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# ORGANOTIN BIOCIDES

## VII *. TRI- AND DIORGANOTIN DERIVATIVES OF PIPERAZINE BIS(DITHIOCARBAMIC) ACID

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## Summary

Eight tri- and diorganotin derivatives of piperazine bis(dithiocarbamic) acid ($H_2$pdtc) of formulae $(R_3Sn)_2$pdtc (R = Me, Bu, Ph, cyclo-$C_6H_{11}$) and $R_2$Snpdtc (R = Me, Bu, Oct, Ph) have been synthesised, along with $(ClBu_2Sn)_2$pdtc, a by-product in the synthesis of $Bu_2$Snpdtc. On the basis of spectroscopic data, compounds of type $(R_3Sn)_2$pdtc are judged to be monomeric, with the tin atoms in a tetrahedral environment distorted towards five-coordinate *cis*-$S_2SnR_3$ each by a weakly bidentate $CS_2$ group. The diorganotin derivatives are polymeric, with a distorted *trans*-$R_2SnS_4$ geometry about the metal. Variable temperature Mössbauer spectroscopic data are presented for $(Me_3Sn)_2$pdtc and $Me_2$Snpdtc.

## Introduction

Alkylene bis(dithiocarbamates) form the basis of a family of fungicides which have been widely exploited over the past forty years. The simplest stable derivative, ethylene bis(dithiocarbamate), is the parent for many of these biocides, which include the manganese and zinc salts commonly known as "maneb" and "zineb". In general, these species have much in common with the simple mono(dithiocarbamates) and their metal salts, although clearly a more extensive range of structural possibilities is presented by the presence of a difunctional ligand. Moreover, the bis(dithiocarbamates) show better foliage adhesion and weathering characteristics, possibly through polymer formation [1].

In view of the fungicidal properties of triphenyltin compounds and the biocidal

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* For part III see ref. 30.

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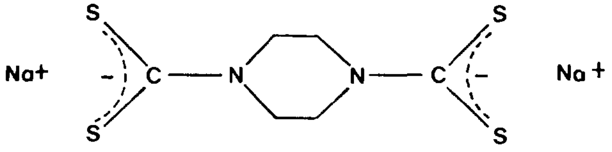
nature of organotins in general [2], we have prepared derivatives of a representative ligand, piperazine bis(dithiocarbamate), available as its disodium salt $Na_2pdtc$ (I).



(I)

Several transition metal salts of this ligand are known [3,4], and there is a brief mention of three organotin compounds, for which synthetic difficulties were noted [5]. In this report we extend the range of known compounds and present spectroscopic evidence for their structures in the solid state.

## Experimental

Infrared spectra were recorded as KBr discs on a Perkin–Elmer 599B spectrophotometer. NMR and mass spectral data were collected on Hitachi/Perkin–Elmer R24B and V.G.70-70E instruments, respectively. Details of our Mössbauer spectrometer and related procedures have been described elsewhere [6]. Microanalyses were performed in part by the Microanalysis service, University College, Dublin (Ireland) but mainly at the University of Bath.

Organotin reagents were either of commercial origin or prepared by published procedures. Piperazine hexahydrate was purchased from Merck and used without further purification. Disodium piperazine bis(dithiocarbamate) dihydrate was prepared by the method of Tombeaux [3], and recrystallised from ethanol. Syntheses of organotin piperazine bis(dithiocarbamates) are typified by the following three examples.

### *Synthesis of bis(tricyclohexylstannyl)piperazine bis(dithiocarbamate)*

Tricyclohexyltin chloride (0.97 g, 2.43 mmol) was dissolved in ethanol (20 $cm^3$) and a warm, ethanolic solution (20 $cm^3$) of $Na_2pdtc \cdot 2H_2O$ (0.39 g, 1.22 mmol) was added with stirring. A white precipitate formed immediately, and stirring was continued for 15 min before isolation of the solid by filtration. The product (0.55 g, 50%) was separated from NaCl by recrystallisation from ethanol.

