Inorganica Chimica Acta, *211* (1993) 155–160

Stereochemistry of hypervalent tin(IV) compounds. NMR and crystallographic studies of organoyltin(IV) complexes with 1,1-dithiolate ligands

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(Received January 18, 1993; revised June 11, 1993)

Abstract

Tin-119 NMR data have been used to examine the effective coordination spheres in dichloromethane solution of a series of organoyltin(IV) 1,1-dithiolate compounds $RSnX_n(S\text{-}S)_{3-n}$ (where R = Ph, Me; X = Cl, Br; n = 0, 1, 2), for S-S = S_2CNEt_2, S_2COEt, $S_2P(OEt)_2$. Intermolecular halide and 1,1-dithiolate exchange are slow on the NMR timescale however the tin-119 chemical shifts are temperature dependent due to the intramolecular equilibrium between monodentate and bidentate coordinated 1,1-dithiolate ligand. The magnitude of the temperature dependence of the tin-119 chemical shifts for the series $RSn(S\text{-}S)_3$ indicates that the order of 1,1-dithiolate ligand donor strength is $Et_2dtc > Etxan > Et_2dtp$. Mixed ligand complexes $PhSn(S\text{-}S)(S\text{-}S)'_2$ may be formed either by redistribution reactions of $PhSn(S\text{-}S)_3$ and $PhSn(S\text{-}S)'_3$ or by addition of 1,1-dithiolate salt to solutions of $PhSnCl_n(S\text{-}S)_{3-n}$ (n = 1,2). The crystal structure of $PhSn(S_2CNEt_2)_3$ has been determined. The geometry about tin in $PhSn(S_2CNEt_2)_3$ is a distorted pentagonal bipyramid with tin–sulfur distances ranging from 2.487(1) to 2.794(2) Å.

Introduction

The halides in $RSnCl_3$ are easily replaced by other ligands such as 1,1-dithiolate anions S-S (where S-S = S_2CNEt_2(Et_2dtc), S_2COEt (Etxan), $S_2P(OEt)_2$ (Et_2dtp)). The coordination at the tin atom depends not only on factors such as stoichiometry, but also whether the 1,1-dithiolates behave as monodentate or bidentate ligands and whether the complexes are monomeric or oligomeric. Effective coordination numbers between four and seven can be contemplated for such a series of complexes.

Coordination of the 1,1-dithiolate ligand to the tin atom is most often asymmetric so that the coordination number of the tin atom may appear ambiguous, depending on the significance placed on Sn–S bonds which are longer than normal covalent bonds but shorter than the sum of the respective van der Waals radii. Both $MeSn(Et_2dtc)_3$ and $^nBuSn(Et_2dtc)_3$ are seven-coordinate and have pentagonal bipyramidal structures in the solid state [1] whereas $PhSnCl(Et_2dtc)_2$ in the solid state contains tin in a distorted octahedral environment [2]. There remains a paucity of data describing such systems in solution. Tin-119 NMR spectroscopy is a particularly sensitive probe for determination of the coordination environment of the tin atom in many of its complexes In general, four-coordinate systems have tin-119 chemical shifts at higher frequency relative to those of five-coordinate which in turn are generally found at higher frequency relative to those with six-coordinate geometries. There are only few data describing seven-coordinate tin complexes in solution [3, 4]. As part of an ongoing study of 1,1-dithiolate complexes of main group elements [5, 6] and of the coordination chemistry of tin compounds [7, 8] we now report the results of a tin-119 NMR investigation on the formation in dichloromethane solution of a series of tin(IV) 1,1-dithiolate complexes. Results for the formation of mixed 1,1-dithiolate complexes $PhSn(S\text{-}S)'(S\text{-}S)_2$ and for the mixed halide compounds PhSnClBr(S-S) are detailed. We also report the crystal structure determination of $PhSn(Et_2dtc)_3$.

