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Complexes of Tin(IV) Halides and Organotin(IV) Halides with Organic Sulphides and Selenides: the Low Temperature Cessation of Sulphur and Selenium Inversion and its Structural Consequences

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We report the preparation and characterisation of the 1:2 complexes [$SnX_4(R_2E)_2$] (R = $C_6H_5CH_2$, Me_3SiCH_2; E = S, Se; X = Cl, Br) and the 1:1 complexes [$SnCl_4$(bmt)] (bmt = 3,4-bis(methylthio)-toluene and [$SnCl_3(C_6H_5)$(dth)] (dth = 2,5-dithiahexane). Variable temperature ^1H NMR studies have confirmed the previously observed cis/trans *isomerism about tin in the [SnX_4L_2] complexes, and we have additionally discovered at low temperature the cessation of the pyramidal atomic inversion about sulphur and selenium. This latter phenomenon is characterised by the observation of prochiral centres in the [SnX_4L_2] complexes and mixtures of* dl *and* meso *isomers in the chelate complexes.*

Introduction

Dynamic nuclear magnetic resonance (DNMR) has been extensively used in the investigation of pyramidal atomic inversion [1] and since the first observations of the sulphur inversion phenomenon in a metal co-ordination complex [2, 3], the technique has been extensively used to obtain both qualitative and quantitative information concerning sulphur and selenium inversions in transition metal complexes [4–10].

To date such observations in main group co-ordination compounds have been almost non-existent [11] which prompted us to the syntheses of specific tin adducts, where the arrest of sulphur and selenium atomic inversion would likely be observable. The two approaches that have proved successful with transition metal adducts were the use of monodentate ligands in which the arrest of ligand atom inversion generates an NMR observable prochiral centre, and the use of bidentate ligands where inversion arrest results in the observation of several different and observable isomers.

Sulphide and selenide complexes of the tin(IV) halides are well known [12, 13], but have rarely been well characterised. Recently, however, a series of papers by Merbach [14–16] has described investigations on the solution equilibria of tin(IV) halide complexes with a range of oxygen, sulphur, selenium and nitrogen bases. In the cases of complexes [$SnX_4(R_2E)_2$] (R = CH_3, C_2H_5; E = S, Se; X = Cl, Br), both *cis* and *trans* isomers were observed in solution and a *cis–trans* equilibrium observed by DNMR. Rapid ligand/complex exchange was noted for the *cis* isomer, with a much slower ligand/complex exchange for the *trans* complex. Our own results with analogous complexes confirm these observations and conclusions. In addition, however, we have observed the low temperature cessation of sulphur and selenium inversion, and this present work is primarily concerned with reporting the structural consequences of this effect.

Experimental

All complexes investigated were extremely moisture sensitive and all preparations and manipulations were performed under an atmosphere of dry nitrogen. All solvents were distilled from appropriate drying reagents immediately prior to use.

Reagents

Bis(trimethylsilylmethyl)-sulphide [17] and -selenide [18] were prepared by previously reported methods, dibenzyl sulphide (Aldrich) was used without further purification, 3,4-bis(methylthio) toluene was prepared by the methylation of toluene-3,4-dithiol(BDH), tin(IV) halides (BDH) were used as supplied, and phenyltrichlorotin was prepared by a literature method [19].

Complexes [$SnX_4(R_2E)_2$]- (R = $C_6H_5CH_2$, Me_3SiCH_2; E = S, Se; X = Cl, Br)

A slight excess of the ligand was added to a solution of the tin(IV) halide in benzene, and the reaction

TABLE I. Characterization of Sulphide and Selenide Complexes of Tin(IV) Halides and Phenyltrichlorotin.