### *Syntheses of dibutylstannylpiperazine bis(dithiocarbamate) and bis(chlorodibutylstannyl)piperazine bis(dithiocarbamate)*

Dibutyltin dichloride (2.61 g, 8.6 mmol) and $Na_2pdtc \cdot 2H_2O$ (2.67 g, 8.4 mmol) were stirred in ethanol for 30 min. Insoluble $Bu_2Snpdtc$ was filtered off, and separated from co-precipitated NaCl by washing with water and finally diethyl ether (Yield 87%). Concentration of the initial reaction filtrate to dryness and recrystallisation from a minimum of hot ethanol yielded $(ClBu_2Sn)_2pdtc$ (60 mg).

### *Synthesis of bis(tributylstannyl)piperazine bis(dithiocarbamate)*

Tributyltin chloride (4.94 g, 15.2 mmol) and $Na_2pdtc \cdot 2H_2O$ (2.42 g, 7.6 mmol) were stirred in ethanol for 30 min. After filtration to remove NaCl, the filtrate was

TABLE 1

PHYSICAL DATA FOR ORGANOTIN PIPERAZINE BIS(DITHIOCARBAMATES)

| Compound | Yield (%) | M.p. (°C) | C [a] | H [a] | N [a] |
|---|---|---|---|---|---|
| $(Me_3Sn)_2$pdtc | 30 [b] | 182–184 | 25.50 (25.56) | 4.46 (4.65) | 4.67 (4.97) |
| $(Bu_3Sn)_2$pdtc | 25 | oil | 44.80 (44.46) | 7.74 (6.72) | 3.08 (3.46) |
| $(Cy_3Sn)$pdtc | 50 [c] | 233–234 | 52.16 (51.86) | 7.79 (7.67) | 2.84 (2.88) |
| $(Ph_3Sn)_2$pdtc | 50 [c] | 244–246 [d] | 54.33 (53.87) | 4.09 (4.09) | 2.89 (2.99) |
| $(ClBu_2Sn)_2$pdtc [e] | 78 [f] | 133–134 | 34.49 (34.20) | 5.96 (5.73) | 3.65 (3.62) |
| $Me_2$Snpdtc | 76 | > 270 (dec.) | 22.61 (24.94) | 3.44 (3.60) | 5.95 (7.27) |
| $Bu_2$Snpdtc | 87 | > 220 (dec.) | 35.38 (35.83) | 5.63 (5.58) | 5.04 (5.97) |
| $Oct_2$Snpdtc | 72 | > 225 (dec.) | 45.54 (45.60) | 7.38 (7.30) | 4.51 (4.83) |
| $Ph_2$Snpdtc | 76 | > 200 (dec.) | 41.70 (42.45) | 3.41 (3.56) | 4.24 (5.50) |

[a] Calculated values in parentheses. [b] Recrystallised from $CHCl_3$. [c] Recrystallised from toluene. [d] Lit. m.p. > 300 (dec.) [5]. [e] Cl, Found: 9.02; calcd.: 9.15%. [f] Recrystallised from EtOH.

concentrated to yield $(Bu_3Sn)_2$pdtc as an oil. This was purified by repeatedly dissolving it in hot ethanol, allowing the solution to cool, reform the oil and decanting off the supernatant liquid. Prolonged drying of the oil in vacuo removed final traces of solvent, to leave an analytically pure sample (Yield 25%).

## Results and discussion

Bis(triorganotin)piperazine bis(dithiocarbamates) have been synthesised by metathesis reactions between triorganotin halides and disodium piperazine bis(dithiocarbamate):

$$2R_3SnCl + Na_2\text{pdtc} \rightarrow (R_3Sn)_2\text{pdtc} + 2NaCl \qquad (1)$$

$(R = Me, Bu, Ph, \text{cyclo-}C_6H_{11})$

In no instance were compounds of type $(R_3Sn)$Napdtc obtained from reactions involving the stoichiometric ratio of eq. 1, as had previously been reported to be the case [5], and there can be no doubt as to the presence of two triorganotin moieties in the products, from both microanalytical data and the presence of ditin fragments in the mass spectra (Table 2).