Experimental

Tin-119 NMR spectra were recorded at 100.75 MHz with broad band proton decoupling, using a JEOL GX

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270 MHz spectrometer, and referenced against external Me_4Sn. Phosphorus-31 spectra were recorded at 109.38 MHz and referenced against external 85% phosphoric acid. Carbon-13 spectra were recorded at 67.94 MHz and referenced against internal TMS. Temperatures were maintained using a JEOL GTV3 control system. Solid state ^{119}Sn NMR spectra were recorded by Dr T.J. Bastow (CSIRO Division of Materials Science and Technology) using a Bruker MSL 400 at 149.21 MHz. The pulse width was 2.5 μs and spinning frequencies for MAS ranged between 4.1 and 4.8 kHz.

Complexes for NMR investigation were generally prepared *in situ* by reaction of the organoyltin(IV) trihalide with appropriate mole ratios of the 1,1-dithiolate ligands as the salts KEt_2dtc, NaExan or $NaEt_2dtp$ in dichloromethane solution. NMR spectra of solutions from which NaCl (or KCl) had been filtered were indistinguishable from spectra of solutions which were not filtered. Complexes were isolated by evaporation of the filtered dichloromethane solution, the solid material dissolved in dichloromethane followed by addition of a second solvent (indicated in brackets) to induce crystallization. $PhSn(Et_2dtc)_3$ (petroleum ether 80/100): m.p. 145–148 °C. *Anal.* Found: C, 39.24; H, 5.64; N, 6.48. Calc. for $C_{21}H_{35}N_3S_6Sn$: C, 39.37; H, 5.51; N, 6.56%. $PhSnCl(Et_2dtc)_2$ (ethanol): m.p. 180–182 °C. *Anal.* Found: C, 36.21; H, 4.86. Calc. for $C_{16}H_{25}ClN_2S_4Sn$: C, 36.40; H, 4.77; N, 5.33%. The X-ray structural determination of $PhSnCl(Et_2dtc)_2$ showed it to be identical to that previously reported [2]. Other complexes could only be isolated as oils.

X-ray diffraction studies

A summary of crystal and intensity data for $PhSn(Et_2dtc)_3$ is reported in Table 1. All X-ray measurements were performed at room temperature on a Enraf-Nonius CAD4 diffractometer using Mo Kα radiation monochromatized with a graphite crystal. The cell parameters were determined by least-squares refinement of the setting angles of 25 randomly selected reflections. Three standard reflections were collected every 2 h (no decay of intensities was observed). Intensity data were corrected for Lorentz–polarization effects. Absorption corrections were determined by the azimuthal-scan method [9]. Atomic scattering factors are those reported in ref. 10 with anomalous dispersion corrections taken from ref. 11. The structure was solved by the heavy atom technique. Refinement was by full matrix least-squares calculations; initially with isotropic thermal parameters and then with anisotropic parameters for all the non-hydrogen atoms. Aliphatic hydrogen atoms were found from a difference Fourier map and their positional and isotropic parameters were successfully refined. The phenyl ring was treated as a rigid body (C–C distances 1.39) and all hydrogen atoms were introduced at calculated positions. The final refinement cycles were performed using the weighting scheme $w = k/(\sigma^2(F) + pF^2)$ ($p = 0.0005$) which gave the smallest variations of the mean value of $w(F_o - F_c)^2$. Final Fourier maps were featureless. See also ‘Supplementary material’.

Results and discussion

Description of the structure of $PhSn(Et_2dtc)_3$

Final atomic coordinates are given in Table 2 and relevant bond lengths and angles in Table 3. A PLUTO diagram of the molecule is presented in Fig. 1.

The geometry about the tin is a distorted pentagonal bipyramid with the phenyl group axial, two dithiocarbamate ligands equatorial and one dithiocarbamate bridging axial-equatorial. Each dithiocarbamate is asymmetrically chelated to tin, the largest asymmetry occurring for the group spanning the axial-equatorial positions. The tin–sulfur bonds range from 2.487(1) to 2.794(2) Å. Atom S(2) is out of the plane formed by Sn S(3) S(4) S(5) S(6) by 0.66 Å and the vector Sn–S(2) lies at 15° to the basal plane. The angle S(1)–Sn–C(1,1) is 165.0(1) which is similar to the corresponding angles in $MeSn(Et_2dtc)_3$ and $^nBuSn(Et_2dtc)_3$ (163.3 and 166.3°, respectively [1]).