Complex	Yield (%)	Colour	M.p./°C	Analysis			
				Calc. (%)		Found (%)	
				C	H	C	H
$[SnCl_4\{S(CH_2C_6H_5)_2\}_2]$	78	white	110	48.8	4.09	48.1	4.11
$[SnBr_4\{S(CH_2C_6H_5)_2\}_2]$	63	pale yellow	93	38.8	3.22	38.7	3.18
$[SnCl_4\{S(CH_2Si(CH_3)_3)_2\}_2]$	69	white	120	28.6	6.52	26.6	6.02
$[SnBr_4\{S(CH_2Si(CH_3)_3)_2\}_2]$	67	pale yellow	83	22.6	5.17	21.9	4.86
$[SnCl_4\{Se(CH_2Si(CH_3)_3)_2\}_2]$	68	white	140	26.1	5.80	25.7	6.04
$[SnCl_4\{3,4(CH_3S)_2C_6H_3CH_3\}]$	72	white	142	24.3	2.68	23.7	2.58
$[SnCl_3(C_6H_5)(CH_3SCH_2CH_2SCH_3)]$	74	white	190–1	28.3	3.53	28.8	3.51

mixture stirred for 1 hour. The product was precipitated by the slow addition of petroleum spirit (b.p. 40–60 °C), recrystallized from benzene/petroleum spirit and dried at 25 °C/0.01 mm. Hg (Table I).

Complexes $[SnCl_4(bmt)]$ and $[SnCl_3(C_6H_5)dth]$ – (bmt = 3,4-bis(methylthio)toluene and dth = 2,5-dithiahexane

A dilute solution of the tin(IV) chloride or phenyltrichlorotin in benzene was added very slowly to a dilute solution of the appropriate ligand in benzene at 0 °C. The resulting mixture was stirred at 0 °C for 30 minutes and then warmed to 25 °C. The white crystalline precipitate was recrystallized from benzene and dried at 25 °C/0.01 mm (Table I).

Spectral Measurements

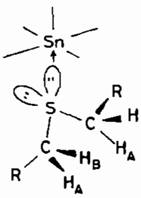
^{1}H NMR spectra were recorded for solutions of the complexes in either CD_2Cl_2 and/or CS_2 solvent mixture, $[SnCl_4\{Se(CH_2Si(CH_3)_3)_2\}_2]$ was recorded in toluene-d^8 to determine the effect of the less polar solvent upon the spectrum. All ^{1}H NMR spectra were obtained on a JEOL PS/PFT–100 spectrometer operating in F.T. mode at 100 MHz. A standard JES-VT3 variable temperature unit was used to control the probe temperature. Temperatures were recorded immediately before and after obtaining a spectrum, using a calibrated copper-constantan thermocouple. All quoted temperatures are considered accurate to $\leqslant$1 °C.

Computer simulations of spectra were performed using the modified DNMR-8 program of Binsch [20].

All spectra were recorded with and without excess ligand present. In the case of $[SnX_4(SR_2)_2]$ complexes this allowed a distinction between line shape changes due to atomic inversion and those due to ligand exchange processes.

Results and Discussion

The static nature of the pyramidal configuration of a sulphur or selenium ligand atom is readily reflected by the presence of a prochiral methylene group [3, 8] as illustrated in I below. Only with rapid interchange of the two lone pairs on the sulphur atom (*i.e.* pyramidal atomic inversion) may the two protons H_A and H_B become equivalent.



(I)

In the presence of a non-inverting sulphur atom the protons H_A and H_B are anisochronous and give rise to an AB quartet. The ligands $(C_6H_5CH_2)_2S$, $((CH_3)_3SiCH_2)_2S$ and $((CH_3)_3SiCH_2)_2Se$ allow the observation of such AB quartets without the complication of these AB protons being coupled to other protons in the ligand molecule.

$[SnX_4(SR_2)_2]$

The ^{1}H NMR spectra obtained for this series of complexes are summarized in Table II. It should be noted in this Table that it was not possible to unambiguously assign the methylene protons H_A and H_B. However, assuming that the preferred conformation of the complex is that depicted in I, and that the coupling $^3J(Sn–S–C–H)$ (*trans*) > $^3J(Sn–S–C–H)$ (*gauche*), then the higher frequency protons H_A will be those *trans* to the tin atom. Spectra obtained over a wide range of temperature indicated the onset of three processes, *cis*/*trans* isomerism about tin, sulphur or selenium ligand exchange

TABLE II. Variable Temperature NMR Data for Sulphide and Selenium Complexes of Tin(IV) Halides.

