopically in benzene or nitrobenzene (Table 1). The compounds are non-conducting in acetonitrile or nitrobenzene. Although vibrational and n.m.r. data revealed structural features and co-ordination at the tin atom, an *X*-ray structure determination of representative members of the series was essential for an unambiguous assignment of spectral data.

Crystal and Molecular Structures.—The molecular structure of compound (**1a**) is shown in Figure 1, and selected bond distances are listed in Table 3. Atomic co-ordinates are given in Table 4. The ligand is monodentate through its sulphur atom [Sn–S 2.453(1) Å]. This is comparable to the distances observed in four-co-ordinated complexes such as $SnPh_3[SP(S)(OEt)_2]$ (S–Sn 2.458 Å)[20] and in $SnMe_3(SCSNMe_2)$(S–Sn 2.47 Å).[21] Reported distances for triphenyltin thiophenolates[22] lie in the range 2.41—2.44 Å. There is no bonding interaction between Sn and O in (**1a**), as shown by the long distance of 3.02 Å. Such a situation is comparable to the four-co-ordinated tricyclohexyltin acetate[23] wherein one oxygen atom is bonded to the tin atom while the other oxygen atom is located at a distance of 2.95 Å.

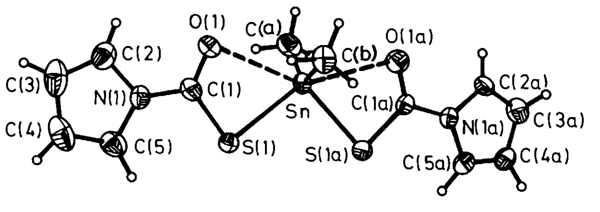


Figure 3. ORTEP plot of the molecular structure of $SnMe_2L_2$, (**2c**). Thermal ellipsoids are represented on a 30% probability level

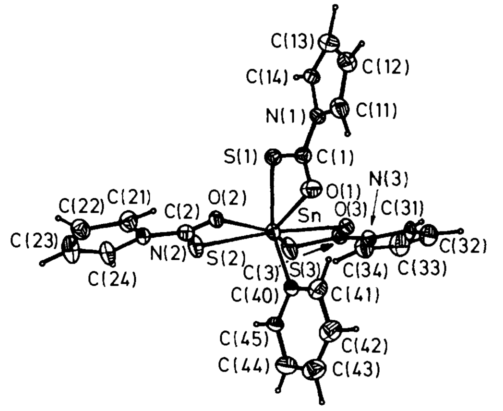


Figure 4. ORTEP plot of the molecular structure of $SnPhL_3$, (**3a**). Thermal ellipsoids represent 30% probability

The geometry around tin in compound (**1a**) is slightly distorted tetrahedral (Figure 2). While the bond angles to the phenyl carbons (110.0, 113.9, and 114.3° respectively) are close to the tetrahedral angle, the SSnC angles are rather irregular ranging from 98.2 and 107.2 to 112.2°. The largest bond angle is probably due to steric interaction of the oxygen atom with H(25) (H $\cdots$ O 2.432 Å). The asymmetry observed can readily be explained by the monodentate nature of the ligand L, which effects strongly the ideal point-group symmetry expected for SnR_3X compounds. A similar deviation from tetrahedral symmetry has been noted for triphenyltin *p*-t-butylbenzenethiolate,[24] $SnPh_3(SC_6H_4Bu^t\text{-}p)$ (CSnC 98.5—114°) as well as for triphenyltin dithiophosphate[20] (CSSn 110—114°) which is an established example of a four-co-ordinate triphenyltin(IV) complex.