Diorganotin piperazine bis(dithiocarbamates) were prepared analogously:

$$R_2SnCl_2 + Na_2\text{pdtc} \rightarrow R_2\text{Snpdtc} + 2NaCl \qquad (2)$$

$(R = Me, Bu, Oct, Ph)$

In one instance (R = Bu) a second product, $(ClBu_2Sn)_2$pdtc, was also isolated in small amounts, probably due to the slight excess of dibutyltin dichloride used in the synthesis. Separation of this compound from the main product, $Bu_2$Snpdtc, is facilitated by the solubility of the chlorinated derivative in organic solvents, in contrast to the total insolubility of all $R_2$Snpdtc species in such media. Support for the formulation of this secondary product comes from the presence of chlorine-containing fragments in the mass spectrum (Table 2).

Structural possibilities for the two series of compounds are shown in II–V. For the $(R_3Sn)_2$pdtc series, the choice is largely between a four-coordinate, tetrahedral geometry at tin, with a unidentate $CS_2$ moiety (II), or if the latter is bidentate a

TABLE 2

CHEMICAL IONISATION (*CI*) AND 70 eV ELECTRON IONISATION (*EI*) MASS SPECTRA OF $(R_2XSn)_2$pdtc (X = R, Cl) [a]

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*$(Me_3Sn)_2$pdtc(EI)* 551 (60%, $Me_3SnS_2C\overline{\underline{NN}}CS_2SnMe_3^+$), 475 (17, $Me_3SnS_2C\overline{\underline{NN}}SnMe_2^+$) 355 (23, $HMeS\overline{\underline{NN}}SnMe^+$), 347 (30, $Me_3SnSSnMe_2^+$), 311 (28, $Me_2SnS_2C\overline{\underline{NN}}H^+$), 185 (7, $HSnS_2^+$), 183 (16, $Me_2SnSH^+$), 165 (100, $Me_3Sn^+$), 135 (24, $MeSn^+$), 120 (7, $Sn^+$).

*$(Ph_3Sn)_2$pdtc (EI)* 657 (1%, $Ph_3SnSSnPh_2^+$), 435 (1, $Ph_2SnS_2C\overline{\underline{NN}}H^+$), 351 (4, $Ph_3Sn^+$), 309 (4, ?), 197 (3, $PhSn^+$), 120 (2, $Sn^+$).

*$(CySn)_2$pdtc (EI)* 401 (6.5%, $Cy_3SnS^+$), 369 (1, $Cy_3Sn^+$), 331 (3, $Cy_2SnSCH^+$), 321 (9, $Sn\overline{\underline{NN}}SnH^+$), 287 (3, $Cy_2SnH^+$), 235 (2, $CySnS^+$), 203 (18, $CySn^+$), 120 (2, $Sn^+$); (*CI*) 796 (2.5, ? ditin), 769 (2, $[Cy_3SnSSnCy_3\text{-}H]^+$), 514 (2, ? ditin), 401 (8, $Cy_3SnS^+$), 369 (15, $Cy_3Sn^+$), 203 (1, $CySn^+$).

*$(Bu_3Sn)_2$pdtc (EI)* 347 (3%, ?), 291 (25, $Bu_3Sn^+$), 269 (100, $H_2BuSnS_2CN^+$), 235 (24, $BuSnSCN^+$), 213 (28, $H_3SnSCN^+$), 177 (50, $BuSn^+$), 155 (20, $H_3SnS^+$ or $SnCl^+$ [b]), 120 (10, $Sn^+$); (*CI*) 743 (2, ? ditin), 615 (7, $Bu_3SnSCNSSnBu_2^+$), 599 (4, $[Bu_3SnSCSSnBu_2\text{-}2H]^+$), 557 (2, $Bu_3SnSSnBu_2^+$), 541 (2, ? ditin), 395 (8, $Bu_2SnS_2C\overline{\underline{NN}}H^+$), 347 (6, ?), 291 (100, $Bu_3Sn^+$), 177 (3, $BuSn^+$), 155 (1, $H_3SnS^+$ or $SnCl^+$ [b]), 121 (1, $SnH^+$).