The chelate rings S(5)–C(11)–S(6) and S(3)–C(6)–S(4) deviate 3.7° from coplanarity whilst the chelates S(5)–C(11)–S(6) and S(1)–C(1)–S(2) are at 89.2° and S(1)–C(1)–S(2) and S(3)–C(6)–S(4) are at 85.5°.

Organoyltin(IV) 1,1-dithiolate complexes – NMR studies

The stepwise substitution of chloride in $RSnCl_3$ (R = Me, Ph) by diethyldithiocarbamate gives the series $RSnCl_2(Et_2dtc)$, $RSnCl(Et_2dtc)_2$ and $RSn(Et_2dtc)_3$ according to

$$RSnCl_3 + M(S\text{-}S) \longrightarrow RSnCl_2(S\text{-}S) + MCl$$

$$RSnCl_2(S\text{-}S) + M(S\text{-}S) \longrightarrow RSnCl(S\text{-}S)_2 + MCl$$

$$RSnCl(S\text{-}S)_2 + M(S\text{-}S) \longrightarrow RSn(S\text{-}S)_3 + MCl$$

The tin-119 chemical shifts (Table 4) accompanying these substitutions move progressively to lower frequency for both R = Me and R = Ph and are consistent with effective increases in coordination of the tin. The chemical shift differences on going from $RSnCl_3$ to $RSnCl_2(Et_2dtc)$ are 308 ppm for R = Me and 290 ppm for R = Ph. Similar differences are observed on changing from $RSnCl_2(Et_2dtc)$ to $RSnCl(Et_2dtc)_2$ (302 ppm for R = Me; 292 ppm for R = Ph). However considerably smaller chemical shift differences accompany the change from $RSnCl(Et_2dtc)_2$ to $RSn(Et_2dtc)_3$ (160 ppm for

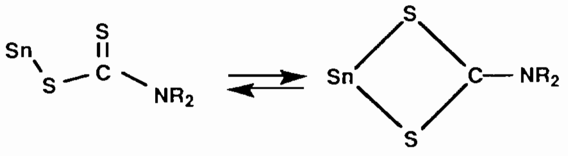
TABLE 1. Summary of crystal data for $PhSn(Et_2dtc)_3$

Formula	$C_{21}H_{35}N_3S_6Sn$
Crystal dimensions (mm)	0.17 × 0.25 × 0.37
Molecular weight	640.61
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.514(1)
b (Å)	13.839(2)
c (Å)	18.740(5)
β (°)	99.14(1)
V (Å^3)	2948.16
Z	4
D_{calc} (g cm^{-3})	1.44
μ(Mo Kα) (cm^{-1})	12.91
Total data	5598
Unique data, $I > 3\sigma(I)$	3232
No. parameters	290
R	0.032
R_w	0.033
Absorption correction: min, max. (%)	89.5, 99.9
Radiation, λ (Å)	graphite-monochromated Mo Kα, 0.71069
Scan type	ω–2θ
2θ Range (°)	5–50
Scan width (°)	$0.8 + 0.35(\tan\theta)$
Scan speed (°/min)	8.24

R = Me; 166 ppm for R = Ph). It appears that the dithiocarbamate ligand is bidentate in all cases and that the tin atom goes from four-coordinate in $RSnCl_3$ to five-coordinate in $RSnCl_2(Et_2dtc)$, six-coordinate in $RSnCl(Et_2dtc)_2$ and seven-coordinate in $RSn(Et_2dtc)_3$. Such a suggestion is in accord with the solid state structures known for $RSnCl(Et_2dtc)_2$ and $RSn(Et_2dtc)_3$.

