Journal of Organometallic Chemistry, 409 (1991) 143–156
Elsevier Sequoia S.A., Lausanne
JOM 21541

Organotin esters of dithiocarbamylacetic acids

Seik Weng Ng [a] and V.G. Kumar Das [b]

[a] *Institute of Advanced Studies and* [b] *Department of Chemistry, University of Malaya, 59100 Kuala Lumpur (Malaysia)*

(Received November 12th, 1990)

Abstract

Twelve di- and tri-organotin derivatives of dithiocarbamylacetic acids of the formula $R_nSn(O_2CCH_2S_2CNR'_2)_{4-n}$ ($R = Me$, ^nBu, ^cHex, Ph; $NR'_2 = NMe_2$, NEt_2, $N(CH_2)_4$, $N(CH_2CH_2)_2O$; $n = 3$, 2) have been prepared. On the basis of IR and Mössbauer spectroscopic data, the trimethyl-, tri-n-butyl- and triphenyltin derivatives are assigned a carboxylate-bridged structure with *trans*-C_3SnO_2 trigonal bipyramidal geometry at tin. The diorganotin dithiocarbamylacetates also adopt a bridged structure with a *trans*-C_2SnO_4 octahedral geometry at tin. The triorganotin esters dissociate into four-coordinate species in solution, as revealed by NMR (^1H and ^{13}C) spectral data. The tri-cyclohexyltin esters, however, are four-coordinate monomers in the solid state and in solution. Three distannoxanes, $[(R''_2SnO_2CCH_2S_2CNMe_2)O_2]_2$ ($R''_2Sn = Bu_2Sn$, BuPhSn, Ph_2Sn), were obtained as adventitious products during attempts to make the diorganotin esters from the diorganotin dihalides; for these distannoxanes the spectral data are interpreted in terms of skew-trapezoidal bipyramidal coordination at the tin atoms.

Introduction

Dithiocarbamates find wide application in analytical chemistry because of their strong metal-binding properties [1], and this feature is central to their behaviour as agricultural biocides [2]. The simplest member of the series, sodium *N,N*-dimethyldithiocarbamate, is a well-established, general purpose fungicide. It is converted by plant tissues into two other fungitoxic products, the β-glucoside and β-alanine derivatives [3], and by microorganisms into its α-aminobutyric acid derivative [4]. Also used as efficient and safe biocidal materials for the control of a small number of important pest and plant diseases are triorganotin compounds such as triphenyl- and tri-cyclohexyltin hydroxides [5,6], and synergism has occasionally been observed when triphenyltin acetate is used in combination with alkali metal dithiocarbamates [6,7]. However, the chemical combination of triphenyltin (as the cation) and dimethyldithiocarbamate (as the anion) is less active [8] than either constituent. We reasoned that the fungicidal activity of the triphenylstannyl-dithiocarbamato system could perhaps be modified by the incorporation of an organic linkage in the dithiocarbamato unit, and for this purpose the methylenecarboxy $-CH_2CO_2-$ grouping was considered, since dimethyldithiocarbamylacetic acid, $Me_2NCS_2CH_2CO_2H$, has been reported to possess plant growth-regulating properties [9]. Results

0022-328X/91/$03.50

[10,11] on the triorganotin ester derivatives of this acid confirmed the improved biological properties. The synthesis and spectroscopic properties of several organotin derivatives of this and other dithiocarbamylacetic acids are described in this report.

Experimental

The dithiocarbamylacetic acids, $R_2NCS_2CH_2CO_2H$ ($R_2N = Me_2N$, Et_2N, $(CH_2)_4N$, $O(CH_2CH_2)_2N$), were prepared by published methods [12] involving displacement of chloride in chloroacetic acid by the dithiocarbamato anion in aqueous alkaline media. The acids were precipitated by adding concentrated hydrochloric acid, and were recrystallized from an ethanol/toluene mixture. Dimethyldithiocarbamylacetic acid was converted into the *S*-benzyl-isothiouronium derivative, $[PhCH_2SC(NH_2)_2][Me_2NCS_2CH_2CO_2]$, m.p. 167–168 °C, upon treatment with *S*-benzyl-isothiouronium chloride. Anal. Found: C, 45.61; H, 5.61, N, 12.10%. $C_{13}H_{19}N_3O_2S_3$ calc.: C, 45.29; H, 5.54; N, 12.16%.

The IR spectra were recorded as Nujol mulls on a Nicolet 5-MX spectrometer. The Mössbauer spectra were recorded at 80 K on a Cryophysics instrument equipped with a 15 mCi $Ca^{119m}SnO_3$ source; for the variable-temperature runs, temperature control (± 0.1 K) was maintained by use of a heating unit manufactured by Lake Shore Cryotronics. The NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer operating at 99.55 MHz for the proton and 25.00 MHz for the carbon spectra. The compounds were dissolved in deuterated chloroform, which also served as internal lock and reference for the ^{13}C spectra. The organotin dithiocarbamylacetates were prepared as described below.

Dimethyltin bis(dimethyldithiocarbamylacetate), $Me_2Sn(O_2CCH_2S_2CNMe_2)_2$

An aqueous solution of dimethyltin dichloride (2.20 g, 10 mmol) was mixed with one containing sodium hydroxide (0.80 g, 20 mmol) and dimethyldithiocarbamylacetic acid (3.58 g, 20 mmol). A white solid was formed immediately, and it was collected, washed several times with water and dried in air. Recrystallization from chloroform gave the pure compound, m.p. 181–182 °C, in 20% yield.

Di-n-butyltin bis(dimethyldithiocarbamylacetate), $^nBu_2Sn(O_2CCH_2S_2CNMe_2)_2$

Di-n-butyltin oxide (2.75 g, 11 mmol) was heated with dimethyldithiocarbamylacetic acid (3.58 g, 20 mmol) in toluene in a Dean–Stark apparatus for 1 h. The mixture was filtered and solvent removed to give a white solid, which was collected and washed with petroleum ether; yield 80%; m.p. 139–142 °C.

Tetra-n-butylbis(dimethyldithiocarbamylacetato)distannoxane, $[(^nBu_2SnO_2CCH_2S_2CNMe_2)_2O]_2$

Sodium dimethyldithiocarbamate was prepared in aqueous ethanol from sodium hydroxide (0.80 g, 20 mol) and dimethyldithiocarbamylacetic acid (3.58 g, 20 mmol), and this solution was added to one of di-n-butyltin dichloride (3.00 g, 10 mmol) in a little ethanol. The solid that separated was collected and washed with water. The pure distannoxane, m.p. 181–182 °C, was obtained in 40% yield by recrystallization from a 1/1 chloroform/ethanol mixture.