*$(ClBu_2Sn)_2$pdtc (EI)* 269 (2%, $Bu_2SnCl^+$), 247 (7, $H_2ClSnS_2CN^+$), 177 (15, $BuSn^+$), 155 (6, $SnCl^+$), 120 (2, $Sn^+$); (*CI*) 573 (1, ? ditin), 325 (1.5, $Bu_2SnS_2CNH^+$), 269 (100, $Bu_2SnCl^+$), 185 (3, $H_2SnS_2^+$), 177 (2, $BuSn^+$), 120 (1, $Sn^+$).

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[a] Based upon $^{120}Sn$, $^{35}Cl$, $^{32}S$, $^{14}N$, $^{12}C$, $^{1}H$. [b] From traces of unreacted $Bu_3SnCl$?

*cis*-$S_2SnR_3$ trigonal-bipyramidal arrangement about the metal (III). Polymeric systems in which each dithiocarbamate acts in a bridging bidentate mode cannot be excluded, but such bonding is unusual for tin-sulphur systems in contrast to its common appearance when bidentate oxygenated ligands are bonded to tin [7]. For the diorganotin series polymeric systems are demanded by the geometry of the ligand, although the coordination number at tin may be four or six depending upon the bonding capacity of each $CS_2$ group. Among the polymeric structures, both

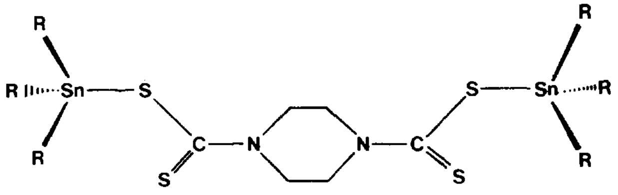
TABLE 3

SELECTED INFRARED ($cm^{-1}$) [a] AND $^1H$ NMR (ppm) [b] SPECTROSCOPIC DATA FOR ORGANOTIN PIPERAZINE BIS(DITHIOCARBAMATES)

| Compound | $\nu$(C–N) | $\nu(CS_2)$ | $\nu_{asym,sym}$(Sn–C) | $\nu$(Sn–S) | $\delta(NCH_2)$ | $\delta(SnCH_3)$ |
|---|---|---|---|---|---|---|
| $Na_2$pdtc | 1461m | 1002vs, 900s | | | 4.52 | |
| $(Me_3Sn)_2$pdtc | 1470m | 1032m, 998s, 910s | 548s, 514m [c] | 382m | 4.29 | 0.64 [d] |
| $(Bu_3Sn)_2$pdtc | 1465m | 1020m, 990s, 910s | | 380w | 4.25 | |
| $(Cy_3Sn)$pdtc | 1460m | 1000m, 990s, 980s, 915s | | 377w | 4.39 | |
| $(Ph_3Sn)_2$pdtc | 1460m | 1020m, 998s, 985m, 912s | | 380w | | |
| $(ClBu_2Sn)_2$pdtc | 1470m | 1025m, 1000s, 912s | | 390m | 4.08 | |
| $(Me_2Snpdtc)$ | 1480 | 1020m, 995s, 912s | 550s, 515m [e] | 360m | | |
| $Bu_2$Snpdtc | 1465m | 1025m, 999s, 912s | | 368m | | |
| $Oct_2$Snpdtc | 1465m | 1025m, 995s, 912s | | 360m | | |
| $Ph_2$Snpdtc | 1475m | 1035m, 1008m, 995m, 912s | | 385w | | |

[a] KBr discs. [b] $CDCl_3$ solution, except $Na_2$pdtc ($D_2O$). [c] Raman: 540m, 516vs. [d] $^2J(^{119}Sn\text{–}C\text{–}^1H)$ 58 Hz. [e] Raman: 556m, 519s.