Further support that the dithiocarbamate is bidentate in these complexes in solution is gained from the observation that stepwise replacement of halide in the series $RSnX_3$ by simple monodentate thiolates, R'S, (where there is no change in coordination number at the tin) leads to the tin-119 NMR shift moving progressively towards higher frequency [12].

It has been claimed that there exist an approximately linear relationship between $\delta(^{119}Sn)$ values and the coordination number of dithiocarbamatotin(IV) complexes [13, 14] but there appears little theoretical basis for such a relationship. Variable temperature experiments are very instructive. The trends for R = Me and R = Ph are similar. There is little change in tin-119 chemical shift for $PhSnCl_2(Et_2dtc)$ and $PhSnCl(Et_2dtc)_2$ as the temperature is lowered to −100 °C (Table 4) indicating no change in the effective coordination of tin and that the equilibrium involving intramolecular monodentate–bidentate dithiocarbamate exchange is unchanged over this temperature range and that the dithiocarbamate ligand is effectively bidentate. However, the tin-119 chemical shift for $PhSn(Et_2dtc)_3$ moves by 75 ppm to lower frequency as the temperature is lowered to −100 °C. The shift to lower frequency is consistent with an effective increase in coordination at the tin atom which would arise from a change in the equilibrium position of intramolecular monodentate–bidentate exchange, bidentate coordination of the dithiocarbamate ligand being favoured as the temperature is lowered. The net effect is to bring about a decrease of the average tin–sulfur bond distances at low temperature probably leading to a geometry similar to that measured in the solid state. This is supported by the fact that the tin-119 chemical shift of $PhSn(Et_2dtc)_3$ at −100 °C in dichloromethane solution (−888 ppm) is very similar to that measured for $PhSn(Et_2dtc)_3$ in the solid state (−894 ppm). Carbon-13 data indicate no evidence for non-equivalent ethyl groups at −100 °C (Table 5) which imply these compounds are still not stereochemically rigid in solution at low temperature.



Analogous reactions between $RSnCl_3$ and ethylxanthate and diethyldithiophosphate ligands lead to complexes of similar stoichiometries as found for the diethyldithiocarbamate series. However in these cases the tin-119 chemical shifts measured at room temperature are consistent with formation of only five- and six-coordinated species, there being no evidence for higher coordination. The tin-119 chemical shift for the xanthate and dithiophosphate complexes are more sensitive to

TABLE 2. Atomic coordinates[a] for $PhSn(Et_2dtc)_3$ with e.s.d.s. in parentheses

Atom	x	y	z
Sn	2250(1)	2333(1)	800(1)
S(1)	4331(1)	2559(1)	1379(1)
S(2)	2977(1)	4246(1)	726(1)
S(3)	2721(1)	681(1)	252(1)
S(4)	3173(1)	2470(1)	−488(1)
S(5)	1559(1)	3214(1)	1945(1)
S(6)	1702(2)	1115(1)	1770(1)
N(1)	682(5)	1956(4)	2786(2)
N(2)	3630(3)	726(3)	−967(2)
N(3)	5223(4)	4312(3)	1322(2)
C(1,1)	498(3)	2530(2)	235(2)
C(2,1)	72(3)	3459(2)	67(2)
C(3,1)	−1074(3)	3589(2)	−294(2)
C(4,1)	−1793(3)	2789(2)	−487(2)
C(5,1)	−1367(3)	1860(2)	−319(2)
C(6,1)	−221(3)	1730(2)	42(2)
C(1)	4266(4)	3774(3)	1158(3)
C(2)	5220(5)	5358(4)	1186(3)
C(3)	4974(8)	5906(5)	1838(4)
C(4)	6374(4)	3880(4)	1612(3)
C(5)	7013(5)	3590(6)	986(3)
C(6)	3224(4)	1242(3)	−471(3)
C(7)	4088(5)	1180(4)	−1570(3)
C(8)	5400(5)	1324(6)	−1412(4)
C(9)	3652(5)	−339(4)	−951(3)
C(10)	2588(7)	−749(5)	−1401(4)
C(11)	1258(5)	2088(4)	2235(3)
C(12)	279(6)	2778(4)	3177(3)
C(13)	−908(6)	3150(5)	2829(4)
C(14)	94(7)	894(5)	2960(4)
C(15)	1019(7)	592(8)	3463(5)

[a]Coordinates multiplied by 10^4.