The molecular structure of dimethyltin(IV) bis(1-pyrrolecarbothioate), (**2c**) is shown in Figure 3. As indicated by the Sn–C, Sn–S, and Sn–O bond distances as well as by the bond angles at the tin atom, the co-ordination polyhedron at the tin atom can be described as a highly distorted tetrahedron. The ligands L are primarily monodentate through their sulphur atoms. However, an alternative description could be that of a highly distorted octahedron or skew-trapezoidal bipyramid[25] (Figure 2), since the tin–oxygen distances (2.670 and 2.645 Å) approach those found in tin–oxygen bonded species (2.11—2.45 Å). In accord with this view is the CSnC angle of 132.9(3)° and the concomitant decrease in the SSnS angle to 92.6(1) (Table 3).

Nevertheless, the SSnC angles lie in a narrow range (105.5—106.8°), close to the tetrahedral angle. These findings are in accord with an increasing co-ordination number at the tin atom, as well as the increased Sn–S bond distance in the bis complex (**2c**) [2.505(2) and 2.501(2) Å] as compared to the analogous distance in the triphenyltin complex (**1a**). The thiocarbamate ligand in $SnMe_2L_2$ can, therefore, be said to possess some degree of anisobidentate bonding. The overall molecular structure of the complex is comparable to that of dimethyltin bis(monothio-β-diketonates), $SnMe_2(RCSCHCOR')_2$,[23] although the latter have comparatively short Sn–O bond lengths (2.489 Å) and acute SSnS bond angles (79.2°).

The molecular structure of phenyltin tris(1-pyrrolecarbothioate), (**3a**), is shown in Figure 4. It contains a seven-co-ordinated tin atom. The three essentially bidentate monothiocarbamate ligands form very acute OSnS bond angles of 62.9(0), 61.7(1), and 62.3(1)° respectively which are less than the ideal 72° for equatorial angles required for a pentagonal-bipyramidal co-ordination. However, if one considers the atoms S(2), S(3), O(3), O(1), and O(2), which lie almost in a plane (sum of bond angles 359.1°), a distorted pentagon can be envisaged. The atoms S(1) and C(40) would then complete the distorted pentagonal-bipyramidal polyhedron [Figure 2(*c*)]. The observed Sn–S distances are 2.529(1), 2.538(1) and 2.448(1) Å. The monothiocarbamate sulphur atom S(1) in the axial position shows a considerable shorter bond length (2.448 Å) than the equatorial ones. This is in accord with similar structures of tris(dithiocarbamate) tin complexes.[26] Although oxygen has a smaller atomic radius than sulphur, the mean Sn–O bond distance (2.506 Å) in complex (**3a**) is comparable with the mean Sn–S distance. However, these Sn–O distances are 0.5 Å shorter than in (**1a**) and 0.14 Å shorter than in (**2c**).

Nevertheless, although an increasing Sn–O interaction is evident in this series, all the three ligands L are bound to the tin atom in a typical anisobidentate fashion. For tin, the isotropic nature does not seem to be restricted to this as well as to monothio-β-diketonates[2] and dithiocarbamates[26] but also occurs with bidentate nitrate[27] and bidentate tropolonate (2-hydroxycyclohepta-2,4,6-trien-1-onate).[28]

The Sn–C distances in the three complexes, (**1a**) [2.140(3), 2.123(3), and 2.123(3) Å], (**2c**) [2.108(5) and 2.111(6) Å], and (**3a**) [2.123(3) Å] are very close to the normal bond lengths expected from the sum of covalent radii (2.14 Å).

In a search for rare eight-co-ordinated tin(IV) complexes, the structure of the tetrakis complex SnL_4, (**4**), was examined. However, as shown in Figure 5, the molecule contains two thiocarbamate ligands functioning as bidentate chelates, and two others which bind as monodentate ligands through sulphur thus leading to a distorted octahedral environment around the tin centre [see Figure 2(*d*)]. The two sulphur atoms of the monodentate ligands are *cis* oriented to one another forming an S(1)SnS(1a) bond angle of 103.2(1)° (Table 3). This is, then, the first example of a complex containing both bi- and monodentate monothiocarbamate ligands.

