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A Multinuclear, (^{77}Se, ^{119}Sn, ^{125}Te) Nuclear Magnetic Resonance Spectroscopic Study of the Series $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$

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Abstract

The complete series of fifteen species of the type $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$, including thirteen new species, has been prepared in equilibrium mixtures in solution by reaction of equimolar amounts of $Sn(EPh)_2$ and $Ph_2E'_2$ (E = E′ = S; E = E′ = Se; E = S, E′ = Se; E = Se, E′ = S; E = S, E′ = Te; E = Se, E′ = Te; E = S/Se mixture, E′ = Te; E = S/Se mixture, E′ = Se/Te mixture) and characterized by ^{119}Sn and ^{77}Se and/or ^{125}Te NMR as appropriate. The reaction is thought to involve oxidative insertion followed by redistribution. Equilibrium mixtures of $Sn(SPh)_x(SePh)_{4-x}$ can also be prepared by redistribution of the known compounds $Sn(SPh)_4$ and $Sn(SePh)_4$, and by the redox reaction of $Sn(EPh)_2$ with PhE′H (E = Se, E′ = S; E = S, E′ = Se). Protonation of $Sn(EPh)_3^-$ (E = S or Se) with CF_3SO_3H or CF_3CO_2H is shown to produce $Sn(EPh)_4$. The ^{119}Sn, ^{77}Se and ^{125}Te NMR chemical shifts and the one-bond ^{119}Sn–^{77}Se and ^{119}Sn–^{125}Te nuclear spin–spin coupling constants can be fitted satisfactorily using established pairwise additivity models. There are smooth correlations between the NMR chemical shifts of the different nuclei, between $^1J(^{119}Sn-^{77}Se)$ and $^1J(^{119}Sn-^{125}Te)$, and between the various sets of chemical shift and spin–spin coupling data. The possible origins of these correlations are discussed.

Introduction

By comparison with the Sn^{IV}–SR and Sn^{IV}–SeR bonds, which have been well-studied (see, for example, Refs. [1–6]), the Sn^{IV}–TeR bond has received little attention. To our knowledge, no compounds of the type $Sn(TeR)_4$ have been characterized, and the Sn^{IV}–TeR bond is known only in a relatively small number of organotin compounds [2, 7–9].

We report here effective insertion of $Sn(SPh)_2$ and $Sn(SePh)_2$ into the Te–Te bond of Ph_2Te_2 to produce, ultimately, equilibrium mixtures of $Sn(SPh)_x(TePh)_{4-x}$ (x = 0–4) and $Sn(SePh)_x(TePh)_{4-x}$ (x = 0–4). The presence of three types of readily-accessible magnetically-active spin-½ nuclei† (^{119}Sn††, ^{77}Se, ^{125}Te†††) in the kernels of these species make them very attractive candidates for scrutiny by multinuclear NMR. To complete the set of NMR data for these model compounds we have extended our study to include the remainder of the fifteen members of the series $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$. Hitherto the only NMR data available for this series were ^{119}Sn NMR chemical shfits for $Sn(SPh)_4$ [5, 6] and $Sn(SePh)_4$ [6], though McFarlane and coworkers have presented various NMR data for other series of the types $Sn(SR)_4$–$Sn(SR')_4$ and $Sn(SR)_4$–$Sn(SeR')_4$ [6].

Experimental

Materials

Diphenyldi-selenide and - telluride were purchased from Strem Chemicals, Inc.; they showed no significant impurities by ^{13}C and ^{77}Se or ^{125}Te NMR and were used as received, as were phenylselenol (Strem Chemicals, Inc.), benzenethiol (Eastman), trifluoroacetic acid (Aldrich) and trifluoromethanesulfonic acid (Aldrich).

Literature syntheses were used for Ph_2S_2 [10], $Sn(EPh)_2$ (E = S or Se) [11]), $(Ph_4As)(Sn(EPh)_3)$ (E = S or Se), and the corresponding Ph_4P^+ salts [12], and $Sn(SPh)_4$ [6]. The last compound was also prepared

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† ^{119}Sn, 8.58% natural abundance, $\mu = -1.8119\ \mu_N$; ^{77}Se, 7.58% natural abundance, $\mu = 0.925\ \mu_N$; ^{125}Te, 6.99% natural abundance, $\mu = -1.537\ \mu_N$.