Di-n-butyldiphenylbis(dimethyldithiocarbamylacetato)distannoxane, $[(^{n}BuPhSnO_2CCH_2S_2CNMe_2)_2O]_2$

A solution of n-butylphenyltin dichloride (3.58 g, 10 mmol) in ethanol was added to an ethanolic solution of diethylaminoethanol (2.34 g, 20 mmol) and dimethyldithiocarbamylacetic acid (3.58 g, 20 mmol). The resulting precipitate was collected and washed with ethanol; yield 30%; m.p. 155–157 ° C.

Tetraphenylbis(dimethyldithiocarbamylacetato)distannoxane, $[(Ph_2SnO_2CCH_2S_2CNMe_2)_2O]_2$

This distannoxane was prepared as described above but from diphenyltin dibromide (4.34 g, 10 mmol), diethylethanolamine (2.34 g, 20 mmol), and dimethyldithiocarbamylacetic acid (3.58 g, 20 mmol). The yield of the product, m.p. 168–170 ° C, was 90%.

Trimethyltin dimethyldithiocarbamylacetate, $Me_3SnO_2CCH_2S_2CNMe_2$

Dimethyldithiocarbamylacetic acid (1.79 g, 10 mmol) was treated with sodium hydroxide (0.40 g, 10 mmol) in 95% ethanol. The sodium salt dissolved on heating. Trimethyltin chloride (1.81 g, 10 mmol) was then added, and the mixture refluxed for 1 h. The sodium chloride formed was filtered off and the solution concentrated to give the product. Recrystallization from chloroform gave the compound in 50% yield; m.p. 144–146 ° C. Variable-temperature Mössbauer plot: a for $80 \leqslant T \leqslant 139$ K (7 points, corr. coeff. -0.998) $= -0.0134$ K^{-1}.

Tri-n-butyltin dimethyldithiocarbamylacetate, $^{n}Bu_3SnO_2CCH_2S_2CNMe_2$

A toluene solution of bis(tri-n-butyltin) oxide (6.00 g, 10 mmol) and dimethyldithiocarbamylacetic acid (3.58 g, 20 mmol) was refluxed for 1 h in a Dean–Stark apparatus. The solvent was removed to have a yellow oil, which solidified when kept under vacuum; yield 50%; m.p. 59–60 ° C.

A similar procedure was used for tri-cyclohexyltin dimethyldithiocarbamate and for the diethylamino-, pyrrolinyl- and morpholinyldithiocarbamylacetato analogues; these were initially isolated as semi-solids. For the preparations, 10 mmol quantities of tri-cyclohexyltin hydroxide and the corresponding acid were used. The dimethyldithiocarbamylacetate was obtained as a solid (yield 40%; m.p. 68–69 ° C) by recrystallization from a 1/1 ether/n-hexane mixture. A 90% yield was obtained, however, from the reaction of tri-cyclohexyltin hydroxide and dimethyldithiocarbamylacetic acid in methanol. The diethyl analogue solidified on exposure to air (yield 90%; m.p. 73–75 ° C); the pyrrolinyldithiocarbamylacetate was obtained as a solid when the initial semi-solid product was treated with n-hexane (yield 60%; m.p. 72–74 ° C); the morpholinyldithiocarbamylacetate was obtained by recrystallization of the crude product from methanol (yield 50%; m.p. 106–108 ° C).

Triphenyltin dimethyldithiocarbamylacetate, $Ph_3SnO_2CH_2S_2CNMe_2$

A solution of triphenyltin hydroxide (3.68 g, 10 mmol) and dimethyldithiocarbamylacetic acid (1.79 g, 10 mmol) in toluene was heated for 1 h. The solution was filtered hot, and the solvent removed on a rotary evaporator to give the product in 60% yield; m.p. 160–161 ° C. Variable-temperature Mössbauer plot: a for $80 \leqslant T \leqslant$ 139 K (7 points, corr. coeff. -0.999) $= -0.0152$ K^{-1}.

Triphenyltin diethyldithiocarbamylacetate, m.p. 129–130 °C, triphenyltin pyrrolinyldithiocarbamylacetate, m.p. 72–74 °C, and triphenyltin morpholinyldithiocarbamylacetate, m.p. 106–108 °C, were prepared similarly in comparable yields from triphenyltin hydroxide and the corresponding dithiocarbamylacetic acids.

Triphenyltin bis(dimethyldithiocarbamyl)acetate · ethanol, $Ph_3SnO_2CCH(S_2CNMe_2)_2 \cdot EtOH$

Ethanol solutions of triphenyltin hydroxide (3.68 g, 10 mmol) and bis(dimethyldithiocarbamyl)acetic acid (2.98 g, 10 mmol) were mixed and the mixture was briefly heated. Cooling of the filtered solution gave the analytically pure product in 60% yield; m.p. 142–143 °C.

The analytical data and melting points of the sixteen organotin dithiocarbamylacetates are shown in Table 1.

Dimethyltin dithiocarbaminoacetate, $Me_2SnS_2CNHCH_2CO_2$, was prepared to enable its infrared and variable-temperature Mössbauer spectra to be compared with those of the organotin dithiocarbamylacetates. This compound, m.p. > 200 °C, precipitated when aqueous solutions containing 2/1 molar amounts of ammonium dithiocarbaminoacetate [13] and dimethyltin dichloride were mixed. Anal. Found: C, 20.24; H, 3.07; N, 4.78; $C_5H_9NO_2S_2Sn$ calc: C, 20.15; H, 3.02; N, 4.70%. The ^{119m}Sn Mössbauer isomer shift (IS 1.31 mm s^{-1}), quadrupole splitting (QS 3.15 mm s^{-1}) and linewidth ($\Gamma_1 = \Gamma_2 = 1.27$ mm s^{-1}) parameters were determined at 80 K. Variable-temperature Mössbauer plot: a for $80 \leqslant T \leqslant 139$ K (7 points, corr. coeff. $-0.994) = -0.0077$ K^{-1}.