The molecule (**4**) possesses a crystallographically imposed two-fold axis, bisecting the S(1)SnS(1a) and O(2)SnO(2a) angles. As a consequence of the bidentate nature of the ligands S(2)C(6)O(2) and S(2a)C(6a)O(2a), acute chelating SCO bond angles of 64.4° are present. This causes serious deviations from the octahedral bond angles, *e.g.* an S(2)SnS(2a) angle of only 139.6(1)° is found instead of the expected ideal 180° for a *trans* arrangement. On the other hand, the S(1)SnS(1a) bond angle of 103.2(1)° involving the monodentate ligands approaches much closer to the expected 90°. The S(1)SnO(2a) bond angles (168°) deviate only by 12° from the ideal 180°. These deviations are the consequences of chelation because the three bond lengths [Sn–O(2) 2.424(3), Sn–S(2) 2.446(1), and Sn–S(1) 2.463(1) Å] are almost equal.

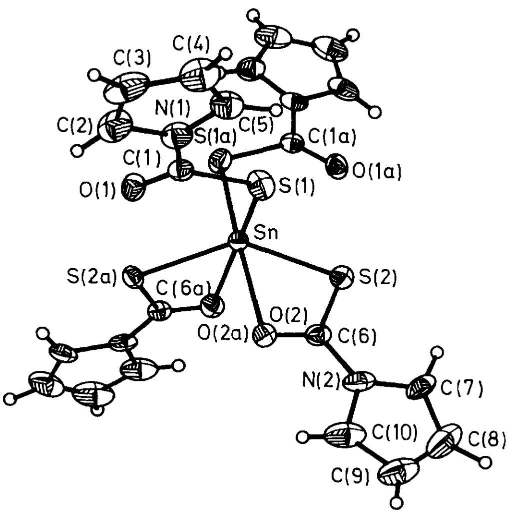


Figure 5. ORTEP plot of SnL_4, (**4a**). Thermal ellipsoids represent 25% probability

The SSnO bond angles of the chelate rings (64.4°) in (**4**) are much smaller [comparable to 61.7—64.6° in $Ti(SCONEt_2)_4$[29] and 69.3° in $Fe(SCONMe_2)_3$[30]] than the corresponding interchelate angle of 108.8°. The very acute bite angles of the ligand are almost certainly the cause of the distortion from the regular octahedron.

The Sn–S bond distance of the chelated ligand L in compound (**4**) [2.446(1) Å] seems to be slightly but significantly shorter than the corresponding distance of 2.463(1) Å when the ligand is acting in a monodentate fashion. This observed difference is not, however, in keeping with the structure of tin tetrakis(diethyldithiocarbamate).[31] In that compound, the Sn–S bonds of the chelate rings are longer than the monodentate ones. The two chelated thiocarbamates still have anisobidentate co-ordination with an Sn–O bond distance of 2.424 Å. This is significantly shorter than the corresponding distance (average 2.506 Å) in (**3a**). In the other two monodentate ligands, the oxygen is too far from the tin atom (intramolecular distance Sn • • • O 3.42 Å) to allow even for any weak interaction.

From the comparative description of the molecular dimensions of the organotin 1-pyrrolecarbothioates (**1a**), (**2c**), (**3a**), and (**4**) some important features can be discerned concerning their electronic structure and the stereochemical pattern around the tin(IV), emphasizing the relative affinity of tin for the mercaptide sulphur.

The bonding within the ligand is of considerable interest, and the resonance structures (**A**)—(**C**) have to be considered. In dialkylmonothiocarbamate complexes of about a dozen transition metals[12] the average ligand bond distances are C–O 1.263, C–N 1.346, and C–S 1.745 Å, while the C–S distances of dithiocarbamate complexes[4] fall in the range 1.70—1.73 Å and C–N bond lengths in the range 1.30—1.35 Å. This implies that, in general, the C–N double-bonded canonical form (**B**) predominates in describing the electronic structures of dialkylmonothiocarbamates and dithiocarbamates. However, from the increase in the C–S bond length it becomes evident that in the monothiocarbamates resonance form (**C**) contributes less to the ground state due to the greater contribution of the C–O double-bonded form (**A**). Comparative dimensions of the SnSCON cores of all the four complexes are summarized in Table 5.