††Tin also contains other spin-½ nuclei that are less favorable for NMR: ^{117}Sn (7.61% natural abundance, $\mu = -1.732\ \mu_N$) and ^{115}Sn (0.35% natural abundance, $\mu = -1.590\ \mu_N$).

†††Tellurium also contains another spin-½ nucleus that is less favorable for NMR: ^{123}Te (0.87% natural abundance, $\mu = -1.275\ \mu_N$, $t_{1/2} = 1.2 \times 10^{13}$ y).

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by oxidative addition of Ph_2S_2 to $Sn(SPh)_2$ (see below); the analogous reaction of Ph_2Se_2 with $Sn(SePh)_2$ yielded $Sn(SePh)_4$.

Manipulations

All solvents were purified by distillation and stored over 3A Molecular Sieves, then thoroughly deoxygenated using a flow of Ar or N_2 before use. All transfers involving PhEH (E = S or Se) and $Sn(EPh)_2$ (E = S or Se) were carried out under an Ar or N_2 atmosphere.

Preparation of Equilibrium Mixtures of $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$ in Solution

(a) $Sn(EPh)_x(E'Ph)_{4-x}$ from $Sn(EPh)_2$ and $Ph_2E'_2$

In a typical experiment an equimolar amount of $Ph_2E'_2$ was added to a suspension of $Sn(EPh)_2$ (200 mg) in CH_2Cl_2 (20 ml). With stirring, the tin(II) compound dissolved within 15 min at room temperature for the E:E′ combinations S:Se, Se:Se, S:Te, and Se:Te, and within 45 min for $Sn(SePh)_2:Ph_2S_2$, but complete dissolution for $Ph_2S_2:Sn(SPh)_2$ mixtures required several days. Solutions of $Sn(SPh)_x(SePh)_{4-x}$ were bright yellow and solutions of $Sn(SPh)_x(TePh)_{4-x}$ and $Sn(SePh)_x(TePh)_{4-x}$ deep red, when the volume of the solutions were reduced to 3 ml for NMR measurements (see below).

(b) $Sn(SPh)_x(SePh)_{4-x}$ from Redistribution of $Sn(SPh)_4$ and $Sn(SePh)_4$

For comparison with the mixtures of $Sn(SPh)_x(SePh)_{4-x}$ prepared by route (a), the same species were prepared from $Sn(SPh)_4$: $Sn(SePh)_4$ mixtures in CH_2Cl_2. As expected from previous work [6], ^{119}Sn NMR measurements (see below) show that redistribution of SPh and SePh moieties is rapid on the preparative but not on the NMR timescale.

(c) $Sn(EPh)_x(E'Ph)_{4-x}$ from $Sn(EPh)_2$ and PhE′H

It was found that suspended $Sn(EPh)_2$ (typically 200 mg) will dissolve completely in CH_2Cl_2 (20 ml) in the presence of two equivalents of PhE′H for the combinations E = E′ = S; E = E′ = Se; E = S, E′ = Se; E = Se, E′ = S. At room temperature, the reaction of $Sn(SePh)_2$ with PhSeH is complete in *ca.* 30 min, while the other reactions require several days for completion.

(d) $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$ from mixtures of $Sn(SPh)_x(SePh)_{4-x}$ with $Sn(SPh)_x(TePh)_{4-x}$, and $Sn(SPh)_x(SePh)_{4-x}$ with $Sn(SePh)_x(TePh)_{4-x}$

Following NMR characterization (see below) of mixtures containing two different phenylchalcogenides, the solutions were combined in various proportions to allow characterization of the three compounds with three different PhE groups.

NMR Spectra

Samples for NMR spectroscopy were prepared in 10 mm o.d. NMR tubes by concentrating the mixtures described above to 3 ml volume *in vacuo.*

All spectra were obtained using a Varian XL-200 NMR spectrometer operating unlocked (field drift ≪ 1 Hz day) in the FT-mode with 2w broadband proton decoupling by the WALTZ-16 [13] sequence. Referencing was by sample interchange, the external references being neat $SnMe_4$ for the 74.60 MHz ^{119}Sn NMR spectra, neat Me_2Se for the 38.15 MHz ^{77}Se NMR spectra and 0.5 M Ph_2Te_2 in CH_2Cl_2 for the 63.14 MHz ^{125}Te NMR spectra. For ^{125}Te NMR, an approximate conversion to external Me_2Te as reference is $\delta Te(Me_2Te, ext.) = \delta Te$ (0.5 M in CH_2Cl_2, ext.) + 422 ppm [14a].