For the purpose of structure–activity correlations in the biological screening tests on the triorganotin dithiocarbamylacetates, two triphenyltin dithiocarbamylpropionates were also prepared: $Ph_3SnO_2C(CH_2)_2S_2CNMe_2$, m.p. 117–120 °C, Anal. Found: C, 52.96; H, 4.74; N, 2.49; $C_{24}H_{25}NO_2S_2Sn$ calc: C, 53.15; H, 4.64; N,

Table 1

Analytical data for organotin dithiocarbamylacetates

Compound	M.p. (°C)	Analysis (Found (calc.) (%))		
		C	H	N
$Me_2Sn(O_2CCH_2S_2CNMe_2)_2$	181–182	27.85 (28.52)	4.27 (4.38)	5.25 (5.54)
$^nBu_2Sn(O_2CCH_2S_2CNMe_2)_2$	139–142	36.60 (36.67)	5.92 (5.81)	4.43 (4.75)
$[(^nBu_2SnO_2CCH_2S_2CNMe_2)_2O]_2$	181–182	36.95 (37.25)	6.24 (6.25)	3.44 (3.34)
$[(^nBuPhSnO_2CCH_2S_2CNMe_2)_2O]_2$	155–157	40.62 (41.02)	5.11 (5.04)	3.13 (3.18)
$[(Ph_2SnO_2CCH_2S_2CNMe_2)_2O]_2$	168–170	43.83 (44.47)	4.18 (3.95)	3.12 (3.05)
$Me_3SnO_2CCH_2S_2CNMe_2$	144–146	27.56 (28.09)	4.99 (5.00)	3.92 (4.09)
$^nBu_3SnO_2CCH_2S_2CNMe_2$	59– 60	43.80 (43.60)	7.60 (7.53)	2.60 (2.99)
$^cHex_3SnO_2CCH_2S_2CNMe_2$	68– 69	51.14 (50.55)	7.72 (7.56)	2.49 (2.56)
$^cHex_3SnO_2CCH_2S_2CNEt_2$	73– 75	52.26 (52.27)	7.70 (7.89)	2.47 (2.43)
$^cHex_3SnO_2CCH_2S_2CN(CH_2)_4$	72– 74	52.71 (52.45)	7.58 (7.57)	2.31 (2.44)
$^cHex_3SnO_2CCH_2S_2CN(CH_2CH_2)_2O$	106–108	51.17 (51.02)	7.42 (7.36)	2.45 (2.38)
$Ph_3SnO_2CCH_2S_2CNMe_2$	160–161	52.56 (52.29)	4.34 (4.38)	2.26 (2.65)
$Ph_3SnO_2CCH_2S_2CNEt_2$	129–130	52.39 (53.97)	4.83 (4.89)	2.49 (2.51)
$Ph_3SnO_2CCH_2S_2CN(CH_2)_4$	162–163	54.17 (54.17)	4.53 (4.54)	2.38 (2.52)
$Ph_3SnO_2CCH_2S_2CN(CH_2CH_2)_2O$	136–137	52.18 (52.65)	4.51 (4.41)	2.43 (2.45)
$Ph_3SnO_2CCH(S_2CNMe_2)_2 \cdot EtOH$	142–143	48.10 (48.49)	4.86 (4.94)	4.09 (4.03)

2.58%; $Ph_3SnO_2CCHMeS_2CNMe_2$, m.p. 119–122°C, Anal. Found: C, 53.49; H, 4.43; N, 2.29; $C_{24}H_{25}NO_2S_2Sn$ calc: C, 53.15; H, 4.64; N, 2.58%.

Results and discussion

The triorganotin dithiocarbamylacetates were prepared by refluxing the organic acid and the triorganotin hydroxide (1/1 stoichiometry) (eq. 1) or bis(triorganotin) oxide (2/1 stoichiometry) (eq. 2) in toluene in a Dean–Stark apparatus, or by reaction of the organotin halide with the sodium salt of the acid (eq. 3). Dimethyltin bis(dimethyldithiocarbamylacetate) was prepared from the dimethyltin dichloride and the sodium salt of the acid (eq. 4), whereas the di-n-butyltin analogue was prepared from di-n-butyltin oxide (eq. 5) by the Dean–Stark method.

$$R_3SnOH + R'_2NCS_2CH_2CO_2H \rightarrow R_3SnO_2CH_2S_2CNR'_2 + H_2O \qquad (1)$$

$$(R = {}^cHex, Ph; NR'_2 = NMe_2, NEt_2, N(CH_2)_4, N(CH_2CH_2)_2O)$$

$$(R_3Sn)_2O + 2R'_2NCS_2CH_2CO_2H \rightarrow 2R_3SnO_2CH_2S_2CNR'_2 + H_2O \qquad (2)$$

$$(R = {}^nBu;\ R' = Me)$$

$$R_3SnCl + R'_2NCS_2CH_2CO_2Na \rightarrow R_3SnO_2CCH_2S_2CNR'_2 + NaCl \qquad (3)$$

$$(R = R' = Me)$$

$$R_2SnCl_2 + 2R'_2NCS_2CH_2CO_2Na \rightarrow R_2Sn(O_2CCH_2S_2CNMe_2)_2 + 2\ NaCl \qquad (4)$$

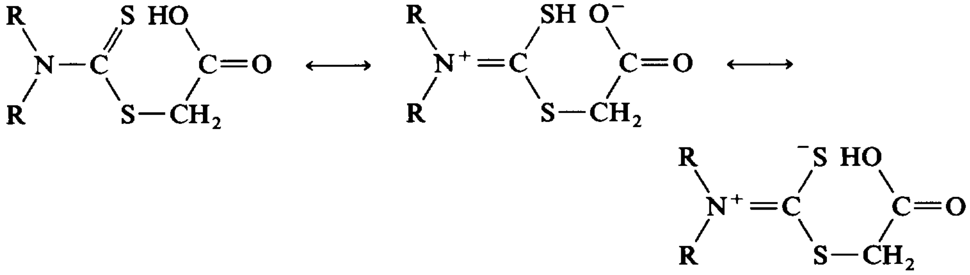
$$(R = R' = Me)$$

$$R_2SnO + 2R'_2NCS_2CH_2CO_2H \rightarrow R_2Sn(O_2CCH_2S_2CNR'_2)_2 + H_2O \qquad (5)$$

$$(R = {}^nBu;\ R' = Me)$$

The $[(R_2SnO_2CCH_2S_2CNMe_2)_2O]_2$ distannoxanes ($R_2Sn = {}^nBu_2Sn$, ${}^nBuPhSn$, Ph_2Sn) were obtained when diorganotin dihalides were treated with the sodium or diethylethanolammonium salt of dimethyldithiocarbamylacetic acid in ethanol.

The dithiocarbamylacetic acids, which are a class of *C*-substituted acetic acids, provide several sites for coordination to the metal atom in the di- and tri-organotin derivatives. Like the dipolar forms that can be written for the dithiocarbamate anion, three resonance structures can be considered for these carboxylic acids:



The evaluation of the preferred bonding mode(s) of the ligand and of the resulting coordination geometries at tin in the stannyl esters are considered in the following sections.