TABLE 3. Selected bond distances (Å) and angles (°) for $PhSn(Et_2dtc)_3$

Sn–S(1)	2.487(1)	S(1)–Sn–S(2)	68.06(4)
Sn–S(2)	2.786(1)	S(3)–Sn–S(4)	65.59(4)
Sn–S(3)	2.599(1)	S(5)–Sn–S(6)	66.77(5)
Sn–S(4)	2.794(2)	S(1)–Sn–C(1,1)	165.0(1)
Sn–S(5)	2.697(2)	S(2)–Sn–C(1,1)	97.0(1)
Sn–S(6)	2.629(2)	S(3)–Sn–C(1,1)	99.0(1)
Sn–C(1,1)	2.142(3)	S(6)–Sn–C(1,1)	96.44(9)
S(1)–C(1)	1.731(5)		
S(2)–C(1)	1.704(5)		
S(3)–C(6)	1.739(5)		
S(4)–C(6)	1.701(5)		
S(5)–C(11)	1.704(6)		
S(6)–C(11)	1.725(6)		

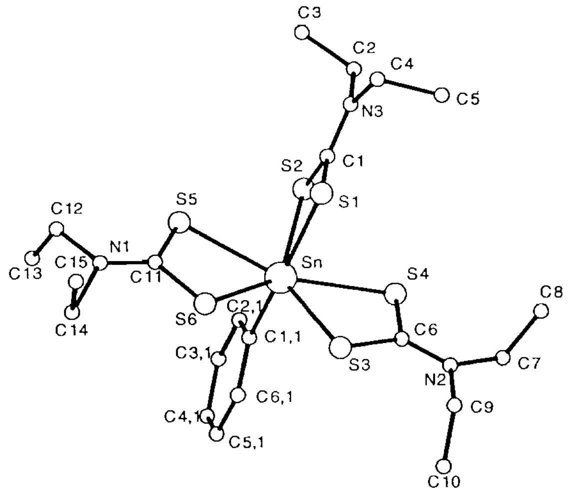


Fig. 1. PLUTO diagram showing structure and numbering scheme of $PhSn[S_2CNEt_2]_3$.

lowering of temperature than are the dithiocarbamate analogues. The tin-119 NMR resonance for $PhSnCl_2(Et_2dtp)$ which appears as a singlet at −303 ppm ($w_{1/2}$ 65 Hz) at room temperature moves to −338 ppm ($w_{1/2}$ 100 Hz) at −100 °C. These observations indicate a change in the position of intramolecular monodentate–bidentate ligand exchange equilibrium with decreasing temperature but the tin-119 chemical shift value is still in accord with overall effective five-coordination at tin. Temperature effects are larger for $PhSnCl(Et_2dtp)_2$ and $PhSn(Et_2dtp)_3$ for which the tin-119 chemical shifts move 142 and 223 ppm, respectively, to lower frequency at −100 °C. Apparently the intramolecular monodentate–bidentate 1,1-dithiolate ligand equilibrium exchange position favours monodentate dithiophosphate coordination as the number of dithiophosphate ligands in the complex is increased. It is interesting to note that the tin-119 chemical shift value for $PhSn(Et_2dtp)_3$ at low temperature is at higher frequency than the value for $PhSnCl(Et_2dtp)_2$. This is consistent with the trend observed when a halide is replaced by a monodentate thiolate [12]. This in turn is consistent with the transformation of $PhSnCl(\eta^2\text{-}Et_2dtp)_2$ to $PhSn(\eta^1\text{-}Et_2dtp)(\eta^2\text{-}Et_2dtp)_2$, the latter containing six-coordinate tin.