The geometry of the chelated and monodentate ligands L differ considerably. The monodentate ligands in $SnPh_3L$ and

Table 4. Atomic co-ordinates (× 10^4)

	X/*a*	*Y*/*b*	*Z*/*c*		*X*/*a*	*Y*/*b*	*Z*/*c*
$SnPh_3L$ (**1a**)							
Sn	1 621(0)	2 289(0)	1 278(0)	C(15)	4 816(4)	1 885(2)	732(1)
S	274(1)	2 859(0)	636(0)	C(20)	2 919(4)	3 149(2)	1 653(1)
C	−1 371(4)	3 345(2)	923(1)	C(21)	4 524(5)	2 949(2)	1 825(1)
O	−1 388(3)	3 420(2)	1 309(1)	C(22)	5 436(5)	3 491(3)	2 073(1)
N	−2 699(3)	3 656(1)	669(1)	C(23)	4 767(5)	4 215(2)	2 149(1)
C(1)	−2 896(4)	3 611(2)	225(1)	C(24)	3 200(5)	4 425(2)	1 983(1)
C(2)	−4 394(5)	3 955(2)	122(1)	C(25)	2 268(5)	3 885(2)	1 738(1)
C(3)	−5 162(4)	4 222(2)	508(1)	C(30)	−333(4)	1 664(2)	1 614(1)
C(4)	−4 134(4)	4 040(2)	837(1)	C(31)	−1 235(5)	1 047(2)	1 430(1)
C(10)	3 462(4)	1 548(2)	963(1)	C(32)	−2 553(5)	676(2)	1 645(1)
C(11)	3 321(4)	737(2)	963(1)	C(33)	−2 976(5)	906(3)	2 054(2)
C(12)	4 496(4)	281(2)	733(1)	C(34)	−2 083(5)	1 502(3)	2 247(1)
C(13)	5 807(4)	624(2)	504(1)	C(35)	−780(5)	1 885(2)	2 027(1)
C(14)	5 983(4)	1 428(2)	505(1)				
$SnMe_2L_2$ (**2c**)							
Sn	1 018(1)	3 565(1)	272(1)	C(5)	2 075(3)	−708(7)	1 612(4)
C(a)	404(3)	3 121(7)	−1 126(4)	S(1a)	1 715(1)	5 216(2)	−123(1)
C(b)	893(3)	4 011(6)	1 717(4)	C(1a)	1 076(3)	6 212(5)	−399(4)
S(1)	1 840(1)	1 917(2)	586(1)	O(1a)	584(2)	5 876(4)	−264(3)
C(1)	1 285(3)	923(5)	877(4)	N(1a)	1 140(2)	7 400(4)	−778(3)
O(1)	755(2)	1 247(4)	746(3)	C(2a)	669(3)	8 243(5)	−1 087(5)
N(1)	1 481(2)	−248(4)	1 294(3)	C(3a)	900(3)	9 282(6)	−1 444(4)
C(2)	1 086(3)	−1 156(6)	1 509(5)	C(4a)	1 526(3)	9 094(6)	−1 346(4)
C(3)	1 425(4)	−2 128(7)	1 956(5)	C(5a)	1 675(3)	7 945(6)	−943(4)
C(4)	2 041(4)	−1 866(7)	2 013(5)				
$SnPhL_3$ (**3a**)							
Sn	8 398(1)	1 886(1)	2 741(1)	C(23)	11 215(6)	7 036(4)	3 140(4)
S(1)	5 654(1)	2 863(1)	2 697(1)	C(24)	10 761(5)	5 860(4)	3 493(3)
S(2)	9 296(1)	3 299(1)	3 875(1)	O(3)	7 377(2)	−105(2)	2 490(2)
S(3)	7 963(1)	191(1)	4 327(1)	C(3)	7 354(3)	−605(3)	3 414(2)
O(1)	7 360(2)	2 355(2)	987(2)	N(3)	6 831(3)	−1 793(2)	3 738(2)
C(1)	6 050(3)	2 787(3)	1 359(2)	C(31)	6 345(4)	−2 516(3)	3 072(3)
N(1)	4 849(3)	3 227(2)	749(2)	C(32)	5 932(5)	−3 611(4)	3 650(3)
C(11)	5 026(4)	3 372(3)	−337(2)	C(33)	6 166(6)	−3 587(4)	4 693(3)
C(12)	3 645(4)	3 894(3)	−661(3)	C(34)	6 720(5)	−2 481(4)	4 741(3)
C(13)	2 546(4)	4 104(4)	223(3)	C(40)	10 575(3)	1 117(3)	1 976(2)
C(14)	3 289(4)	3 702(3)	1 073(3)	C(41)	10 834(4)	1 011(3)	928(3)
O(2)	9 045(3)	4 098(2)	1 920(2)	C(42)	12 293(5)	473(4)	499(3)
C(2)	9 475(3)	4 357(3)	2 710(2)	C(43)	13 468(4)	49(4)	1 137(4)
N(2)	10 113(3)	5 485(2)	2 690(2)	C(44)	13 229(4)	157(4)	2 182(4)
C(21)	10 194(4)	6 468(3)	1 840(3)	C(45)	11 759(4)	689(3)	2 607(3)
C(22)	10 864(5)	7 412(3)	2 108(3)				
SnL_4 (**4**)							
Sn	0	789(1)	2 500	C(5)	2 085(3)	−2 631(5)	3 486(4)
S(1)	912(1)	−727(1)	3 392(1)	C(6)	418(2)	2 667(4)	4 190(3)
S(2)	−260(1)	1 625(1)	4 250(1)	O(2)	704(2)	2 603(3)	3 380(2)
C(1)	1 287(2)	−1 085(4)	2 232(3)	N(2)	631(2)	3 551(3)	5 042(3)
O(1)	1 110(2)	−635(3)	1 310(3)	C(7)	375(3)	3 741(5)	6 012(4)
N(1)	1 849(2)	−1 929(3)	2 516(3)	C(8)	750(4)	4 706(6)	6 604(5)
C(2)	2 279(2)	−2 191(5)	1 782(4)	C(9)	1 236(3)	5 124(6)	6 026(6)
C(3)	2 752(2)	−3 039(6)	2 289(6)	C(10)	1 185(3)	4 437(4)	5 079(5)
C(4)	2 644(3)	−3 312(5)	3 383(6)				