Table 2

Infrared data (2000–600 cm^{-1}) for organotin dithiocarbamylacetates, dimethyldithiocarbamylacetic acid and *S*-benzyl-isothiouronium dimethyldithiocarbamylacetate

Compound	Infrared stretching frequencies (cm^{-1})
$Me_2NCS_2CH_2CO_2H$	1703vs, 1697vs, 1693vs, 1505s, 1495s, 1355s, 1305s, 1255s, 1215s, 1187s, 1145m, 1002m, 948m, 910m, 871m, 675s
$[PhCH_2C(NH_2)_2][Me_2NCS_2CH_2CO_2]$	1693s, 1590vs, 1495s, 1433s, 1353s, 1266s, 1228m, 1207w, 1145m, 1135m, 1117m, 1092w, 991m, 923w, 915w, 890w, 781m, 730s, 718s
$Me_2Sn(O_2CCH_2S_2CNMe_2)_2$	1600vs, 1505s, 1340s, 1256s, 1274s, 1143m, 998m, 980m, 880m, 795m, 705m
$^nBu_2Sn(O_2CCH_2S_2CNMe_2)_2$	1640m, 1590vs, 1500vs, 1345s, 1255s, 1238m, 1226s, 1182w, 1136m, 1080w, 1048w, 977s, 890s, 796m, 710m, 688s
$[(^nBu_2SnO_2CCH_2S_2CNMe_2)_2O]_2$	1655s, 1647s, 1638s, 1508s, 1365vs, 1340s, 1320s, 1255s, 1215s, 1179m, 1154m, 1079w, 976m, 893s, 793w, 722w, 680m
$[(^nBuPhSnO_2CCH_2S_2CNMe_2)_2O]_2$	1665s, 1647s, 1640s, 1582w, 1563w, 1507s, 1427s, 1363s, 1307s, 1253s, 1218s, 1205s, 1178s, 1153s, 1077w, 1069w, 1020w, 997m, 975s, 795w, 733s, 695s, 681s
$[(Ph_2SnO_2CCH_2S_2CNMe_2)_2O]_2$	1680s, 1633s, 1505s, 1430s, 1336s, 1300s, 1254s, 1218s, 1202s, 1180s, 1154m, 1075w, 1065w, 1021w, 998m, 978s, 890s, 793w, 730vs, 724vs, 694vs
$Me_3SnO_2CCH_2S_2CNMe_2$	1585vs, 1565vs, 1502s, 1410s, 1395vs, 1252s, 1237s, 1148s, 997s, 984s, 890m, 783vs, 755s, 705vs
$^nBu_3SnO_2CCH_2S_2CNMe_2$	1604vs, 1580vs, 1575vs, 1570vs, 1505m, 1495m, 1448m, 1360vs, 1260s, 1281s, 1145m, 1075w, 1000m, 987m, 887w, 877w, 867w, 795w
$^cHex_3SnO_2CCH_2S_2CNMe_2$	1665vs, 1500s, 1455vs, 1360s, 1325vs, 1255s, 1209s, 1171m, 1145m, 990s, 979s, 888m, 841w, 722w, 692w
$^cHex_3SnO_2CCH_2S_2CNEt_2$	1665s, 1660vs, 1652s, 1495s, 1487s, 1445vs, 1420s, 1356s, 1326s, 1283m, 1270m, 1220s, 1201s, 1167m, 1133m, 1085m, 990s, 919m, 880s, 835m, 829m, 796m, 725m, 693m
$^cHex_3SnO_2CCH_2S_2CN(CH_2)_4$	1680vs, 1673vs, 1434vs, 1379s, 1329s, 1316vs, 1251m, 1208vs, 1151s, 1085w, 1040m, 1007s, 991s, 955s, 880s, 841w, 797w, 723w, 686w

Table 2 (continued)

Compound	Infrared stretching frequencies (cm^{-1})
$^{c}\mathrm{Hex_3SnO_2CCH_2S_2CN(CH_2CH_2)_2O}$	1667s, 1660s, 1445s, 1435s, 1425s, 1367s, 1328s, 1298m, 1265s, 1230s, 1214m, 1170s, 1115s, 1030s, 994s, 911w, 882m, 866m, 841w, 701w
$\mathrm{Ph_3SnO_2CCH_2S_2CNMe_2}$	1583s, 1575s, 1555vs, 1546vs, 1429s, 1414m, 1350m, 1263m, 1243w, 1151w, 1075w, 1025w, 998w, 982w, 888w, 735s, 725s, 695s
$\mathrm{Ph_3SnO_2CCH_2S_2CNEt_2}$	1588s, 1580s, 1576s, 1567s, 1564s, 1557vs, 1548s, 1538s, 1487s, 1435w, 1417w, 1355w, 1304w, 1271m, 1207m, 1144m, 1080m, 1035w, 1013w, 998m, 916m, 994m, 831m, 733s, 699s
$\mathrm{Ph_3SnO_2CCH_2S_2CN(CH_2)_4}$	1670s, 1590s, 1582s, 1577s, 1557vs, 1482s, 1440s, 1435s, 1380s, 1325s, 1254w, 1210s, 1184m, 1166m, 1080m, 1036w, 1012m, 996m, 965m, 884m, 801w, 736vs, 728vs, 699vs
$\mathrm{Ph_3SnO_2CCH_2S_2CN(CH_2CH_2)_2O}$	1589m, 1575s, 1553vs, 1430s, 1378vs, 1270m, 1230m, 1215w, 1115m, 1078w, 1030w, 998m, 734s, 697s
$\mathrm{Ph_3SnO_2CCH(S_2CNMe_2)_2\cdot EtOH}$	1630vs, 1505s, 1498s, 1488s, 1430s, 1330m, 1315m, 1250m, 1145w, 1076w, 1040w, 966m, 869w, 841m, 780w, 731s, 725s, 691s

Infrared spectra

The infrared data of the organotin esters in the 2000–600 cm^{-1} range are listed in Table 2, along with data for dimethyldithiocarbamylacetic acid and its *S*-benzylisothiouronium salt. For the parent acid, the carbonyl stretching band appears as a multiplet centered around 1700 cm^{-1}; for the ionic salt it is split into two strong bands at 1700 and 1590 cm^{-1}.

In the spectrum of trimethyltin dimethyldithiocarbamylacetate, the asymmetric carbonyl stretches appear at 1585 and 1565 cm^{-1} and the symmetric stretch at 1395 cm^{-1}. The difference of < 150 cm^{-1} between the asymmetric and symmetric stretching frequencies, which is also seen for the tri-n-butyl- and triphenyl-tin esters (the carbonyl bands appearing typically below 1600 cm^{-1}), suggests that the carboxylato group is engaged in strong bridging interactions. This difference is expected to exceed 200 cm^{-1} in non-bridged carboxylates [14]. For the tri-cyclohexyltin esters, the difference is large, and is indicative of negligible or weak bridging interactions. The asymmetric carbonyl bands appear at about 1670 cm^{-1}, and the positions are similar to those found for the structurally characterized tri-cyclohexyltin acetate and tri-cyclohexyltin trifluoroacetate [15] esters, whose structures were interpreted [16] in terms of very weak intermolecular bridges. A large difference was also taken as strong evidence against a carboxylate-bridged structure for a series of trialkyltin aminoacetates [17].