chain (IV) or sheet (V) formulations are plausible, and in all possibilities mentioned distortions from regular geometries are possible. Infrared data (Table 3) are of only limited use in structure evaluation in these types of system due to the complexity of the spectra. The so-called "thioureide" band, $\nu(C\simeq N)$, arising from contributions from canonical form (VIII) to the electron distribution within the ligand, generally appears above 1500 $cm^{-1}$ for bidentate $CS_2$ units [8], and the



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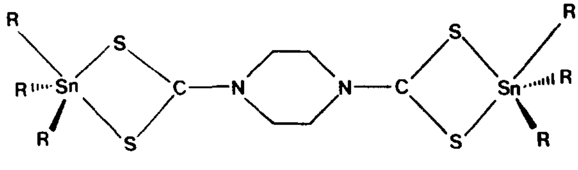
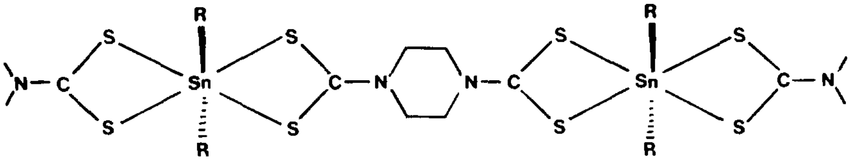


(III)



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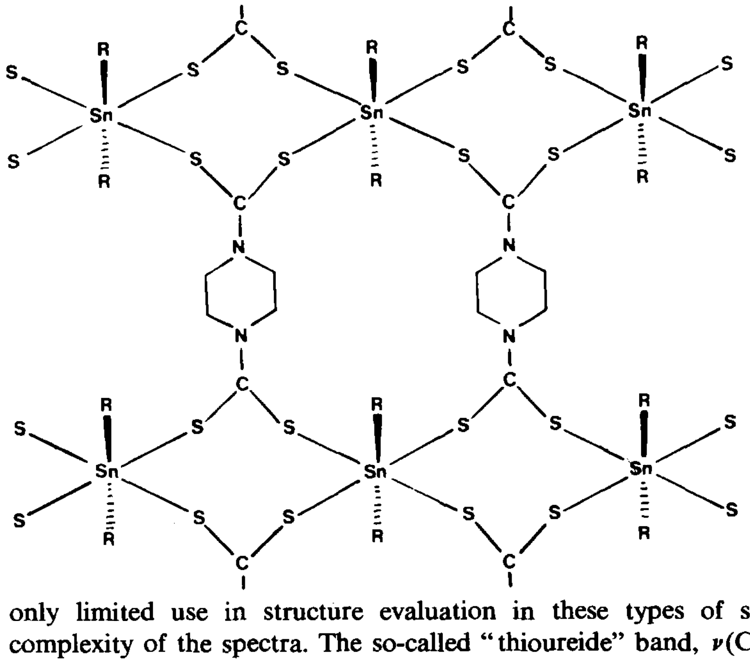
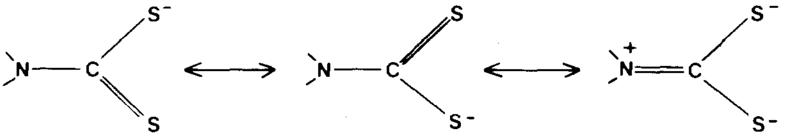


(V)

position of this band for all the organotin derivatives studied (1460–1480 $cm^{-1}$) argues in favour of a unidentate $CS_2$ group, although strongly anisobidentate behaviour cannot be excluded. Our assignments of the vibrations which involve the $CS_2$ group are tentative. The C=S stretch appears over a wide range centred ca. 1000 $cm^{-1}$ [9], with claims for a pure $\nu$(C=S) at 1299 $cm^{-1}$ in $RhCl(CS)(PPh_3)_2$ [10], although in dithiocarbamates the vibration is most likely in the 1030–960 $cm^{-1}$ region [11]. For the four coordinate zinc complex $Zn(S_2CNEt_2)_2$ only one band appears in this region (995 $cm^{-1}$), while for $Et_2NCS_2Et$ a doublet at 1005 and 983 $cm^{-1}$ is observed [12]. Our spectra are complicated by the presence of in-plane C–H deformations of phenyltins [13] and $CH_2$ twisting modes of some alkyltins [13,14] in this region. However, the general complexity of our spectra in the range 1040–900 $cm^{-1}$ would argue against purely bidentate chelation, and more in favour of a unidentate or weakly bidentate system.