Similar trends in tin-119 chemical shift with decreasing temperature are observed for the ethylxanthate complexes $PhSnCl_2(Etxan)$, $PhSnCl(Etxan)_2$ and $PhSn(Etxan)_3$ but the magnitude of the changes are smaller than for the dithiophosphate series. The effective coordination numbers for $PhSnCl_2(Etxan)$, $PhSnCl(Etxan)_2$ and $PhSn(Etxan)_3$ at low temperature are assigned as five, six and six, respectively. A comparison of the low temperature values for $PhSn(S\text{-}S)_3$ indicates that the ligand donor strength order is $Et_2dtc > Etxan > Et_2dtp$. It is noteworthy that monodentate–bidentate 1,1-dithiolate exchange becomes increasingly important as the number of 1,1-dithiolate ligands is increased.

Evidence for the direct involvement of the halide in coordination to tin is gained from tin-119 chemical shift values for the bromo analogues which are all to lower frequency than the corresponding chloride containing

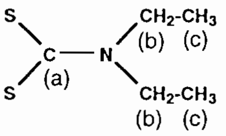
TABLE 4. Tin-119 NMR data for monoorganoyltin(IV)dithiolate complexes in dichloromethane solution at 25 °C. Values in parentheses are $\delta(^{119}Sn)$ at −100 °C

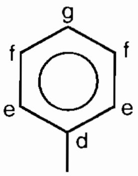
Species	$\delta(^{119}Sn)$	Species	$\delta(^{119}Sn)$	Species	$\delta(^{119}Sn)$
$MeSnCl_3$	12				
$MeSnCl_2(Et_2dtc)$	−296 (−297)	$MeSnCl_2(Etxan)$	−230 (−230)	$MeSnCl_2(Et_2dtp)$[c]	−189 (−229)
$MeSnCl(Et_2dtc)_2$	−598 (−599)	$MeSnCl(Etxan)_2$	−454 (−565)	$MeSnCl(Et_2dtp)_2$[d]	−246 (−316)
$MeSn(Et_2dtc)_3$[a]	−752 (−820)	$MeSn(Etxan)_3$	−423 (−568)	$MeSn(Et_2dtp)_3$[i]	−160 (−184)
$PhSnCl_3$	−65				
$PhSnCl_2(Et_2dtc)$	−355 (−354)	$PhSnCl_2(Etxan)$	−313 (−324)	$PhSnCl_2(Et_2dtp)$	−303 (−338)[g]
$PhSnCl(Et_2dtc)_2$[b]	−647 (−652)	$PhSnCl(Etxan)_2$	−599 (−629)	$PhSnCl(Et_2dtp)_2$	−523 (−665)[h]
$PhSn(Et_2dtc)_3$[b]	−813 (−888)	$PhSn(Etxan)_3$	−600 (−680)	$PhSn(Et_2dtp)_3$[e]	−318 (−541)
$PhSnBr_3$	−228				
$PhSnBr_2(Et_2dtc)$	−472 (−474)	$PhSnBr_2(Etxan)$	−417 (−424)	$PhSnBr_2(Et_2dtp)$	−384 (−433)
$PhSnBr(Et_2dtc)_2$	−704 (−711)	$PhSnBr(Etxan)_2$	−661 (−688)	$PhSnBr(Etdtp)_2$	−557 (−694)
$PhSnClBr(Et_2dtc)$	−419 (−419)	$PhSnClBr(Etxan)$	−377 (−381)	$PhSnClBr(Et_2dtp)$	−374 (−374)
$PhSn(Et_2dtc)_2(Etxan)$	−645	$PhSn(Etxan)_2(Et_2dtp)$	−565	$PhSn(Et_2dtp)_2(Etxan)$	−570
$PhSn(Et_2dtc)_2(Et_2dtp)$[f]	−689	$PhSn(Etxan)_2(Et_2dtc)$	−590	$PhSn(Et_2dtp)_2(Et_2dtc)$	−491