The carboxylato group in dimethyltin bis(dimethyldithiocarbamylacetate) absorbs strongly at 1600 cm^{-1}, as does that in the di-n-butyltin analogue, and so both compounds are also carboxylate-bridged. On the other hand, the tin–oxygen interactions in the distannoxanes are divided into two types as two strong asymmetric carbonyl bands are observed in the spectra. For example, in the case of the tetraphenyldistannoxane, the 1680 cm^{-1} band is probably associated with a weak interaction and the 1633 cm^{-1} band with a stronger interaction.

Two Sn–C stretching bands, at 555 and 544 cm^{-1} for trimethyltin dimethyldithiocarbamylacetate, and at 586 and 555 cm^{-1} for dimethyltin dimethyldithiocarbamylacetate, indicate [18] distortions from planar C_3Sn and linear C_2Sn skeletal geometry, respectively. The C=S stretching bands in the spectra of all the compounds prepared are weak, and are not readily assigned. The tin–sulfur band, which has been observed at around 385 cm^{-1} in organotin dithiocarbamates [19], could not be located in the spectra of the organotin dithiocarbamylacetates, and this may be taken as evidence against any tin–sulfur interaction.

Dimethyltin dithiocarbaminoacetate, $Me_2SnS_2CNHCH_2CO_2$, prepared for comparison purposes, displays bands at 3250 (N–H), 1630, 1330 (CO_2), 1510 (C–N), 978 (C–N coupled with C–S), 565, 543 (Sn–C) and 440 (Sn–S) cm^{-1}.

Mössbauer spectra

The Mössbauer quadrupole splitting (*QS*) and isomer shift (*IS*) values at 80 K for the organotin dithiocarbamylacetates are listed in Table 3. Except for $Ph_3SnO_2CCH_2S_2CNEt_2$, which displays a three-line spectrum that is discussed later, all the other compounds studied exhibit well-resolved doublet spectra.

A guide to the coordination status of tin in di- and tri-organotin compounds is provided by the *QS/IS* ratio, which has a value > 2.1 for higher-than-four

Table 3

Mössbauer data [a] for organotin dithiocarbamylacetates

Compound	*IS*	*QS*	Γ_1	Γ_2
$Me_2Sn(O_2CCH_2S_2CNMe_2)_2$	1.31	3.80	0.96	1.07
$^nBu_2Sn(O_2CCH_2S_2CNMe_2)_2$	1.47	3.92	1.16	1.26
$[(^nBu_2SnO_2CCH_2S_2CNMe_2)_2O]_2$	1.30	3.57	0.98	1.04
$[(^nBuPhSnO_2CCH_2S_2CNMe_2)_2O]_2$	1.23	3.32	1.08	1.01
$[(Ph_2SnO_2CCCH_2S_2CNMe_2)_2O]_2$	1.14	3.23	0.92	0.95
$Me_3SnO_2CCH_2S_2CNMe_2$	1.29	3.87	1.10	1.12
$^nBu_3SnO_2CCH_2S_2CNMe_2$	1.45	3.93	0.97	0.99
$^cHex_3SnO_2CCH_2S_2CNMe_2$	1.49	3.06	1.09	1.09
$^cHex_3SnO_2CCH_2S_2CNEt_2$	1.48	2.94	0.98	1.07
$^cHex_3SnO_2CCH_2S_2CN(CH_2)_4$	1.46	2.83	1.07	1.09
$^cHex_3SnO_2CCH_2S_2CN(CH_2CH_2)_2O$	1.25	3.61	0.96	1.06
$Ph_3SnO_2CCH_2S_2CNMe_2$	1.26	3.61	1.02	1.01
$Ph_3SnO_2CCH_2S_2CNEt_2$ [b]	0.58	2.31	1.01	1.05
	1.27	3.68	1.01	1.00
$Ph_3SnO_2CCH_2S_2CN(CH_2)_4$	1.23	3.11	1.36	1.43
$Ph_3SnO_2CCH_2S_2CN(CH_2CH_2)_2O$	1.47	2.92	1.01	0.97
$Ph_3SnO_2CCH(S_2CNMe_2)_2 \cdot EtOH$	1.25	3.61	0.91	0.91

[a] In mm s^{-1}. [b] Three-line spectrum fitted as two doublets sharing a common lower-velocity wing.

coordination at tin [20]. Such ratios are observed for all the triorganotin compounds except for the four tri-cyclohexyltin derivatives, $^{c}Hex_3SnO_2CCH_2S_2CNR_2$ ($NR_3 = NMe_2$, NEt_2, $N(CH_2)_4$), $N(CH_2CH_2)_2O$) for which the ratio lies in the 1.94 to 2.05 range. On the basis of this ratio, the trimethyl-, tri-n-butyl and triphenyltin dithiocarbamylacetates are assigned a five-coordinate, *trans*-C_3SnO_2 trigonal bipyramidal geometry [21].

The four tri-cyclohexyltin derivatives are probably four-coordinate tetrahedral species as their *QS* values fall in the 2.83–3.06 mm s^{-1} range. This structural feature is typical of tri-cyclohexyltin carboxylates [15,22,23] and can be attributed to the bulk of the cyclohexyl rings.

For the diorganotin bis(dimethyldithiocarbamylacetates), *trans*-[SnR_2] octahedral geometries are predicted on the basis of the magnitudes of their *QS* values. The dimethyldithiocarbamylacetato ligand in these structures is considered to bridging, as indicated by the infrared data. However, crystallographic evidence for a carboxylate-bridged, *trans*-octahedral diorganotin dicarboxylate is still awaited [24].

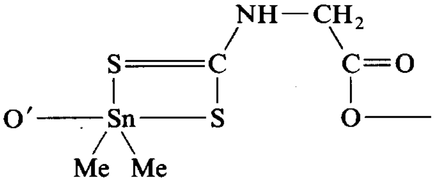
In the old literature, distannoxanes were formulated as either $(R_2SnX)_2O$ or $R_2SnX_2 \cdot R_2SnO$, but recent structural evidence has shown that they are tetranuclear species. The $X = R'CO_2$ derivatives are generally centrosymmetric dimers containing an $Sn^{I}_2O_2$ ring that has two $R_2Sn^{II}O_2CR'$ units attached to its oxygen atoms. One $R'CO_2$ ligand bridges the Sn^{I}–O–Sn^{II} fragment (to give rise to a six-membered $\underline{Sn^{I}\text{–O–}Sn^{II}\text{–O–C–O}}$ ring), whereas the other chelates the Sn^{II} atom in an anisobidentate manner (to give rise to a four-membered $\underline{Sn^{II}\text{–O–C–O}}$ ring). The two tin atoms adopt skew-trapezoidal bipyramidal geometries [25]. The Mössbauer spectra of the present three distannoxanes are doublets with rather narrow linewidths. On the basis of the proven correlations between *QS* values and crystallographically determined carbon–tin–carbon bond angles in diorganotin compounds [26], the skew-trapezoidal bipyramidal geometry (C_2Sn angles in the range of 135 to 155°C [27]) can be assigned to the three distannoxane compounds. The *IS* and *QS* values for the $R_2Sn = {}^{n}BuPhSn$ compound are intermediate between those of the $R_2Sn = {}^{n}Bu_2Sn$ and $R_2Sn = Ph_2Sn$ analogues. This observation is consistent with the greater donor strength of the alkyl than of the aryl group.

