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Phosphorus-31 and Tin-119 NMR Studies on Tin(IV) Halides and their Adducts

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Tin-119 NMR spectra have been recorded for SnX_4 (X = Cl, Br, I) and mixtures thereof. All fifteen possible $SnCl_xBr_yI_z$ (x + y + z = 4) species were observed. Tin-119 NMR spectra were observed for SnX_5^- and SnX_6^{2-} (X = Cl, Br) and for an equimolar mixture of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ which gave all ten possible isomers of $[SnCl_xBr_{6-x}]^{2-}$ in the statistical distribution.

Phosphorus-31 and tin-119 NMR spectra were observed for $SnX_4(PBu_3)_2$ (X = Cl, Br) and a mixture gave all six possible trans *phosphine isomers in the statistical distribution. $[SnX_5(PBu_3)]^-$ (X = Cl, Br) species show some disproportionation, although the $[SnX_5(PBu_3)]^-$ ion is the dominant species in solution. A mixture of $[SnCl_5(PBu_3)]^-$ and $[SnBr_5(PBu_3)]^-$ gave a complex mixture in solution, but all twelve isomers of the $[SnCl_5Br_{5-x}(PBu_3)]^-$ series were identified.*

The well known pairwise additivity model fits well within the tetrahalide or hexahalide anion series and it is shown that the chemical shift of tin in both tetrahedral and octahedral environments may be predicted from a single set of interaction parameters if geometrical factors are taken into account. The same interaction parameters are of use in identifying the mixed tin halide–phosphine complexes.

Introduction

The Lewis acid character of tin(IV) halides has been extensively studied over recent years with many 1:1 and 1:2 adducts, SnX_4L and SnX_4L_2, having been isolated for L as either a neutral or anionic monodentate Lewis base [1]. Adducts SnX_4L_2 involving neutral oxygen, sulphur, selenium or nitrogen donors have been particularly well characterised by Raman, infrared and Mössbauer spectroscopy and they may exist as either *cis* or *trans* isomers in the solid state [2, 3]. More recently, *cis–trans* equilibria of SnX_4L_2 adducts in solution were studied by ^1H, ^{19}F and ^{31}P NMR spectroscopy [4]. However, there is only a single report [5] of phosphorus-31 NMR of phosphine adducts, namely $SnCl_4(PEt_3)_2$ and $SnCl_4(PEt_2Ph)_2$, but there have been no reports of tin-119 NMR studies for this type of complex.

Although tin-119 NMR spectra of the tin tetrahalides and mixtures thereof were first observed by Burke and Lauterbur [6] using continuous wave methods some twenty years ago, no tin spectra have been reported for the SnX_5^- or SnX_6^{2-} systems.

In this paper we report tin-119, and where appropriate phosphorus-31, NMR studies to investigate the structures of SnX_5^-, SnX_6^{2-}, $SnX_4(PBu_3)_2$ and the new species $[SnX_5(PBu_3)]^-$ in solution. The pairwise additivity model has been applied to these systems. It is shown that if geometrical factors are taken into account, then the same interaction parameters may be used in both tetrahedral and octahedral complexes, and these parameters are useful in identifying species in complex mixtures.

Experimental

All NMR spectra were recorded on a JEOL FX 100 spectrometer, phosphorus-31 at 40.26 MHz and tin-119 at 37.06–37.08 MHz. Dichloromethane was the solvent in all cases except for the mixed tetrahalide species when carbon disulphide was used. An external ^7Li lock was used and temperatures were maintained using a JEOL NM 5471 controller. Tin-119 NMR spectra were referenced against external $SnMe_4$ and phosphorus-31 spectra against 85% H_3PO_4. High frequency positive convention is used.

Tin tetrabromide was prepared by bromination of tin at 400 °C in a flow system and purified by distillation. Tetrabutylammonium salts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ were prepared by interaction of the appropriate tin tetrahalide and tetrabutylammonium halide in concentrated hydrohalic acid. The product was filtered, dried and recrystallised from dichloromethane. All other compounds were from commercial sources.