[a] Ref. 3 gives $\delta(^{119}Sn)$ −786 ppm for $MeSn(Me_2dtc)_3$. [b] Ref. 3 gives $\delta(^{119}Sn) = -361$ ppm for $PhSnCl(Me_2dtc)_2$ and $\delta(^{119}Sn) = -659$ ppm for $PhSn(Me_2dtc)_3$. We have repeated these experiments and find the following values $PhSnCl_2(Me_2dtc)$ − 361 ppm; $PhSnCl(Me_2dtc)_2$ − 660 ppm; $PhSn(Me_2dtc)_3$ − 885 ppm. [c] $\delta(^{31}P) = 84.3$ ppm, $J(Sn–P)$ 20 Hz. [d] $\delta(^{31}P) = 87.8$ ppm. [e] $\delta(^{31}P) = 90.2$ ppm, $J(Sn–P)$ 24 Hz. [f] Doublet resonance, $J(Sn–P)$ 42 Hz. [g] $\delta(^{31}P) = 85.0$ ppm, $J(Sn–P)$ 23 Hz at −100 °C. [h] $\delta(^{31}P) = 91.1$ ppm, $J(Sn–P)$ 30 Hz at −100 °C. [i] $\delta(^{31}P) = 89.1$ ppm.

TABLE 5. Carbon-13 data for phenyltin(IV) dithiocarbamate complexes in CD_2Cl_2 solution at −100 °C

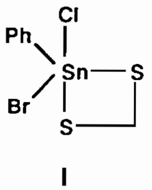
Compound	$C_{(a)}$	$C_{(b)}$	$C_{(c)}$	$C_{(d)}$	$C_{(e)}$	$C_{(f)}$	$C_{(g)}$
$PhSnCl_2(Et_2dtc)$	188.03	51.52	11.97	139.32	133.23	128.52	130.99
$PhSnCl(Et_2dtc)_2$	194.82	51.00	11.65	155.63	131.09	128.18	128.93
$PhSn(Et_2dtc)_3$	199.58	50.04	12.01	157.32	130.56	127.82	128.27





species. This normal halogen dependence of the tin-119 shift implies that the halide is indeed coordinated to the tin in the various compounds. Likewise, the bromo derivatives show similar trends in tin-119 chemical shift changes with lowering of temperature (Table 4).

Further evidence that intermolecular exchange processes for these systems are slow on the NMR timescale is gained from the following mixed ligand experiments. The tin-119 spectrum at room temperature of a dichloromethane solution containing $PhSnCl_3$, $PhSnBr_3$ and $NaEt_2dtc$ in the molar ratio 1:1:2 shows three moderately broad resonances which are attributed to $PhSnCl_2(Et_2dtc)$, $PhSnBr_2(Et_2dtc)$ and the mixed halide species $PhSnClBr(Et_2dtc)$ (Table 4). Cooling this solution to −60 °C causes no change other than a sharpening of the resonances whilst cooling to −100 °C causes all three resonances to broaden. A similar result is obtained when $NaEt_2dtc$ is replaced by KEt_2dtp and no $J(Sn–P)$ coupling is observed. However, when KEtxan is used there are notable differences. At room temperature the tin-119 spectrum of a dichloromethane solution containing $PhSnCl_3$, $PhSnBr_3$ and KEtxan in the molar ratio 1:1:2 shows three broad singlets which are attributed to the species $PhSnCl_2(Etxan)$ ($w_{1/2}$ 150 Hz), $PhSnBr_2(Etxan)$ ($w_{1/2}$ 100 Hz) and $PhSnClBr(Etxan)$ ($w_{1/2}$ 120 Hz). At very low temperature (i.e. near −110 °C) the resonance due to the mixed halide species $PhSnClBr(Etxan)$ becomes much broader



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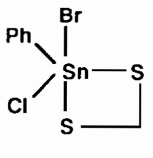

II

($w_{1/2}$ 500 Hz) than do the resonances attributed to $PhSnCl_2(Etxan)$ ($w_{1/2}$ 140 Hz) and $PhSnBr_2(Etxan)$ ($w_{1/2}$ 90 Hz). We interpret this broadening to result from a slowing of intramolecular processes such as fluxional exchange between the two possible five-coordinate structures, **I** and **II**, of PhSnClBr(Etxan).