There is little difference between the Mössbauer parameters for triphenyltin dimethyldithiocarbamylacetate and those for the bis(dimethyldithiocarbamyl)acetate · ethanol adduct. The two compounds can be regarded as having the *trans*-trigonal bipyramidal geometry, but comparison of their infrared data reveals that the carbonyl bands in the ethanol adduct are not much shifted compared with those for the parent acid. Thus, although triphenyltin dimethyldithiocarbamylacetate is unequivocally carboxylate-bridged, the ethanol compound is probably a monomeric, ethanol-coordinated triphenyltin ester. Ethanol, though a weak Lewis base, is known to coordinate to the triphenyltin acceptor [28], and a methanol adduct of a triphenyltin ester [29] has also been structurally characterized.

An indication of how tightly bound a tin atom is in a lattice, and hence the degree of molecular association, is provided by the magnitude of the temperature coefficient of the Mössbauer recoil-free fraction, which can be determined from variable-temperature studies. A survey of several methyltin, c-hexyltin and phenyltin compounds has revealed that rigid polymeric structures yield $-a$ values of $< 1.1 \times 10^{-2}$ K^{-1}, whereas polymers possessing more flexible tertiary structures that permit greater vibrational freedom for the tin atom give $-a$ values approaching those of non-associated structures, i.e., in the range 1.3×10^{-2}–2.8×10^{-2} K^{-1} [30,31]. In the present study, trimethyl- and triphenyl-tin dimethyldithiocarbamylacetates yielded $-a$ values of 1.29×10^{-2} and 1.52×10^{-2} K^{-1}, respectively. As these values are similar to those for carboxylate-bridged triphenyltin acetate and triphenyltin chloroacetate [32], both of which adopt stretched helical conformations, the two dithiocarbamates are judged to have a similar lattice structure.

Triphenyltin diethyldithiocarbamylacetate displays a three-line Mössbauer spectrum that was fitted as two Lorentzian doublets sharing a common lower-velocity wing. The Mössbauer parameters for the doublets are *IS* 0.58, *QS* 2.31 and *IS* 1.72, *QS* 3.68 mm s^{-1}. The second pair of parameters can be confidently assigned to a *trans*-trigonal bipyramidal geometry, whereas the first could arise from a tetrahedral geometry. A three-line spectrum is also displayed by the triphenyltin derivative of the related ethylxanthylacetic acid, $Ph_3SnO_2CCH_2S_2COEt$, and an identical interpretation has been advanced [33].

The $-a$ value for dimethyltin dithiocarbaminoacetate is 0.77×10^{-2} K^{-1}, which is consistent with a strongly bound, rigid conformation. Its rather low *QS* value of 3.15 mm s^{-1} rules out a *cis*-SnC_2 octahedral geometry, but could arise from a five-coordinate *cis*-SnC_2 trigonal bipyramidal geometry [21]. The two sulfur atoms of the ligand are considered to engage the tin in chelation, so that the negatively charged oxygen end of the ligand is constrained to bond with another tin to give a strongly bound polymeric structure. The inability to attain six-fold coordination at tin may thus be seen as the consequence of decreased Lewis acidity associated with the presence of two tin–sulfur bonds in the molecule [34].



NMR spectra

Dimethyldithiocarbamylacetic acid displays two *N*-methyl resonances in both the ^1H and ^{13}C NMR spectra because the rotation about the C–N bond is restricted. This feature is also apparent in the triorganotin esters. In trimethyltin dimethyldithiocarbamylacetate, the *N*-methyl resonances are separated by 11.0 Hz. The magnitude of the the two-bond ^{119}Sn–Me coupling constant (57.6 Hz) for this compound is similar to that for tetrahedral trimethyltin chloride in non-polar solvents [35]. The ^1H NMR spectrum of the $[(Me_2SnO_2CCH_2S_2CNMe_2)_2O]_2$ appears to be anomalous; multiple Sn-Me signals are observed, along with broadenend *N*-Me and methylene resonances, indicative of complex equilibria in solution.

The ^{13}C NMR data (Table 4) are most informative for the tri-n-butyl- and triphenyl-tin dimethyldithiocarbamates, since direct spectral comparison can be made with data for other triorganotin carboxylates. In particular, the one-bond ^{119}Sn–$^{13}C_{ipso}$ (for the triphenyltin system) and ^{119}Sn–$^{13}C_{\alpha}$ (for the tri-n-butyltin system) coupling constants fall in a narrow range, and they can be fairly diagnostic of the coordination status at tin. The ^1J values fall in the 550–660 Hz range for the triphenyltin systems, and in the 330–390 Hz range for the tri-n-butyltin systems

Table 4

^{13}C NMR data [a] for triorganotin dithiocarbamylacetates

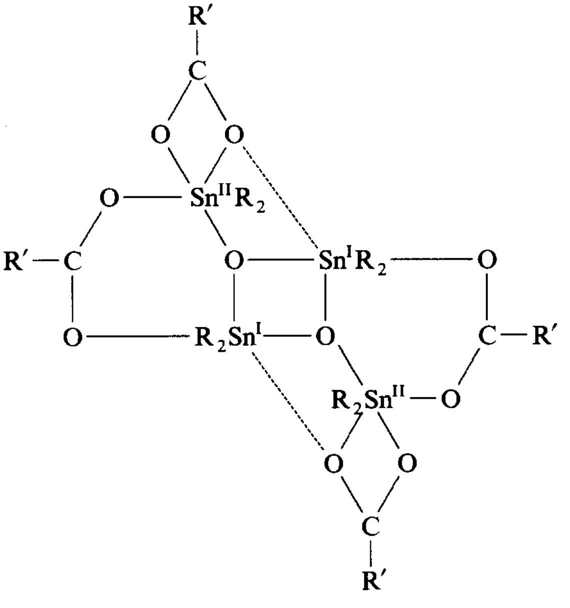
$R_3SnO_2CCH_2S_2CNMe_2$	$\delta(^{13}C)$				
	R	CO_2	CH_2	CS_2	$N(CH_3)_2$
$Me_3SnO_2CCH_2S_2CNMe_2$	−2.0 (398.6)	173.1	40.4	196.0	41.5, 45.4
$^nBu_3SnO_2CCH_2S_2CNMe_2$	16.4 [b] (354.6) 27.4 [c] (20.5) 26.7 [d] (64.5) 13.3 [e] (< 5)	172.5	40.1	195.6	41.4, 45.0
$^cHex_3SnO_2CCH_2S_2CNMe_2$ [f]	33.7 [b] (333.0) 30.6 [c] (14.7) 28.5 [d] (64.5) 26.5 [e] (< 5)	172.2	40.2	195.6	41.0, 44.9
$Ph_3SnO_2CCH_2S_2CNMe_2$	137.7 [g] (644.0) 136.9 [h] (48.3) 128.9 [i] (64.9) 130.2 [j] (13.7)	174.1	40.1	199.9	41.4, 45.5