Typically, the ^{77}Se NMR spectra were measured using 17° (3 μs) pulses applied at 40 min^{-1} using a 1.5 s acquisition time and a 10^4 Hz spectral width, with a 16 or 32 K transform. Under these conditions spectra with reasonable S/N were obtained in $6-10 \times 10^3$ transients. To obtain the ^{125}Te NMR spectra, 75° (10 μs) pulses were applied at 40 min^{-1}, the acquisition time was 0.6 s, the spectral window 25 kHz and the final transform one of 64 K points; to obtain spectra with good S/N needed $3-14 \times 10^3$ transients. For the ^{119}Sn NMR spectra, the spectral window used was 2×10^4 Hz for $Sn(SPh)_x(SePh)_{4-x}$ mixtures and 5×10^4 Hz for all other mixtures, the associated acquisition times being 1.5 and 0.6 s. In both cases 60° (8 μs) pulses were applied at 20 min^{-1} and 64 K data points were Fourier transformed. The spin–lattice relaxation time of a typical sample of $Sn(SPh)_4$ was measured by the inversion recovery method and found to be 6.0 ± 0.1 s; the NOE factor of the sample was −0.06.

Results and Discussion

Equimolar quantities of $Sn(EPh)_2$ (E = S or Se) and $Ph_2E'_2$ (E′ = S, Se or Te) react together in CH_2Cl_2 causing dissolution of the tin(II) salt. NMR spectroscopy (see below) shows that the mixtures in which E = E′, contain only a single species, $Sn(EPh)_4$; however, when E ≠ E′ the product solutions contain all five species $Sn(EPh)_x(E'Ph)_{4-x}$ (x = 0–4), with populations approximately binomially distributed. Most probably effective insertion of $Sn(EPh)_2$ into the E′–E′ bond of $Ph_2E'_2$ occurs first*, and is followed by redistribution of the PhE and PhE′ groups about the tin(IV) centre:

$$\begin{tikzcd}
Sn(EPh)_2 + Ph_2E'_2 \arrow[r, "\text{insertion}"] & \{Sn(EPh)_2(E'Ph)_2\} \arrow[d, "\text{redistribution}"] \\
 & Sn(EPh)_x(E'Ph)_{4-x}
\end{tikzcd}$$

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*For footnote, see on facing page.

TABLE I. Tin-119, Selenium-77 and Tellurium-125 NMR Data for $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$ at 295 ± 1 K[a] in CH_2Cl_2.

Species	δ_{Sn}[b] (ppm)	δ_{Se}[c] (ppm)	δ_{Te}[d] (ppm)	$^1J(^{119}Sn-^{77}Se)$[e] (Hz)	$^1J(^{119}Sn-^{125}Te)$[e] (Hz)
$Sn(SPh)_4$	49.5[f]				
$Sn(SePh)_4$	−132.7[g]	183.4		1584 ± 2	
$Sn(TePh)_4$	−570.5		264		3379 ± 5
$Sn(SPh)_3(SePh)$	7.8	149.8		1750 ± 2	
$Sn(SPh)_2(SePh)_2$	−36.4	162.4		1693 ± 2	
$Sn(SPh)(SePh)_3$	−83.2	173.6		1636 ± 2	
$Sn(SPh)_3(TePh)$	−63.8		139		4776 ± 5
$Sn(SPh)_2(TePh)_2$	−202.9		197		4218 ± 5
$Sn(SPh)(TePh)_3$	−369.2 ± 0.5		236		3765 ± 5
$Sn(SePh)_3(TePh)$	−221.8	198.1	201	1499 ± 5	4164 ± 10
$Sn(SePh)_2(TePh)_2$	−324.0	207.5	229	1419 ± 5	3888 ± 10
$Sn(SePh)(TePh)_3$	−439.8 ± 0.6	213.0	249	1329 ± 10	3625 ± 10
$Sn(SPh)_2(SePh)(TePh)$	−113.6	181.8	162	1588 ± 5	~4606
$Sn(SPh)(SePh)_2(TePh)$	−166.1	190.3	183	1535 ± 10	~4356
$Sn(SPh)(SePh)(TePh)_2$	−261.6	201.6	213	1454 ± 10	4026 ± 10