SnL_4 possess typical C–O double-bond distances [1.207(4) and 1.192(5) Å], comparatively long C–S bonds [1.762(3) and 1.771(5) Å)], and C–N bond lengths [both 1.402(4) Å] approaching the corresponding single-bond lengths (C–S 1.81, C–N 1.47 Å). The C–O bond lengths, similar to those in ketones and aldehydes, are, so far, the shortest reported for any monothiocarbamate complex. The C–S bond lengths lie surprisingly close to that in the triphenyltin thiolate $SnPh_3(SC_6H_4Bu^t\text{-}p)$ (C–S 1.784 Å).[24] It is shorter than the single-bond distance in bis(1-indolecarbonyl) disulphide,[32] 1.801 Å, suggesting some double-bond character. This implies that within non-chelating 1-pyrrolecarbothioates, the charge distribution is such that most of the negative charge resides on the sulphur atom and that the CO double-bonded canonical form (**A**) contributes primarily to the ground state. Positive charge on the amine nitrogen atom would destabilize the aromatic system in the CN double bonded form (**B**). Nevertheless, a fairly long CN bond (Pauling single-bond distance 1.47 Å) and the almost coplanar

Table 5. Structural parameters (lengths in Å, angles in °) of the 1-pyrrolecarbothioate ligand