Complex	Solvent	Temperature(s) /°C	Isomer(s)	NMR Data		$^3J(^{119,117}Sn-H)/Hz$	Others/Hz
				C_6H_5 or $(CH_3)_3Si$	δ/ppm[a] CH_2	These data are for *trans* isomers only	
$SnCl_4\{S(CH_2C_6H_5)_2\}_2]$	CD_2Cl_2/CS_2	25	*cis + trans*	7.22	3.90		
		−82	*cis*	7.06	4.07 s,sh	$^3J(Sn-H_A) = 57.6$;	$\nu_A = 489.0; \nu_B = 411.0$;
			trans	7.25	4.50 (AB quartet)	$^3J(Sn-H_B)$[b]	$\Delta\nu_{AB} = 78.0; {}^2J_{AB} = 13.8$
$[SnBr_4\{S(CH_2C_6H_5)_2\}_2]$	CD_2Cl_2/CS_2	25	*cis + trans*	7.50	3.72		
		−102	*cis*	7.01	4.07b		$\nu_A = 482.3; \nu_B = 399.1$;
			trans	7.30	4.41 (AB quartet)	$^3J(Sn-H)$[b]	$\Delta\nu_{AB} = 83.2; {}^2J_{AB} = 13.5$
$[SnCl_4\{S(CH_2Si(CH_3)_3)_2\}_2]$	CD_2Cl_2	32	*cis + trans*	0.19	2.26b		
		−46	*cis*	0.12	vb	$^3J(Sn-H_A) = 81.7$;	$\nu_A = 285.2; \nu_B = 198.1$;
			trans	0.18	2.41 (AB quartet)	$^3J(Sn-H_B) = 48.0$	$\Delta\nu_{AB} = 87.1; {}^2J_{AB} = 14.7$
$[SnBr_4\{S(CH_2Si(CH_3)_3)_2\}_2]$	CD_2Cl_2	25	*cis + trans*	0.12	1.96		
		−54	*cis*	0.20	2.26b	$^3J(Sn-H_A) = 88.6$;	$\nu_A = 277.7; \nu_B = 197.4$;
			trans	0.28	2.38 (AB quartet)	$^3J(Sn-H_B) = 42.3$	$\Delta\nu_{AB} = 80.3; {}^2J_{AB} = 14.8$
$[SnCl_4\{Se(CH_2Si(CH_3)_3)_2\}_2]$	Toluene-d^8	25	*cis + trans*	0.08	2.36 vb		
		−26	*cis*	0.058	1.66 b	$^3J(Sn-H_A) = 81.9$;	$\nu_A = 325.8; \nu_B = 167.4$;
			trans	0.065	2.45 (AB quartet)	$^3J(Sn-H_B) = 62.5$	$\Delta\nu_{AB} = 158.4; {}^2J_{AB} = 14.0$

[a] Chemical shifts relative to $SiMe_4$ signal, slightly temperature dependent; s = singlet; sh = sharp; b = broad, vb = very broad. [b] Not clearly discernible due to overlapping signals.

involving the *cis* species, and pyramidal sulphur or selenium atomic inversion in the *trans* adduct. The first two processes have already been closely studied by Merbach [14–16], and our own spectra confirm the previous observations and trends. We have confined our present studies to the ligand inversion process in the more abundant *trans* isomers.

In the low temperature (~−70 °C) spectra of all the complexes studied it was possible to observe the *trans* isomer in which sulphur or selenium pyramidal inversions were arrested (showing an AB quartet with appropriate tin satellites due to $^3J(Sn-S-C-H)$ coupling), along with a signal corresponding to rapid exchange of ligand and *cis* isomer. At lower temperatures (*ca.* −100 °C for $[SnCl_4\{S(CH_2C_6H_5)_2\}_2]$ for example), overlapping AB quartets corresponding both to the *cis* and *trans* isomers were obtained, and a separate sharp peak for free ligand indicated the absence of any exchange of either species. On warming $[SnCl_4\{S(CH_2C_6H_5)_2\}_2]$, at −82 °C a sharp AB quartet (with tin couplings) was retained for the *trans*-complex, but a broad band at δ = 4.07 ppm resulted from ligand exchange with the *cis* adduct. At −36 °C the *trans* AB quartet had collapsed to a broad singlet (4.45 ppm) with the onset of pyramidal inversion, but remained separated from the ligand/*cis* isomer signal (4.05 ppm). Further raising of the temperature resulted in coalescence of the *trans* signal with the ligand/*cis* isomer signal at the onset of *cis-trans* isomerism. The same pattern of events, upon temperature increase was observed for all of the complexes listed in Table II.