[a] This temperature is nominal, 2w broad band decoupling was used in all cases and the sample temperature will be higher. [b] Relative to external $SnMe_4$ (neat) at 295 ± 1 K. Reproducibility between different samples is ±0.3 ppm or better, except where noted otherwise. [c] Relative to external Me_2Se (neat) at 295 ± 1 K. Reproducibility between different samples is ±0.3 ppm or better. [d] Measured relative to external Ph_2Te_2 (0.5 M in CH_2Cl_2) and converted to external neat Me_2Te as reference using δ_{Te} (ext. Me_2Te) = δ_{Te} (ext. Ph_2Te_2) + 422 ppm [14a]. Reproducibility between different samples is ±1 ppm or better. [e] Errors given are reproducibility found between different samples and/or nucleus observed. [f] For a saturated solution in CH_2Cl_2, δ_{Sn} = 44 ppm by $^1H-\{^{119}Sn\}$ double resonance [5]. [g] For a saturated solution in CH_2Cl_2, $\delta_{Sn} = -135 \pm 2$ ppm by $^1H-\{^{119}Sn\}$ double resonance [6].

Ligand scrambling reactions of tin(IV) compounds are very well known (see, for example, Refs. [2, 6, 17]); for all the cases reported here the redistribution gives close-to-statistical [18] product populations.

The compounds $Sn(EPh)_2$ (E = S or Se) also dissolve in CH_2Cl_2 in the presence of two equivalents of PhE′H. By comparison with the very recent work of Tzschach *et al.* [19], we formulate this overall reaction as:

$$\begin{tikzcd}
Sn(EPh)_2 + 2PhE'H \arrow[r] & \{Sn(EPh)_2(E'Ph)_2\} + H_2 \arrow[d, "\text{redistribution}"] \\
& Sn(EPh)_x(E'Ph)_{4-x}
\end{tikzcd}$$

It is likely, though, that the species $HSn(EPh)_2(E'Ph)$, formed by effective insertion of $Sn(EPh)_2$ into the E′H bond, is involved here. We find that addition of one equivalent of CF_3CO_2H or CF_3SO_3H to $Sn(EPh)_3^-$ (E = S or Se, as the Ph_4As^+ or Ph_4P^+ salts) in CH_2Cl_2 quickly[§§] produces $Sn(EPh)_4$ together with insoluble $Sn(EPh)_2$. A plausible reaction sequence[§§] is:

$$\begin{tikzcd}
Sn(EPh)_3^- + HA \arrow[r] & \{HSn(EPh)_3\} + A^- \arrow[d, "\text{redistribution}"'] \arrow[dr] & \\
& Sn(EPh)_4 & \{H_2Sn(EPh)_2\} \arrow[d] \\
& & Sn(EPh)_2 + H_2
\end{tikzcd}$$

NMR parameters measured in the present study are given in Table I, which includes data from studies of the nuclei ^{119}Sn, ^{77}Se and ^{125}Te[†].

The ^{119}Sn NMR chemical shifts found for $Sn(EPh)_4$ (E = S or Se) produced from $Sn(EPh)_2$ and Ph_2E_2, $Sn(EPh)_2$ and PhEH, or protonation of $Sn(EPh)_3^-$ (see above) are identical, and in accord with those reported earlier by McFarlane and coworkers

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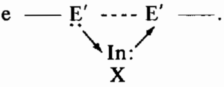
[*] Very recently, Peppe and Tuck [15] have reported the insertion of InX into $Ph_2E'_2$ (E′ = S or Se, but not Te) in the presence of py to give XIn $(E'Ph)_2py_2$. They have suggested that such insertion requires simultaneous donor and acceptor behavior by the indium centre, and proceeds through the intermediate  The same type of intermediate may be involved for the oxidative insertion reported here; donation by tin(II) centres is well-established [16], and $Sn(EPh)_2$ (E = S or Se) are acceptors (see, for example, Refs. [11] and [12]).

[§§] We were unable to detect an intermediate in many attempts.

[†] See footnote p. 1.