Mixed 1,1-dithiolate complexes $PhSn(S\text{-}S)(S\text{-}S)'_2$ are formed either by reaction of $PhSn(S\text{-}S)X_2$ with the alkali metal salt of (S-S)′ or by mixing $PhSn(S\text{-}S)_3$ with $PhSn(S\text{-}S)'_3$. In mixtures of the latter, there are separate signals for each possible combination of the mixed 1,1-dithiolate species indicating that intermolecular 1,1-dithiolate exchange is rapid on the preparative timescale but slow on the NMR timescale.

Conclusions

Caution must be exercised in attempting to assign coordination numbers to tin in complexes containing 1,1-dithiolate ligands. Intramolecular monodentate–bidentate 1,1-dithiolate exchange equilibria depend on both the Lewis acidity of the tin center and the basicity of the 1,1-dithiolate. Consequently, the effective coordination number of the tin atom may change as a function of temperature. Mixing experiments show that halide and 1,1-dithiolate ligand exchange are both rapid on the preparative timescale but slow on the NMR timescale. There is some implicit evidence that five-coordinate species such as PhSnClBr(Etxan) may still be fluxional in solution at −100 °C.

Supplementary material

Complete tables of hydrogen coordinates, bond lengths and angles, lists of calculated and observed structure factors are available from authors C.M. and D.M.

Acknowledgements

We are grateful to Dr T.J. Bastow, CSIRO Division of Materials Science and Technology, for solid state ^{119}Sn NMR spectra and to the Austrilian Research Council (ARC) for financial assistance.

References

1 (a) J.S. Morris and E.O. Schlemper, *J. Cryst. Mol. Struct., 8* (1978) 295; (b) *9* (1979) 1.

2 P.G. Harrison and A. Mangia, *J. Organomet. Chem., 120* (1976) 211.

3 J. Otera, A. Kusaba, T. Hinoishi and Y. Kawasaki, *J. Organomet. Chem., 228* (1982) 223.

4 J. Otera, T. Hinoishi and R. Okawara, *J. Organomet. Chem., 202* (1980) C93.

5 (a) D. Dakternieks, R. Di Giacomo, R.W. Gable and B.F. Hoskins, *J. Am. Chem. Soc., 110* (1988) 6753; (b) *110* (1988) 6541; (c) *110* (1988) 6762; (d) D. Dakternieks, R. Di Giacomo, R.W. Gable and B.J. Hoskins, *J. Organomet. Chem., 353* (1988) 35.

6 B.A. Abrahams, G.W. Winter and D. Dakternieks, *Inorg. Chim. Acta, 162* (1989) 211.

7 (a) D. Dakternieks and C.L. Rolls, *Inorg. Chim. Acta, 161* (1989) 105; (b) R. Colton and D. Dakternieks, *Inorg. Chim. Acta, 148* (1988) 31; (c) *143* (1988) 151.

8 D. Dakternieks, H. Zhu, D. Masi and C. Mealli, *Inorg. Chem., 31* (1992) 3601.

9 A.C.T. North, D.C. Philips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.

10 D. Cromer and J. Waber, *Acta Crystallogr., 18* (1965) 104.

11 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974.

12 B. Wrackmeyer, *Annu. Rep. NMR Spectrosc., 16* (1985) 73.

13 (a) O.S. Jung, J.H. Jeong and Y.S. Sohn, *Polyhedron, 8* (1989) 1413; (b) *8* (1989) 2557.

14 O.S. Jung and Y.S. Sohn, *Bull. Korean Chem. Soc., 9* (1988) 365.