[a] Chemical shifts in ppm; coupling constants (in parenthesis) reported for $^nJ(^{119}Sn-^{13}C)$ in Hz. [b,c,d,e] C_α, C_β, C_γ and C_δ, respectively. [f] δ ppm (J Hz) for $^cHex_3SnOH$: C_α 31.9 (352.7), C_β 31.0 (15.1), C_γ 28.6 (46.4), C_δ 26.9 (< 7). [g,h,i,j] C_{ipso}, C_{ortho}, C_{meta} and C_{para}, respectively.

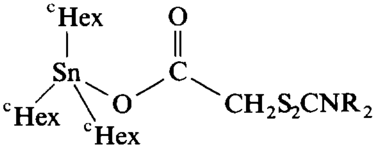
[36,37]. The ^1J values for the tri-n-butyltin and triphenyltin dimethyldithiocarbamylacetates are 354.6 and 644.0 Hz, respectively, and are indicative of four-coordinate tin. There is little information available on the one-bond coupling constants for tri-cyclohexyltin compounds, but they are expected to be of a similar magnitude to those for the tri-n-butyltin system, since four chemically different aliphatic carbons are also present. The ^1J value for $(4\text{-Me-}^cHex)_3Sn\text{-}^iPr$ is 312 Hz [38]; for $(^cHex)_nSnMe_{4-n}$ it is 406 Hz for $n = 1$ and 340 Hz for $n = 2$ [39]. The value for tri-cyclohexyltin hydroxide, assigned a tetrahedral structure from its ^{119}Sn chemical shift [40], is 352.7 Hz. The value of 330.0 Hz observed for tri-cyclohexyltin dimethyldithiocarbamylacetate agrees well with these literature values.

Conclusion

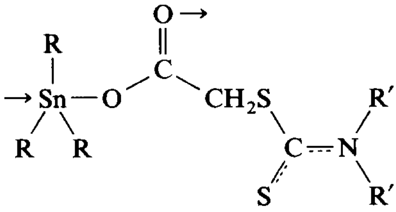
The dithiocarbamylacetato distannoxane derivatives are assigned a skew-trapezoidal bipyramidal geometry at tin essentially on the basis of Mössbauer evidence, and by analogy with the few crystallographically-characterized [25] distannoxanes; they are considered also to be tetranuclear compounds, as depicted (I). On the other hand there have been many structural studies of triorganotin carboxylates, and these have shown the compounds to be generally polymeric, with carboxylate-bridged structures [16,36,41]. Among the notable exceptions are several tri-cyclohexyltin carboxylates [15,23]. The tri-cyclohexyltin dithiocarbamylacetates are therefore assigned a tetrahedral structure (II) in which the carbonyl oxygen points into one face of the tetrahedron around the tin, distorting the geometry somewhat. For the other triorganotin derivatives of the dithiocarbamylalkaloic acids, the carboxylate-bridged structure with *trans*-C_3SnO_2 trigonal bipyramidal geometry at tin is envisaged, and the spectroscopic data supporting this conclusion are corroborated by crystallographic studies reported recently for tri-n-butyltin *N*-methyl-*N*-phenyldithiocarbamylacetate [42] and tri-n-butyltin pyrrolidinyldithiocarbamyl-3-propionate [43]. The repeat distances in these two esters are 5.117 and 4.990 Å, respectively, and are typical of those found in other carboxylate-bridged triorganotin esters [16]. In the methylphenyldithiocarbamylacetate, the intermolecular Sn–O bond (2.393 Å) is longer than the intramolecular Sn–O bond (2.190 Å), and the O–Sn–O skeleton is bent (173.9°) [42]. In the pyrrolidinyldithiocarbamylpropionate, the two Sn–O bonds are also unequal (2.117, 2.399 Å [43]). In both structures, the C_2N-CS_2 fragment is flat, and the dithiocarbamyl sulfur atom is not involved in coordination to tin. The present trimethyl-, tri-n-butyl- and triphenyl-tin dithiocarbamylacetates are best represented by the bridged structure (III).



(I)



(II)



(III)

That the intermolecular bonds in the triorganotin dithiocarbamylacetates are weak is also borne out by mass spectral data. Thus, for triphenyltin dimethylditiocarbamylacetate, the parent ion was observed but higher molecular-weight fragments were not; the loss of the phenyl group and the elimination of carbon dioxide lead to the stable $[Ph_2SnCH_2S_2CNMe_2]^+$ ion-fragment. There is some evidence, however, of disproportionation in the gas phase, as the $[Sn(O_2CCH_2S_2CNMe_2)_3]^+$ ion and its decarboxylated fragments were also observed.

Acknowledgements

This research was supported by the Tin Industry (R & D) Board, the National Science Council for R & D (Grant No. 2-07-04-06) and the University of Malaya (PJP 286/89).