[5, 6]. Reaction of $Sn(EPh)_2$ (E = S or Se) with $Ph_2E'_2$ (E′ = Se or S) or of $Sn(SPh)_4$ with $Sn(SePh)_4$ produces solutions containing the expected three new mixed-ligand species, which can be characterized using ^{119}Sn and ^{77}Se NMR. The ^{119}Sn NMR chemical shifts for the series $Sn(SPh)_x(SePh)_{4-x}$ increase monotonically though not linearly with increase in x, as was also found in the series $Sn(SMe)_x(SeMe)_{4-x}$ [6]. The selenium-containing species have ^{119}Sn NMR signals flanked by ^{77}Se satellites[†]; the magnitude of $^1J(^{119}Sn-^{77}Se)$ (which is known to have an absolute positive sign [4]) also increases with increase in x, whereas the satellite/total intensity ratio for each signal in the ^{119}Sn NMR spectrum has the reverse x-dependence[§§§]. The differing values of $^1J(^{119}Sn-^{77}Se)$ allow unambiguous assignment of the ^{77}Se NMR spectra of $Sn(SPh)_x(SePh)_{4-x}$ in which $^{117/119}Sn$ satellites[†,††] are observed; the ^{77}Se chemical shift decreases non-linearly with increase in x for x = 0–3. The observed changes in δ_{Sn}, $^1J(^{119}Sn-^{77}Se)$ and δ_{Se} with x are qualitatively similar to those found for the analogous parameters in the ^{113}Cd and ^{77}Se NMR spectra of the isoelectronic series $[Cd(SPh)_x(SePh)_{4-x}]^{2-}$ [20]; it seems that $^1J(^{113}Cd-^{77}Se)$ must be positive like $^1J(^{119}Sn-^{77}Se)$. (Both ^{113}Cd and ^{119}Sn have negative magnetogyric ratios so that the reduced coupling constants, $^1K(M-^{77}Se)$ must both be negative). However, the x-dependences of δ_{Sn} and δ_{Se} are the reverse of those reported for the tin(II) complexes $[Sn(SPh)_x(SePh)_{3-x}]^-$ [11].

When $Sn(SPh)_2$ is treated with an equimolar amount of Ph_2Te_2, the ^{119}Sn NMR spectrum of the product solution shows a signal due to $Sn(SPh)_4$ together with four new signals, as expected for the series $Sn(SPh)_x(TePh)_{4-x}$. The new resonances are all shielded relative to the $Sn(SPh)_4$ signal and all show ^{125}Te satellites[†]; in the ^{125}Te NMR spectrum there occur the corresponding four signals with $^{117/119}Sn$ satellites[†,††]. By analogy with the NMR spectroscopic properties of the species $Sn(SPh)_x(SePh)_{4-x}$ (see above), the ^{119}Sn and ^{125}Te resonances can be assigned readily to various members of the series $Sn(SPh)_x(TePh)_{4-x}$ on the basis of the observed monotonic changes with x of δ_{Sn}, $^1J(^{119}Sn-^{125}Te)$, δ_{Te}, and the ^{125}Te satellite intensities[*] in the ^{119}Sn NMR spectrum.

A total of five ^{119}Sn NMR signals is found for $Sn(SePh)_2-Ph_2Te_2$ mixtures. That of highest chemical shift is due to $Sn(SePh)_4$ and that of lowest to $Sn(TePh)_4$, the latter already observed in the $Sn(SPh)_2-Ph_2Te_2$ mixtures (see above). The resonances of mixed species of the $Sn(SePh)_x(TePh)_{4-x}$ series can be assigned on the basis of their monotonic changes in δ_{Sn} and $^1J(^{119}Sn-^{125}Te)$. Both ^{77}Se and ^{125}Te NMR spectra of the mixture show four lines, one due to the appropriate parent $Sn(EPh)_4$ (E = Se or Te); the new resonances can be assigned on the basis of the now anticipated monotonic changes in δ_{Se} and δ_{Te}, as well as the magnitudes of the one-bond $^{117/119}Sn$ satellite splittings that were observed.

In the series $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$ there should be three species having three different chalcogenide groups: those with x = 1 and y = 1, x = 1 and y = 2, and x = 2 and y = 1. The ^{119}Sn, ^{77}Se and ^{125}Te NMR spectra all show evidence for three new species when solutions of $Sn(SPh)_x(SePh)_{4-x}$ and $Sn(SPh)_x(TePh)_{4-x}$, or $Sn(SPh)_x(TePh)_{4-x}$ and $Sn(SePh)_x(TePh)_{4-x}$ are mixed. All the new resonances are assignable on the basis of empirical correlations in the chemical shifts and $^{119}Sn-^{77}Se/^{125}Te$ coupling constants (see following).