Due to the complexity of the spectra and the competing effects of the intermolecular exchange processes, (see Fig. 1 for the full range of spectral changes associated with $[SnCl_4\{S(CH_2Si(CH_3)_3)_2\}_2]$ in CD_2Cl_2 solution), it was not possible to obtain very accurate thermodynamic parameters for the atomic inversion rate processes. However, estimates of $\Delta G^{\ddagger}$ have been made by computer simulation of the spectra of [*trans*-$SnCl_4\{S(CH_2C_6H_5)_2\}_2$] and [*trans*-$SnBr_4\{S(CH_2C_6H_5)_2\}_2$] around their coalescence temperatures, producing values of 45 (227 K) and 41.5 (204 K) kJ mol^{-1} respectively. A higher collapse temperature for the AB quartet in [*trans*-$SnCl_4\{Se(CH_2Si(CH_3)_3)_2\}_2$], compared to its sulphur analogue, suggested a higher activation energy for selenium atomic inversion in this class of complex. Merbach reports $\Delta G^{\ddagger}$ for the ligand exchange reactions in [*trans*-$SnCl_4(R_2S)_2$] and [*trans*-$SnBr_4(R_2S)_2$] as 59.5 and 53.3 kJ mol^{-1} respectively. Such values are considerably higher than our above estimates of $\Delta G^{\ddagger}$ for the pyramidal inversions in these species, which is in accord with values for analogous processes in several transition metal complexes [7]. The processes involved in these complexes may thus be summarized.