References

1 G.D. Thorn and R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, Amsterdam, 1962.
2 A. Kaars Sijpesteijn and M.J. Janssen, Antonie van Leeuwenhoek, 25 (1959) 422.
3 J. Kaslander, A. Kaars Sijpesteijn and G.J.M. van der Kerk, Biochim. Biophys. Acta, 52 (1961) 396; 60 (1962) 417.
4 A. Kaars Sijpesteijn, J. Karslander and G.J.M. van der Kerk, Biochim. Biophys. Acta, 62 (1962) 587.
5 C.J. Evans and S. Karpel, J. Organomet. Chem. Libr., 16 (1985) 1.
6 R. Block, Pest. Rev., 79 (1981) 2.
7 K. Haertel, Tin Its Uses, 61 (1964) 7.
8 V.G. Kumar Das, in Ungku A. Aziz, Y.H. Yip and C.P. Ling (Eds.), Int. Symp. Tech. Cult. Develop., University of Malaya Press, Kuala Lumpur, 1984, pp. 576–613.
9 G.J.M. van der Kerk, M.H. van Raalte, A. Kaars Sijpesteijn and R. van der Veen, Nature, 176 (1955) 308; C.H. Fawcett, R.L. Wain and F. Wightman, Nature, 178 (1956) 972.
10 V.G. Kumar Das, A.J. Kuthubutheen, S. Balabaskaran and S.W. Ng, Main Group Met. Chem., 12 (1989) 389; V.G. Kumar Das, A.J. Kuthubutheen, S.W. Ng and W.K. Ng, Malaysian Patent, Pl 8700031, 1987.
11 A.J. Kuthubutheen, Y. Salahudin and V.G. Kumar Das, in V.G. Kumar Das, S.W. Ng and M. Gielen (Eds.), Chemistry and Technology of Silicon and Tin, Oxford University Press, 1991, in press.
12 K.A. Jensen, J. Prakt. Chem., 159 (1941) 189; Chem. Zentralbl., 1 (1942) 605; Chem. Abstr., 37 (1943) 27182; G. Nachmias, Ann. Chem., 7 (1952) 584; C.W. Pluijgers, Direct and systemic antifungal action of dithiocarbamic acid derivatives, Thesis, Utrecht, 1959; S.S. Tiwari and V.G. Pandey, J. Indian Chem. Soc., 51 (1974) 440.
13 O. Budevsky, E. Russeva and B. Mesrob, Talanta, 13 (1966) 277.
14 G.B. Deacon, F. Huber and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227; idem, Inorg. Chim. Acta, 104 (1985) 41.
15 N.W. Alcock and R.E. Timms, J. Chem. Soc. A, (1968) 1876; S. Calogero, P. Ganis, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 191 (1980) 381.
16 S.W. Ng, Chen Wei and V.G. Kumar Das, J. Organomet. Chem., 345 (1988) 59.
17 B.Y.K. Ho and J.J. Zuckerman, Inorg. Chem., 12 (1973) 1552.
18 V.S. Petrosyan, N.S. Yashina and O.A. Reutov, Adv. Organomet. Chem., 14 (1976) 63.
19 V.G. Kumar Das, Chen Wei and E. Sinn, J. Organomet. Chem., 290 (1985) 291.
20 R.H. Herber, H.A. Stöckler and W.T. Reichle, J. Chem. Phys., 42 (1965) 2447; J.J. Zuckerman, Adv. Organomet. Chem., 9 (1970) 21.
21 G.M. Bancroft, V.G. Kumar Das and K.B. Butler, J. Chem. Soc., Dalton Trans., (1974) 2355; G.M. Bancroft, V.G. Kumar Das, T.K. Sham and M.G. Clark, J. Chem. Soc., Dalton Trans., (1976) 643.
22 K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann and J.J. Zuckerman, Organometallics, 5 (1986) 85; K.C. Molloy, T.G. Purcell, M.F. Mahon and E. Minshall, Appl. Organomet. Chem., 1 (1987) 507.
23 R.-J. Wang, H.-G. Wang, X.-K. Yao, Q.-L. Xie, M.-D. Wang and C. Li, Acta Chim. Sinica, 47 (1989) 209.
24 G.K. Sandhu, N. Sharma and E.R.T. Tiekink, J. Organomet. Chem., 371 (1989) C1; S.W. Ng, V.G. Kumar Das, B.W. Skelton and A.H. White, J. Organomet. Chem., 377 (1989) 221; S.W. Ng, V.G. Kumar Das, W.-H. Yip, R.-J. Wang and T.C.W. Mak, J. Organomet. Chem., 393 (1990) 201; S.W. Ng, Chen Wei, A. Zainudin, V.G. Kumar Das, W.-H. Yip, R.-J. Wang and T.C.W. Mak, J. Crystallogr. Spectrosc. Res., 21 (1991) 39.
25 C.S. Parulekar, V.K. Jain, T.K. Das, A.R. Gupta, B.F. Hoskins and E.R.T. Tiekink, J. Organomet. Chem., 372 (1989); C.S. Parulekar, V.K. Jain, T. Kesavadas and E.R.T. Tiekink, J. Organomet. Chem., 387 (1990) 163.
26 T.K. Sham and G.M. Bancroft, Inorg. Chem., 14 (1975) 2281.

27 S.W. Ng, Chen Wei, V.G. Kumar Das and T.C.W. Mak, J. Organomet. Chem., 334 (1987) 295.
28 S.W. Ng, Chen Wei, V.G. Kumar Das and T.C.W. Mak, J. Organomet. Chem., 373 (1989) 21.
29 N.W. Alcock and S.M. Roe, J. Chem. Soc., Dalton Trans., (1989) 1589.
30 S. Matsubara, M. Katada, K. Sato, I. Motoyama and H. Sano, J. Phys., Colloq. C2, 40 (1979) 363.
31 K.C. Molloy and K. Quill, J. Chem. Soc., Dalton Trans., (1985) 1417.
32 K.C. Molloy, T.G. Purcell, K. Quill and I.W. Nowell, J. Organomet. Chem., 267 (1984) 237; S.W. Ng, K.L. Chin, Chen Wei, V.G. Kumar Das and R.J. Butcher, J. Organomet. Chem., 376 (1989) 277.
33 S.W. Ng, A.J. Kuthubutheen, A. Zainudin and V.G. Kumar Das, in V.G. Kumar Das, S.W. Ng and M. Gielen (Eds.), Chemistry and Technology of Silicon and Tin, Oxford University Press, 1991, in press.
34 S.W. Ng and A.L. Rheingold, J. Organomet. Chem., 378 (1989) 339.
35 V.S. Petrosyan, Prog. NMR Spectrosc., 11 (1977) 115.
36 S.W. Ng, V.G. Kumar Das and A. Syed, J. Organomet. Chem., 364 (1989) 353.
37 S.W. Ng and V.G. Kumar Das, Malays. J. Sci., 10 (1988) 39; C.K. Yap, L.T. Hong, R. Hill, K.M. Lo, S.W. Ng and V.G. Kumar Das, J. Trop. For. Sci., 1 (1989) 390.
38 H.A. Olszowy and W. Kitching, Organometallics, 3 (1984) 1676.
39 H.G. Kuivila, J.L. Considine, R.H. Sharma and R.J. Mynott, J. Organomet. Chem., 111 (1976) 179.
40 S.J. Blunden and R. Hill, Inorg. Chim. Acta, 98 (1985) L7.
41 M. Amini, S.W. Ng, K.A. Fidelis, M.J. Heeg, C.R. Muchmore, D. van der Helm and J.J. Zuckerman, J. Organomet. Chem., 365 (1989) 103.
42 S.W. Ng, Chen Wei, V.G. Kumar Das, C.K. Yap and R.J. Butcher, in V.G. Kumar Das, S.W. Ng and M. Gielen, (Eds.) Chemistry and Technology of Silicon and Tin, Oxford University Press, 1991, in press.
43 J. Lokaj, V. Vrabel, E. Kellö and V. Ratay, Coll. Czech. Chem. Commun., 54 (1989) 684.