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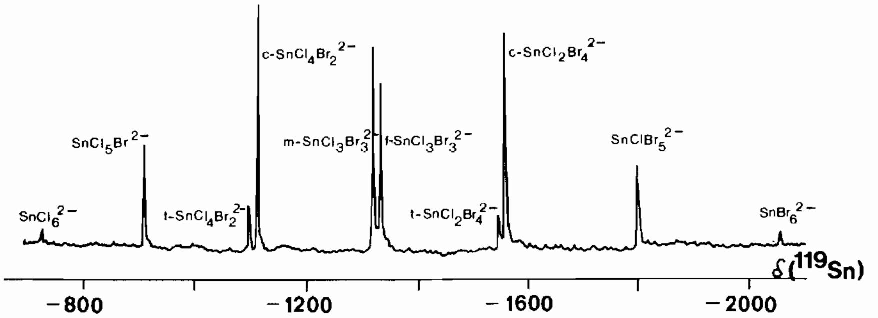

Fig. 1. The tin-119 NMR spectrum at −30 °C of a solution prepared by mixing SnCl$_6^{2-}$ and SnBr$_6^{2-}$ in 1:1 proportions.

TABLE I. Tin-119 NMR Data for Tin Tetrahalides in CS$_2$ at −30 °C.[a]

	δ (rel SnMe$_4$) (ppm)	δ (rel SnCl$_4$) (ppm)	
		Expt.	Calc.
SnCl$_4$	−150	0	0
SnCl$_3$Br	−265	−115	−115
SnCl$_2$Br$_2$	−382	−232	−232
SnClBr$_3$	−502	−352	−352
SnCl$_3$I	−543	−393	−399
SnBr$_4$	−623	−473	−473
SnCl$_2$BrI	−663	−513	−517
SnClBr$_2$I	−783	−633	−636
SnBr$_3$I	−905	−755	−757
SnCl$_2$I$_2$	−927	−787	−785
SnClBrI$_2$	−1057	−907	−906
SnBr$_2$I$_2$	−1176	−1026	−1028
SnClI$_3$	−1320	−1170	−1163
SnBrI$_3$	−1438	−1288	−1285
SnI$_4$	−1679	−1529	−1529

[a] Interaction parameters: Cl–Cl = 0, Br–Br = −79, I–I = −254.7, Cl–Br = −38.3, Cl–I = −133.1, Br–I = −173.5.

Results

The tin-119 NMR spectra of the tetrahalides SnX$_4$ were easily observed. Pairwise mixtures of 1:1 stoichiometry gave five resonances at room temperature which were a little broad, but cooling the solutions to −30 °C gave sharp resonances. The five resonances for each mixed solution correspond to the mixed halides SnX$_x$Y$_{4-x}$ (X, Y different halogens) which occurred in the statistical distribution expected for the random distribution of the halogens. A mixture of SnCl$_4$, SnBr$_4$ and SnI$_4$ in equimolar proportions showed all fifteeen possible species, although only three of these (those containing three different halogens) were new species not previously observed in the pairwise mixtures. The chemical shifts for the mixed tin(IV) halides are given in Table I and agree well with those reported previously [6]. The assignments and determination of the calculated chemical shifts for these tetrahalides and for all subsequent compounds will be given in the Discussion section.

These mixtures were observed in carbon disulphide solution, rather than dichloromethane which is the preferred solvent for the other types of compound, because SnI$_4$ is only sparingly soluble in dichloromethane. However, it was shown that the chemical shifts for SnCl$_4$ and SnBr$_4$, which are most important for later discussions, were almost unchanged in the two solvents.

The tin-119 NMR spectra of SnCl$_6^{2-}$ and SnBr$_6^{2-}$ were easily observed in dichloromethane solutions of the tetrabutylammonium salts. No signal could be found for SnI$_6^{2-}$ nor for mixtures of anions containing SnI$_6^{2-}$. However, an equimolar mixture of SnCl$_6^{2-}$ and SnBr$_6^{2-}$ showed the presence of all ten possible mixed halides [SnCl$_x$Br$_{6-x}$]$^{2-}$ in the statistical proportions as shown in Fig. 1. Exactly the same spectrum was obtained using a mixture of SnCl$_4$, SnBr$_4$ and NBu$_4$Br in the proportions 3:1:8, which is stoichiometrically equivalent to SnCl$_6^{2-}$ and SnBr$_6^{2-}$ in 1:1 proportions. Thus the halides freely exchange in solution, although this exchange is slow on the NMR time scale. Chemical shifts at −30 °C (to allow direct comparison with the SnCl$_4$/SnBr$_4$ mixtures) are given in Table II.