It is clear from the NMR data for the three series $Sn(EPh)_x(E'Ph)_{4-x}$ (Table I) that neither the chemical shifts nor the one-bond coupling constants can be accounted for on the basis of simple additive substituent effects. However, the different sets of chemical shifts and one-bond coupling constants give good agreement with a second-order pairwise additivity model [21], in which, for example, the differential change in an NMR parameter P for $Sn(EPh)_x(E'Ph)_{4-x}$ is correlated with the empirical pairwise interaction constants η:

$$\Delta P = P(Sn(EPh)_x(E'Ph)_{4-x}) - P(Sn(EPh)_4)$$
$$= \Sigma\eta_{E_i-E_j}$$

Here the summation is over all E – E′ and E′ – E′ interactions along the edges of the coordination tetrahedron. The empiricism is readily extended to the whole series $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$, and $\Delta\delta_{Sn}$, $\Delta\delta_{Se}$, $\Delta\delta_{Te}$, $\Delta^1J(^{119}Sn-^{77}Se)$, and $\Delta^1J(^{119}Sn-^{125}Te)$, derived from the data in Table I, have been fitted using a least-squares technique. The values of η that give the best fit to each ΔP, are listed in Table II. The results in Table II show that $\Delta\delta_{Sn}$, $\Delta\delta_{Se}$, $\Delta\delta_{Te}$ and $\Delta^1J(^{119}Sn-^{77}Se)$ can be fit with standard errors less than 1% of their respective ranges of values. The somewhat larger standard error in the fit of $\Delta^1J(^{119}Sn-^{125}Te)$ may reflect the more approximate nature of the data (Table I). Nonetheless, the good overall fit can be taken as confirmation of the assignments given in Table I.

From the data in Tables I and II it is evident that the sensitivities of the various NMR observables to the nature of the substituents in $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$ are as follows: ^{119}Sn nuclear shielding, TePh > SePh > SPh; ^{77}Se and ^{125}Te nuclear shield-

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[†,††] See footnote p. 1.

[*] From statistical considerations [18], the percentage populations of kernels with one ^{77}Se nucleus are 7.6, 14.0, 19.4 and 23.9% for $Sn(SPh)_x(SePh)_{4-x}$ with x = 3, 2, 1 and 0, respectively, when ^{77}Se is in natural abundance (7.58%). Similarly, the kernels with one ^{125}Te nucleus in $Sn(SPh)_x(TePh)_{4-x}$ have populations 7.0, 13.0, 18.1 and 22.5% for x = 3, 2, 1 and 0, respectively, when ^{125}Te is in natural abundance.

TABLE II. Empirical Correlation of Chemical Shifts (ppm) and One-Bond Coupling Constants (Hz) of $Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}$ by Pairwise Interactions.[a]

ΔP	$\eta_{S,S}$	$\eta_{S,Se}$	$\eta_{Se,Se}$	$\eta_{S,Te}$	$\eta_{Se,Te}$	$\eta_{Te,Te}$	Intercept	Number of Points	Standard Error	(% of) (Range)
$\delta_{Sn} - \delta_{Sn}(Sn(SPh)_4)$	–	−13.6	−30.2	−36.9	−59.8	−102.9	−0.9	14	0.5	(0.08)
$\delta_{Se} - \delta_{Se}(Sn(SePh)_4)$	−7.9	−3.4	–	3.7	4.7	4.9	0.5	10	0.5	(0.8)
$\delta_{Te} - \delta_{Te}(Sn(TePh)_4)$	−32.4	−23.0	−15.8	−7.8	−3.7	–	−4.2	9	0.7	(0.6)
$^1J(^{119}Sn-^{77}Se) - {}^1J(^{119}Sn-^{77}Se)(Sn(SePh)_4)$	38.0	19.5	–	−18.4	−25.7	−56.4	2.8	9	2.8	(0.66)
$^1J(^{119}Sn-^{125}Te) - {}^1J(^{119}Sn-^{125}Te)(Sn(TePh)_4)$	341.9	260.7	177.9	110.7	67.0	–	49.5	9	23.4	(1.7)

[a] See text.