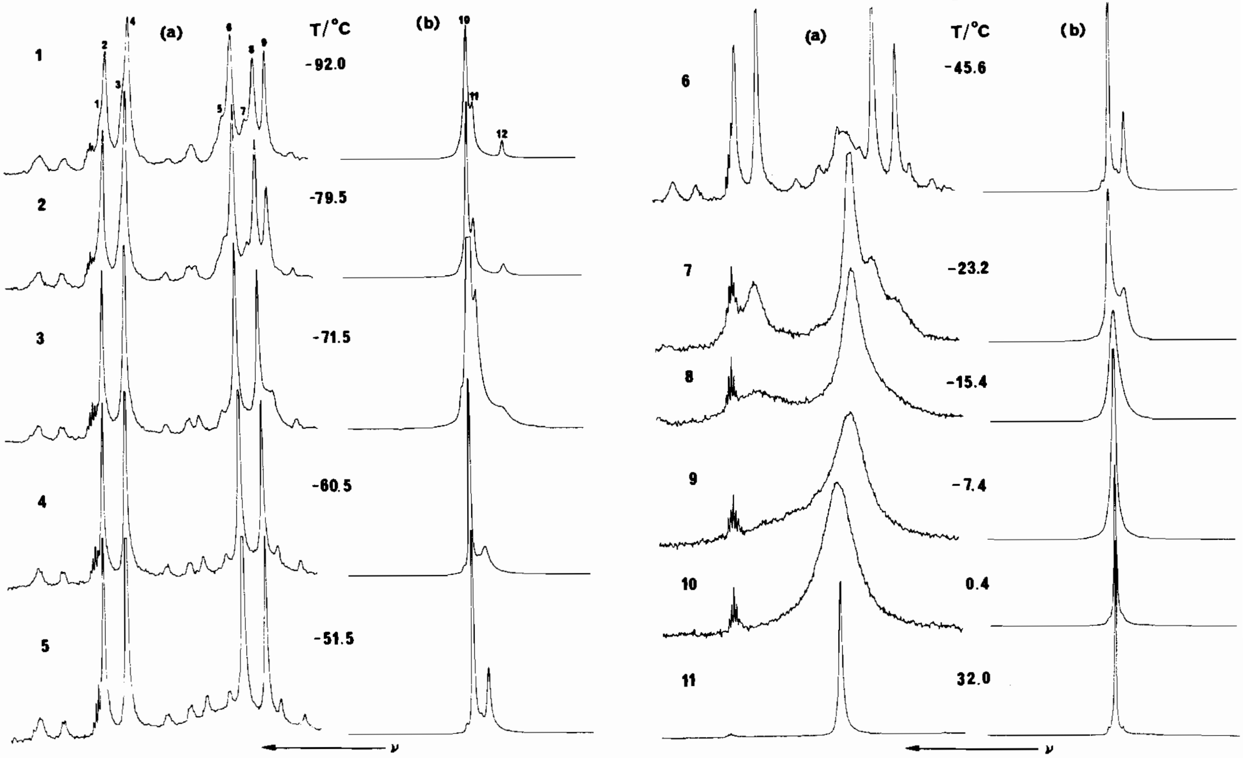


Fig. 1. Variable temperature 100 MHz ^1H spectra of (a) the methylene and (b) the methyl absorptions of $[SnCl_4\{S(CH_2Si(CH_3)_3)_2\}_2]$ in CD_2Cl_2 solution without excess ligand added. A small amount of free ligand arising from slight dissociation of the complex is detectable in the lowest temperature spectra (Nos. 1–3, signals 9 and 12). The high frequency multiplet in the methylene region spectra is a solvent impurity (CD_2HCl?). The other weak bands are ^{117}Sn, ^{119}Sn satellites (in the methylene region) and ^{29}Si satellites (in the methyl region).

Spectrum 1	'Static' spectrum showing the *cis* and *trans* isomers and free $S(CH_2Si(CH_3)_3)_2$ with no S inversion or exchange processes occurring. Band assignments are: *cis* isomer (signals 1, 3, 5, 7 in (a) and 11 in (b)), *trans* isomer (signals 2, 4, 6, 8 in (a) and 10 in (b)) and free ligand (signals 9 in (a) and 12 in (b)).
Spectrum 2	The onset of *cis*/free ligand exchange is shown by the broadening of signals, 1, 3, 5, 7, 9 in (a) and 11, 12 in (b).
Spectrum 3	The *cis* isomer and free ligand signals are further broadened.
Spectrum 4	The *cis* isomer and free ligand signals in (a) are no longer separable and are visible only as a broad envelope under signals 6–8. In (b) the *cis* isomer and free ligand signals have coalesced.
Spectrum 5	In (a) the coalescence point of the *cis*/free ligand signals has been reached whereas in (b) the coalesced band has sharpened.
Spectrum 6	Both regions (a) and (b) show further sharpening of the coalesced bands due to the faster rate of *cis*/free ligand exchange.
Spectrum 7	The onset of S inversion in the *trans* isomer is apparent by broadening of all the *trans* isomer lines in (a). Slight broadening of the lines in (b) could be due to some *trans-cis*/free ligand exchange.
Spectrum 8	S inversion in the *trans* isomer has removed the distinction between the AB methylene protons in (a). *Trans-cis*/free ligand exchange must also be appreciable since the methyl signals in (b) have coalesced.
Spectrum 9	The inversion/*cis-trans* exchange rate is now slightly slower than that required for coalescence in region (a) and greater than that required for coalescence in region (b).
Spectrum 10	A single broad band in (a) represents the coalescence point for the *trans-cis*/free ligand exchange whereas in (b) the spectrum is above the coalescence point.
Spectrum 11	Both regions (a) and (b) exhibit sharp lines due to all rate processes being fast on the NMR time scale.

$$\begin{tikzcd}
& \text{Ligand} & \\
{[\mathit{cis}\text{-}SnX_4(R_2S)_2]} \arrow[ur, shift left, "k_1"] \arrow[rr, shift left, "k_2"] & & {[\mathit{trans}\text{-}SnX_4(R_2S)_2]} \arrow[ul, shift left, "k_3"'] \arrow[ll, shift left]
\end{tikzcd}$$

$k_1 \geqslant k_i$ (inversion) $\geqslant k_2 \approx k_3$

It is likely that k_i (*trans*) $\geqslant k_i$ (*cis*), but the ligand exchange process precludes any accurate assessment of k_i (*cis*).