	Monodentate		Anisobidentate		
	(4)	**(1a)**	**(2c)**	**(3a)**	**(4)**
Sn–S	2.463(1)	2.453(1)	2.505(2) 2.501(2) av. 2.503	2.448(1) 2.529(1) 2.538(1) av. 2.505	2.446(1)
C–O	1.192(5)	1.207(4)	1.214(7) 1.224(7) av. 1.219	1.224(3) 1.227(4) 1.237(3) av. 1.229	1.241(5)
C–S	1.771(5)	1.762(3)	1.757(6) 1.750(6) av. 1.753	1.750(3) 1.742(3) 1.741(4) av. 1.744	1.739(4)
C–N	1.402(5)	1.402(4)	1.390(7) 1.382(7) av. 1.386	1.375(4) 1.380(4) 1.380(4) av. 1.378	1.366(5)
Sn–O	3.242*	3.02*	2.65*	2.517(2) 2.523(2) 2.480(2) av. 2.506	2.424(3)
Angle at S	100.3(1)	94.5(1)	85.2(2) 86.5(2) av. 85.8	83.9(1) 82.9(1) 82.0(1) av. 82.9	81.9(1)
Angle at C (L)	125.3(3)	124.2(2)	122.0(4) 121.5(4) av. 121.8	120.5(2) 120.4(2) 120.4(2) av. 120.4	120.0(3)

* Non-bonded distance.

Table 6. Spectroscopic data

	I.r. (cm^{-1})[a]			δ(^{119}Sn)[b]	δ(^{13}C)[c] (p.p.m.)		I.s.	Q.s.
Complex	ν(CO)	ν(CN)	ν(CS)	p.p.m.	C(O)S	Allyl or aryl	mm s^{-1}	
(1a)	1 640vs	1 273s	979m	−82	168.3	136.9, 136.3, 129.4, 128.4	1.46	1.95
(1b)	1 642vs	1 275s	982m	+88	169.2	28.3, 26.7, 14.9		
(1c)	1 637vs	1 275s	980m	+93	169.2	14.1		
(2a)	1 588vs	1 289s	984m	−206	135.7	131.8, 131.1, 129.9		
(2b)	1 596s	1 283s	1 022m	−97	28.7	27.1, 16.4, 14.6		
(2c)	1 600vs	1 290s	981m	−80	6.1			
(3a)	1 604s, br	1 290s	980m	−237	134.5	129.7, 129.5, 123.2		
(3b)	1 604s, br	1 302s	978m	−175	36.1	23.4, 21.7, 9.7		
(4)	1 645s 1 550m	1 273s	979m	−392	—	—	1.07	0.85

[a] Spectra recorded in the range 4 000—2 000 cm^{-1} as Nujol mulls or liquid films [(**1**)—(**3**)] or in chloroform solution [(**4**)] on CsI discs; s = strong, v = very, m = medium, br = broad; ν_{asym}(SnC) and ν_{sym}(SnC) for type (**a**) compounds are found at 300/335 and 261—315 cm^{-1} respectively, for type (**b**) and (**c**) at 508—604 and 550 cm^{-1}; ν(SnS) is rather constant (385—398 cm^{-1}, s to m), and the ν(SnO) band for (**2**)—(**4**) is found in the range 487—508 cm^{-1}. [b] In CDCl$_3$ with SnMe$_4$ as a reference in sealed capillaries [(**3a**), reference is external SnMe$_4$]. [c] In CDCl$_3$ with SiMe$_4$ as internal reference; pyrrole-carbon resonances are observed for α-C as singlets (^{1}H-decoupled) in the range 119.9—120.9 and for β-C in the range 111.9—114.5 p.p.m.; δ(^{1}H) for the pyrrole unit at 7.26—7.30 for α-CH and 6.15—6.3 for β-CH.