ing, SPh > SePh > TePh; $^1J(^{119}Sn-^{77}Se)$ and $^1J(^{119}Sn-^{125}Te)$, SPh > SePh > TePh. In fact, there are smooth non-linear correlations between any two of δ_{Sn}, δ_{Se}, δ_{Te}, $^1J(^{119}Sn-^{77}Se)$ and $^1J(^{119}Sn-^{125}Te)$ when the various data for the individual members of the series are compared. Correlation between one-bond coupling constants and the chemical shifts of the coupled nuclei have been observed before (*e.g.* Refs. [21] and [22]. On theoretical grounds, Vladimiroff and Malinowski [21] have argued that the observation of pairwise additivity in both the chemical shifts of the coupled nuclei and the coupling constants is indicative of a coupling in which the Fermi term is not dominant.

For tetrahedral tin(IV) compounds, ^{119}Sn NMR chemical shifts depend on several factors including (a) the coordination number, (b) the effective electronegativity of the substituents, (c) the geometry of the bonds at the tin atom, (d) π-bonding, and (e) the 'bulky atom effect' [23, 24]. Only factor (a) can be ruled out with certainty in the present case, but it seems unlikely that factor (c) could produce changes of the magnitude we observe. Disentanglement of (b), (d) and (e) is difficult here, as the atoms directly attached to tin change from species to species: decrease in the electronegativities of the donor atoms should lead to increased ^{119}Sn shielding, as should increase in their polarizabilities and, probably, extent of π-donation [23]. Changes in $^1J(^{119}Sn-^{77}Se)$ are those expected from changes in the electronegativity of the atoms attached to tin, provided the Fermi contact term is mainly affected and the effective electronegativities are SPh > SePh > TePh (see below). This order of electronegativities is consistent with the Pauling scale of neutral atom electronegativities for the chalcogens, but it should be noted that the ordering of S and Se in electronegativity scales is contentious (see, for example, Ref. [25]). In terms of π-bonding, changes in the ^{13}C NMR chemical shifts of C_4 in Ph_2E (E = S, Se, Te) [26] can be interpreted [27] in terms of slight variation in π-donor ability in the order SPh > SePh > TePh. Probably, then replacement of SPh by SePh or TePh, or replacement of SePh by TePh, should lead to an overall decrease in E → Sn π-donation and deshielding of the ^{119}Sn nucleus, the opposite of what is observed.

Tentatively, we ascribe the ^{119}Sn shielding sequence TePh > SePh > SPh to a combination of changes in the electronegativities and polarizabilities of the donor atoms.

It has been pointed out [4] that due to changes in the Fermi contact term (which may not be dominant in the present case (see above)), the magnitude of the positive $^1J(^{119}Sn-^{77}Se)$ in organotin(IV) selenides should increase as the electronegativities of the other groups attached to tin increase. If the changes we observe in ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se})$ in the series $\mathrm{Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}}$ are similarly dependent on changes in the Fermi contact term, this implies that the overall electron-withdrawing abilities of the PhE groups are in the order SPh > SePh > TePh. Then, for instance, ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se})$ should change in the order $\mathrm{(PhS)_3Sn(SePh)}$ > $\mathrm{(PhSe)_3Sn(SePh)}$ > $\mathrm{(PhTe)_3Sn(SePh)}$, as observed.

Whatever the exact mechanism of nuclear spin–spin coupling, it is clear from their parallel response to changes in substituents on tin that the same factors effect ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se})$ and ${}^{1}J({}^{119}\mathrm{Sn}-{}^{125}\mathrm{Te})$. The observed parallelism is consistent with ${}^{1}J({}^{119}\mathrm{Sn}-{}^{125}\mathrm{Te})$ being negative, so that the reduced coupling constants ${}^{1}K({}^{119}\mathrm{Sn}-\mathrm{E})$ are both positive, ${}^{77}\mathrm{Se}$ and ${}^{125}\mathrm{Te}$ having magnetogyric ratios of oppositive sign. Opposite signs for ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se})$ and ${}^{1}J({}^{119}\mathrm{Sn}-{}^{125}\mathrm{Te})$ have been established for $\mathrm{(Me_3Sn)_2E}$ ($\mathrm{E} = {}^{77}\mathrm{Se}$ or ${}^{125}\mathrm{Te}$) [7].