(VI) (VII) (VIII)

Both $\nu_{asym}$(Sn–C) and $\nu_{sym}$(Sn–C) are observed in the infrared and Raman spectra of the two methyltin compounds, with the former the stronger in the IR and the pattern reversed in the Raman. For the triorganotin derivative this rules out a structure containing a planar $[C_3Sn]$ moiety, which would only arise in the case of a symmetrically bridging $CS_2$ group, but cannot be used to distinguish between structures II and III. However $^2J(^{119}Sn–C–H)$ coupling for $(Me_3Sn)_2$pdtc of 58 Hz is in good agreement with the value for $Me_3SnS_2CNMe_2$ of 57 Hz [16] where a tetrahedral geometry distorted towards *cis*-$S_2SnMe_3$ (Sn–S: 2.47, 3.16 Å) is found in the solid [17] and is presumably maintained in solution. In the case of $Me_2$Snpdtc, the data rule out a linear $[C_2Sn]$ fragment, again arising in the presence of a symmetrically bidentate $CS_2$ group, but are consistent with both tetrahedral and distorted octahedral (C–Sn–C $< 180°$) geometries at tin. Sn–S vibrations were found in the range 390–360 $cm^{-1}$, which is consistent with values obtained for other organotin dithiocarbamates such as $R_2Sn(S_2CNEt_2)_2$ and $R_2XSn(S_2CNEt_2)$ (R = Me, i-Pr, n-Bu, Ph; X = halogen) which exhibit $\nu$(Sn–S) in the 392–364 $cm^{-1}$ range [15].

Mössbauer spectroscopic data (Table 4) provide the clearest insight into the solid state structures of the novel organotin compounds. Quadrupole splitting (*QS*) values for the triorganotin derivatives (1.81–2.32 mm $s^{-1}$) are consistent with either tetrahedral or *cis*-$S_2SnR_3$ geometries about tin [18]. $(Me_3Sn)_2$pdtc and $(Ph_3Sn)_2$pdtc both show *QS* values (2.07, 1.81 mm $s^{-1}$, respectively) close to those for the dithiocarbamates $Me_3SnS_2CNMe_2$ (2.33 mm $s^{-1}$; [16]) and $Ph_3SnS_2CNEt_2$ (1.77 mm $s^{-1}$; [15]), and both mono- and bis-dithiocarbamate series can be assumed isostructural, involving a tetrahedral geometry distorted towards the five-coordinate *cis*-structure by a long, secondary Sn ← :S interaction, which is observed for $Me_3SnS_2CNMe_2$ (3.16, 3.33 Å; [17]) and $Ph_3SnS_2CNEt_2$ (3.11 Å; [19]).

TABLE 4

MÖSSBAUER SPECTROSCOPIC DATA (78 K) [a] FOR ORGANOTIN PIPERAZINE BIS(DITHIOCARBAMATES)

| Compound | *IS* [b] | *QS* [c] | $\Gamma_1$ [d] | $\Gamma_2$ [d] | C–Sn–C (deg) [c] |
|---|---|---|---|---|---|
| $(Me_3Sn)_2$pdtc | 1.31 | 2.07 | 0.96 | 0.94 | |
| $(Bu_3Sn)_2$pdtc | 1.46 | 2.28 | 1.03 | 0.98 | |
| $(Cy_3Sn)_2$pdtc | 1.54 | 2.32 | 1.07 | 1.05 | |
| $(Ph_3Sn)_2$pdtc | 1.29 | 1.81 | 0.92 | 0.91 | |
| $(ClBu_2Sn)_2$pdtc | 1.57 | 3.13 | 1.00 | 1.03 | |
| $Me_2$Snpdtc | 1.45 | 2.94 | 0.96 | 0.94 | 126 |
| $Bu_2$Snpdtc | 1.57 | 3.05 | 1.27 | 1.23 | 129 |
| $Oct_2$Snpdtc | 1.61 | 2.99 | 0.89 | 0.84 | 127 |
| $Ph_2$Snpdtc | 1.29 | 2.34 | 1.04 | 1.05 | 114 |

[a] All values in mm $s^{-1}$. [b] ±0.02 mm $s^{-1}$. [c] ±0.04 mm $s^{-1}$. [d] Full width at half height. [e] Calculated using eq. 3 and {Alk} −1.03 mm $s^{-1}$, {Ph} −0.95 mm $s^{-1}$.