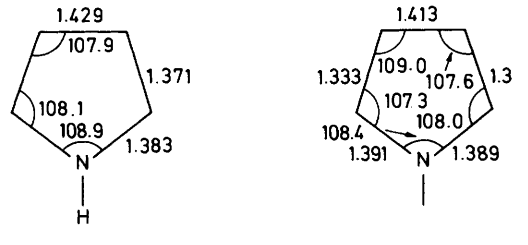
arrangement of the pyrrole ring with the NC(S)O plane (Table 3) indicate that some CN π bonding is present.

For the essentially anisobidentate thiocarbamate ligands some trends can be recognized in the average C–O, C–S, and C–N bond lengths in compounds (**2c**), (**3a**), and (**4**). Data in Table 5 show that the C–S and C–N distances gradually become shorter while the C–O distance increases. This suggests that the π-electron delocalization involving all atoms of the NC(S)O unit increases from (**2c**) to (**4**).

Within monodentate and chelating 1-pyrrolecarbothioates, significant differences can be noted in the intrachelate angles subtended at sulphur. For the non-chelated ligands, 94.5(1)° is found in (**1a**) and at 100.3(1)° in (**4**), and this angle on chelation (by oxygen co-ordination) tends to close up in the series from (**2c**) (85.8°) and (**3a**) (82.9°) to (**4**) (81.9°). The angles at carbon also differ from chelating to non-chelating L but less significantly (see Table 3). The comparison of structural parameters of the ligand L is affected by its bonding mode to the tin atom. Usually the pyrrole ring is coplanar with the respective COS plane. However, in (**4**) the planar pyrrole ring containing atom N(1) is twisted by 8.5° with respect to the O(1)C(1)S(1) plane, while the pyrrole ring at N(2) is almost coplanar (0.5°) with the plane O(2)C(6)S(2).

According to the *X*-ray data, the bonds in the pyrrole ring in all four species examined are almost identical. Compared with pyrrole, whose structure has been determined by a microwave study, the pyrrole unit in L is less symmetrical, as can be seen from Figure 6.

Complexes of type (**1**) display a strong band in the region 1 637—1 642 cm^{-1} owing to ν(C$\cdots$O) absorption, typically for a monodentate sulphur-bonded ligand.[33] Complexes (**2**) show intense CO bands at 1 588—1 600 cm^{-1}, to distinctly



(*a*) (*b*)

Figure 6. Structural data (distances in Å, angles in °) for (*a*) pyrrole (V. Shomaker and L. Pauling, *J. Am. Chem. Soc.*, 1939, **39**, 1769) and (*b*) the pyrrole ring in the ligand L

lower frequency in comparison to SnR_3L compounds. The positions are intermediate between those corresponding to mono- and bi-dentate[17] modes of sulphur attachment. The ν(C$\overset{\cdots}{-}$O) absorptions for complexes of type (**3**) occur around 1 604 cm^{-1}. Thus, the data on (**2**) and (**3**) are consistent with an anisobidentate bonding pattern. Two absorptions at 1 645 and 1 550 cm^{-1} in the solution spectra of (**4**) correspond to mono- and bi-dentate ligands respectively.

An intense band appearing in the range 1 273—1 302 cm^{-1} can be assigned to the ν(C$\overset{\cdots}{-}$N) vibration.[18] The medium-intensity absorption in the region 978—1 022 cm^{-1} arises from ν(C$\overset{\cdots}{-}$S) vibration.[32] Complexes (**1**) and (**2**) display two additional modes around 583—604 and 544—558 cm^{-1} due to ν_{sym} and ν_{asym}(S–C) vibrations[34] in accord with the non-linearity of the C–Sn–C moiety. Complexes (**1a**) and (**2a**) exhibit ν(Sn–C) frequencies around 335 and at 261—315 cm^{-1} [34] while (**3b**) displays a ν(Sn–C) absorption at 592 cm^{-1}. In the spectrum of (**3a**) a band at 300 cm^{-1} may result from a ν[Sn–C(Ph)] mode. All the complexes display a band of medium intensity around 385—390 cm^{-1} due to the ν(Sn–S) mode.[35] The vibration ν(SnO) is found in the range 487—508 cm^{-1}.[36] This, however, is not fully compatible with the *X*-ray result, where one would expect a significant decrease in ν(Sn–O) on going from complex (**4**) *via* complexes (**3**) to (**2**).