Selenium-77 NMR chemical shifts are affected by the electronegativity of the substituents attached to selenium; generally there is an increase in δ_{Se} with increase in the effective electronegativity of the substituents on selenium [14, 28]. Provided the effective electronegativities are SPh > SePh (see above), this is the behaviour exhibited by the stannous complexes $[\mathrm{Sn(SPh)_x(SePh)_{3-x}}]^{-}$ and (several related series of species) [11]. However, the reverse behaviour is found here for the stannic species, $\mathrm{Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}}$, the influence of the tin substituents on δ_{Se} of SePh being TePh > SePh > SPh, with parallel substituent sensitivity evident for δ_{Te} of TePh. We have noted above that the π-donor ability of the phenylchalcogenides is PhS > PhSe > PhTe, as least in $\mathrm{Ph_2E}$, and in addition it is known that involvement of selenium (and presumably, therefore, tellurium also) in multiple bonding leads to deshielding of the chalcogen nucleus [14]. Thus it seems feasible that the observed variations in δ_{Se} and δ_{Te} are due to either small increases in E → Sn π-donation as the π-donor abilities of the other groups on tin decrease or small increases in E → phenyl π-donation as the electronegativities of the other substituents on tin decrease. It is noteworthy that the orbital contribution to ${}^{1}J({}^{119}\mathrm{Sn}-\mathrm{E})$, which by the criteria of Vladimiroff and Malinowski (see above) could be significant in $\mathrm{Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}}$, also requires multiple bond character in the tin–chalcogen linkage [22].

As a general rule, changes in δ_{Te} are larger than the changes in δ_{Se} when analogous compounds are compared [14]. For the kernels of $\mathrm{Sn(SPh)_x(SePh)_y(TePh)_{4-x-y}}$, the ratio of the chemical shift differences $(\delta_{\mathrm{Te}}(\mathrm{S_3SnTe}) - \delta_{\mathrm{Te}}(\mathrm{Te_3SnTe}))/(\delta_{\mathrm{Se}}(\mathrm{S_3SnSe}) - \delta_{\mathrm{Se}}(\mathrm{Se_3SnSe}))$ is 2.36, reasonably close to the slope of *ca.* 1.8 found from a plot of δ_{Te} *vs.* δ_{Se} for a wider range of compounds [14]. Similarly, the ratio of the analogous differences in ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se}/{}^{125}\mathrm{Te})$ is 3.32, not out of line with the ratio of *ca.* 2–3 found for a wider range of one-bond couplings to ${}^{77}\mathrm{Se}$ and ${}^{125}\mathrm{Te}$ [14].

The value of ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se})$ for $\mathrm{Sn(SePh)_4}$, 1584 ± 2 Hz, is comparable to the value of 1520 ± 10 Hz found for $\mathrm{Sn(SeMe)_4}$ [5], but larger than the 710 ± 10 Hz reported for $[\mathrm{Sn(SePh)_3}]^{-}$ [11]. The differences in ${}^{1}J({}^{119}\mathrm{Sn}-{}^{77}\mathrm{Se})$ between both $\mathrm{Sn(SePh)_4}$ and $\mathrm{Sn(SeMe)_4}$, and $\mathrm{Sn(SePh)_4}$ and $[\mathrm{Sn(SePh)_3}]^{-}$ are in the direction expected on the basis of electronegativity arguments (see above). Similarly the relative magnitudes of ${}^{1}J({}^{119}\mathrm{Sn}-{}^{125}\mathrm{Te})$ in $\mathrm{Sn(TePh)_4}$ (3379 ± 5 Hz) and $\mathrm{SnTe_4}^{4-}$ (2804 Hz [29]) are consistent with predictions based on electronegativity.

Finally, it may be noted that the chemical shift separation ratio $(\delta_{\mathrm{Sn}}(\mathrm{Sn(SPh)_4}) - \delta_{\mathrm{Sn}}(\mathrm{Sn(SePh)_4}))/(\delta_{\mathrm{Sn}}(\mathrm{Sn(SPh)_4}) - \delta_{\mathrm{Sn}}(\mathrm{Sn(TePh)_4}))$ is 0.29, near the close-to-average [30] value of 0.31 for the Cl–Br/Cl–I separation ratio in the ${}^{119}\mathrm{Sn}$ NMR chemical shifts of the tin tetrahalides [17], even though the range of δ_{Sn} for $\mathrm{Sn(EPh)_4}$ is only 41% of the range for $\mathrm{SnX_4}$.

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