The *QS* value for $(Bu_2ClSn)_2$pdtc is somewhat larger (3.13 mm $s^{-1}$), and is indicative of a clear coordination number expansion at tin to five in a *cis*-$S_2SnR_3$ arrangement, as expected from the increased Lewis acidity at tin concomitant with the substitution of Cl for Bu on the metal. This value agrees well with data for compounds of type $R_2ClSnS_2CNR^1_2$ (R = Me, Bu; $R^1$ = Me, Et), where the *QS* values fall in the range 2.71–3.14 mm $s^{-1}$ [20]. The crystal structure of $ClMe_2SnS_2CNMe_2$ confirms the more symmetrical chelation of the $CS_2$ group, with Sn–S distances of 2.48 and 2.79 Å [21]. *QS* values for the diorganotin series are generally ca. 3.00 mm $s^{-1}$, with a somewhat lower value (2.34 mm $s^{-1}$) for $Ph_2$Snpdtc. These data are consistent with a tetrahedral geometry at tin distorted towards *trans*-$R_2SnS_4$, but with anisobidentate $CS_2$ moieties and $C\text{–}Sn\text{–}C \ll 180°$, as indicated by the IR data for $Me_2$Snpdtc (vide supra). An approximate measure of these distortions can be gained by application of the Bancroft and Sham model [22], which has:

$$QS = 4\{R\}[1 - 3\cos^2\theta \sin^2\theta]^{1/2} \tag{3}$$

where $\{R\}$ is the partial quadrupole splitting of the hydrocarbon groups and C–Sn–C = $(180 - 2\theta)°$. The C–Sn–C angles calculated for $R_2$Snpdtc (R = Me, Bu, Oct) are 126, 129 and 127°, respectively, with estimated potential errors of ±13° based upon our analysis of this model [23]. The predicted C–Sn–C for $Ph_2$Snpdtc is close to tetrahedral (114 ± 13°), and in all cases the structures are close to those found in analogous mono(dithiocarbamates) e.g. $Me_2Sn(S_2CNMe_2)_2$ C–Sn–C 136° [24]; $Me_2Sn[S_2CN(CH_2)_3CH_2]$, 129.7° [19]; $Ph_2Sn(S_2CNEt_2)_2$, 101.4 [19].

The two alternative polymeric arrangements for the $R_2$Snpdtc series, IV and V, can potentially be distinguished by variable temperature Mössbauer spectroscopy. The temperature coefficient of the natural logarithm of the recoil-free fraction, *f*, (or resonance area *A*):

$$a = \frac{-\mathrm{d}\ln f}{\mathrm{d}T} = \frac{-\mathrm{d}\ln A}{\mathrm{d}T} \tag{4}$$

is an indicator of the rigidity with which the Mössbauer atom is held within the lattice [25 and references therein], and *a* diminishes as the lattice stiffens. Thus,