N.m.r. data (Table 6) are fully in accord with the *X*-ray results. Thus, complexes (**1a**) and (**2a**) show values of the coupling constant $^2J(^{119}Sn^1H)$ consistent with the four-co-ordinated structure[37] for trimethyltin complexes and a structure somewhere between four- and six-co-ordinated tin for SnR_2L_2 complexes. The ^2J value for complex (**2a**) indicates a distortion of the CSnC bond angle from *trans* orientation as compared with the octahedral complex $SnMe_2(MeCOCHCOMe)_2$.[38,39] The value, however, is very close to that reported for $SnMe_2(S_2CNMe_2)_2$ possessing a distorted octahedral structure with a CSnC angle of 136°.[40,41] The ^{119}Sn resonance for (**4**) is found at rather high field, which indicates six-co-ordination also in solution. The ^1H n.m.r. spectra of the tin(IV) 1-pyrrolecarbothioates display two sets of triplets due to the pyrrole protons. Therefore, irrespective of the nature of the ligands L in the solid state, these become equivalent in solution, due to rapid intramolecular exchange.

The value of the coupling constant $^1J(^{119}Sn^{13}C)$ = 376 Hz for complex (**1b**) is consistent with a four-co-ordinated structure.[42] The value for (**2c**) (530 Hz) corresponds to those of structurally similar bis(dithiocarbamates)[43] (552 Hz) of co-ordination number six and lies far below that for $SnMe_2(MeCOCHCOMe)_2$ (966 Hz).[44] The tin-119 n.m.r. chemical shifts for complex (**1**) are consistent with four-co-ordinated tin in related thiolate complexes.[45,46] Substitution of n-butyl for methyl groups seems to result in a better shielded tin nucleus. The values for the triphenyltin complexes are found at much higher field; this may be accounted for in terms of an increased polarizability of the phenyl groups.[47,48]

The $\delta(^{119}Sn)$ values for complexes (**2**) are intermediate between those of four-co-ordinated diorganotin(IV) dithiolates[44,48] (122—144 p.p.m.) and of six-co-ordinated dimethyltin(IV) bis(β-diketonates) (−365 p.p.m.)[49,50] or $SnMe_2L'_2$ complexes[51] [L′ = tropolonate, kojate (5-hydroxy-2-hydroxymethyl-4*H*-pyran-4-onate) or benzoate; $\delta(^{119}Sn)$ = −125 to −197 p.p.m.].

The values of $\delta(^{119}Sn)$ for complexes of type (**3**) are found at much lower field than expected for seven-co-ordinated tin(IV) complexes (δ = −409 to −695 p.p.m.).[50] However, they are at higher field than those reported for four-co-ordinated trithiolates $SnR(SR')_3$ (65—167 p.p.m.).[45,49] The results may therefore be rationalized in terms of the anisobidentate nature of the ligands L and fluxional character in solution.

Further evidence for the structure of the tin(IV) 1-pyrrolecarbothioate complexes in the solid state was derived from ^{119}Sn Mössbauer studies (see Table 6). The magnitude of the ratio of the quadrupole splitting (q.s.) and the isomer shift (i.s.) = 1.34 for complex (**1a**) is close to the range 1.22—1.29 for tetrahedral tin(IV) dithiocarbamates.[50,52–54] Such values for five-co-ordinated trialkyltin carbamates range from 2.63 to 2.69. This further supports four-co-ordination at the tin atom of (**1a**). In contrast, data for (**4**) (q.s./i.s. = 0.79) reflect six-co-ordinated tin as found for $Sn(S_2CNEt_2)_4$ (q.s./i.s. = 0.77).[54]

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