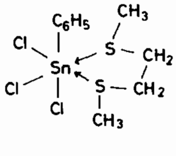
TABLE III. Low Temperature NMR Data for Chelate Sulphur Complexes of Tin(IV).

Complex	Solvent	Temperature/ °C	Isomer	NMR Data (–S–CH$_3$) (Hz)				
				meso (1)	*meso* (2)	^{3}J(Sn–H)	*dl*	^{3}J(Sn–H)
[SnCl$_4${(CH$_3$S)$_2$C$_6$H$_3$(CH$_3$)}]	CD$_2$Cl$_2$/CS$_2$	−101	*cis*	317.4	317.4	40.0	315.7	43.5
			cis	297.4	297.4		289.1	
[SnCl$_3$(C$_6$H$_5$){CH$_3$SCH$_2$CH$_2$SCH$_3$}]	CD$_2$Cl$_2$/CS$_2$	−95	*cis*	275.4		a	258.3	57.4
			cis		241.9	47.4	235.4	

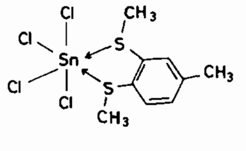
[a] Not clear due to overlapping signals.

[SnCl$_4$(S$_2$chelate)]

We found the previously reported [21] chelate complex of tin(IV) chloride with 2,5-dithiahexane to be either very insoluble, or unstable in all solvents suitable for NMR measurements. We have therefore prepared the corresponding *cis* complexes of phenyltrichlorotin (II below) and also the 3,4-bis(methylthio)toluene complex of tin(IV) chloride (III below); both complexes have excellent solubility characteristics and stability.

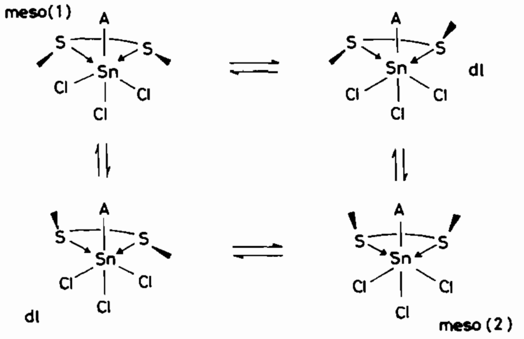


(II)



(III)

In these complexes the slowing down and eventual cessation of sulphur inversion is clearly demonstrated by the NMR observation of the resultant isomers. In the case of (III) the presence of the ring-methyl substituent further splits the S–CH$_3$ pattern, but does not materially differentiate between the inversion energies of the two sulphur atoms. The sulphur atoms in both complexes undergo independent inversions which produce the four isomers illustrated (Fig. 2).



A = Cl or C$_6$H$_5$

Fig. 2. Isomers resulting from independent sulphur. Inversions in [SnCl$_3$A(S$_2$chelate)] complexes.

The two degenerate *dl* isomers are present in equal amounts, and of course are indistinguishable from NMR measurements. In the case of the tin(IV) chloride the two *meso* forms are also degenerate and are observed as one species. In contrast the phenyltrichlorotin complex has one less plane of symmetry and the two *meso* isomers become different and identifiable species (Table III).

These isomeric species are clearly observable in solution below ~−95 °C, but upon warming coalescence takes place. It appears likely that these line shape changes are due to the onset of both pyramidal inversion at sulphur and ligand exchange processes. It is not surprising that these two effects commence simultaneously in such *cis* complexes, as a previous observation [16] has put $\Delta G^{\ddagger}$ for ligand exchange in [*cis*-$SnCl_4(R_2S)_2$] complexes as ~41 kJ mol^{-1}. Now $\Delta G^{\ddagger}$ for inversion in [*trans*-$SnCl_4(R_2S)_2$] was ~45 kJ mol^{-1} and, although not measurable, $\Delta G^{\ddagger}$ (inversion) for the corresponding *cis* complexes would probably be somewhat lower; thus our results imply k (ligand exchange) ≈ k_i (atomic inversion) for these complexes.

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