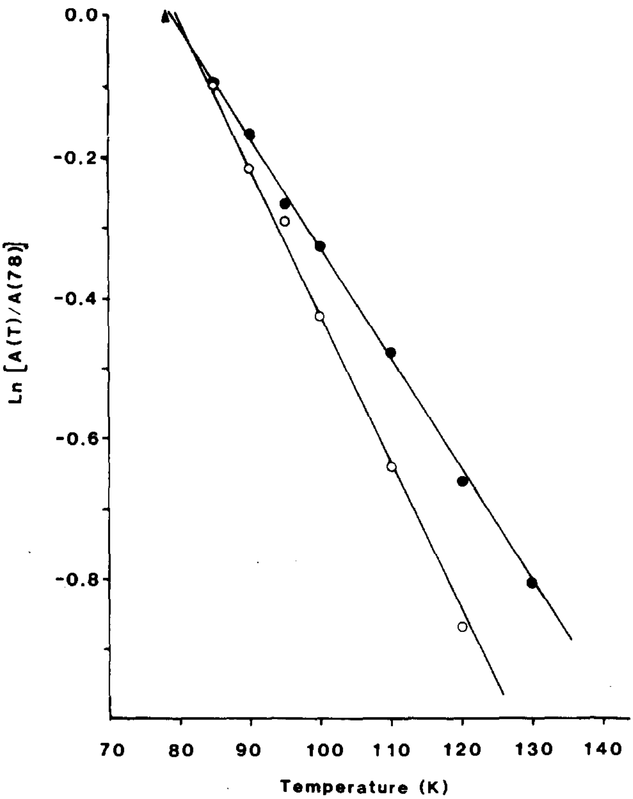


Fig. 1. Variable temperature Mössbauer spectroscopic data for $(Me_3Sn)_2$pdtc (○) and $Me_2$Snpdtc (●). Data for the former are $a$ $2.12\times10^{-2}$ $K^{-1}$, $(78 \leqslant T \leqslant 120)$, correlation coefficient $r$ $-0.997$ (7 pts) and the later $a$ $1.58\times10^{-2}$ $K^{-1}$ $(78 \leqslant T \leqslant 130)$, $r$ $-0.999$ (8 pts). The point ▲ (78, 0.0) is common to both plots.

monomeric lattices (consisting of isolated monomers, dimers etc.) and highly coiled polymers allow the tin a greater vibrational freedom than more linear chains or sheet arrangements. Variable temperature Mössbauer spectroscopic data for $(Me_3Sn)_2$pdtc and $Me_2$Snpdtc are depicted in Fig. 1 as $\log_e$ $A(T)/A(78)$ vs. $T$ plots, with normalisation of the resonance area $A(T)$ to the 78K datum point to facilitate intersample comparison. For $(Me_3Sn)_2$pdtc, $a$ $2.12 \times 10^{-2}$ $K^{-1}$ and reflects the lack of association between individual ditin molecules. Comparisons can be made with $[Me_2SnS]_3$ ($10^2a$ 2.46 $K^{-1}$; [26]) or $Ph_3SnSnPh_3$ (2.09; [25]). The data, taken in isolation, are also consistent with a severely coiled (Class 3 or 4 [25]) polymer, such as was proposed [27] for $Me_3SnOH$ ($10^2a$ 1.99 $K^{-1}$; [28]), but such a situation is unlikely on the basis of other spectroscopic evidence, particular the small $QS$ value.

For $Me_2$Snpdtc ($10^2a$ 1.58 $K^{-1}$) there is a more rigid lattice, but this is relatively flexible compared to those of other known (or inferred) methyltin polymers e.g. $Me_2SnO$ ($10^2a$ 0.87 $K^{-1}$; [29]). If a distorted $R_2SnS_4$ local geometry at tin occurs, as suggested by ancillary spectroscopic data, this must arise by polymer formation, but the flexibility of this polymer from the variable temperature Mössbauer experiment would be more in keeping with the 1-D chain arrangement (IV) than the 2-D sheet

(V). Furthermore, the relatively high *a* value for a chain polymer can be correlated with three features of the polymer construction. Firstly, flexibility is enhanced by the weakness of the secondary Sn ← :S bonds, as deduced from Mössbauer *QS* data. Secondly, the ligand possesses a "concertina-like" contraction/expansion afforded by the chair conformation of the piperazine heterocycle, and finally the length of the bridging ligand is likely to import some non-linearity (Class 2 or 3) to the spacial disposition of tin atoms and ligands. We have observed an analogous situation and made similar inferences regarding polymer Class for $[Ph_2Sn(OC_6H_4O)]_n$ ($10^2a$ 1.73 $K^{-1}$; [25]).

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