It is of interest to compare these results with those of Clark and coworkers [7] who prepared individual mixed halides by rapid precipitation reactions. They obtained clear evidence from Raman spectroscopy that single compounds were obtained by this technique. However, use of the tetrabutylammonium cation renders the salts soluble and in solution the halides exchange. We have found that interaction of SnCl$_4$ and two moles of NBu$_4$Br in dichloromethane gives all the mixed halides observed by mixing SnCl$_6^{2-}$ and SnBr$_6^{2-}$ (although of course the abund-

TABLE II. Tin-119 NMR Data for Hexahalostannate(IV) Anions in CH_2Cl_2 at –30 °C.[a]

	δ (rel $SnMe_4$) (ppm)	δ (rel $SnCl_4$) (ppm)	
		Expt.	Calc.
$SnCl_6^{2-}$	–732	–582	–569
$SnCl_5Br^{2-}$	–912	–762	–754
t-$SnCl_4Br_2^{2-}$	–1092	–942	–939
c-$SnCl_4Br_2^{2-}$	–1115	–965	–960
m-$SnCl_3Br_3^{2-}$	–1322	–1172	–1165
f-$SnCl_3Br_3^{2-}$	–1336	–1186	–1186
t-$SnCl_2Br_4^{2-}$	–1548	–1386	–1392
c-$SnCl_2Br_4^{4-}$	–1559	–1409	–1413
$SnClBr_5^{2-}$	–1800	–1650	–1660
$SnBr_6^{2-}$	–2064	–1914	–1929

[a] Interaction parameters: Cl–Cl = 0, Br–Br = –79 ppm (as for the tetrahalides). After correction for geometrical factors (see text) these become 0 and –113.3 ppm. δ_{charge} = –569 ppm. Cl–Br = –46.2 ppm which is the mean of values derived from $SnCl_5Br^{2-}$ and $SnClBr_5^{2-}$.

ances are weighted towards the chloride rich species.

Soluble salts of the pentahalo anions $SnCl_5^-$ and $SnBr_5^-$ were prepared by interaction of tin(IV) halide and one mole of NBu_4X in dichloromethane [8]. Their tin-119 NMR spectra were easily observed at –479 ppm ($SnCl_5^-$) and –1381 ppm relative to $SnMe_4$, but an equimolar mixture of the compounds gave no signal at room temperature. Attempts to observe mixed halide anions at low temperatures were thwarted by poor solubility.

The reactions between $SnCl_4$ or $SnBr_4$ and tributylphosphine give rise to insoluble products except when the phosphine is present in 2:1 proportion, or greater, and under these circumstances the only tin species present in solution is $SnX_4(PBu_3)_2$. At room temperature the phosphorus-31 NMR spectrum of each of these solutions consists of a sharp signal flanked by tin-117 and -119 satellites, but the resonance due to excess phosphine was quite broad. Cooling the solutions to –30 °C caused the resonance due to free phosphine to become very sharp. The tin-119 NMR spectrum consists of a sharp triplet whose coupling constant agrees with that derived from the phosphorus spectrum.

Reaction of SnI_4 with tributylphosphine gave quite different results. All stoichiometric ratios of halide to phosphine at all temperatures to as low as –100 °C gave only a single phosphorus resonance with no metal satellites. The position of the resonance varied with phosphine concentration and these results indicate that SnI_4 adducts with this phosphine are labile on the NMR time scale.

An equimolar mixture of $SnCl_4$ and $SnBr_4$ was treated with an excess of PBu_3. At room temperature the phosphorus-31 NMR spectrum showed six sharp resonances with tin satellites and a broad resonance due to the excess phosphine as shown in Fig. 2, but

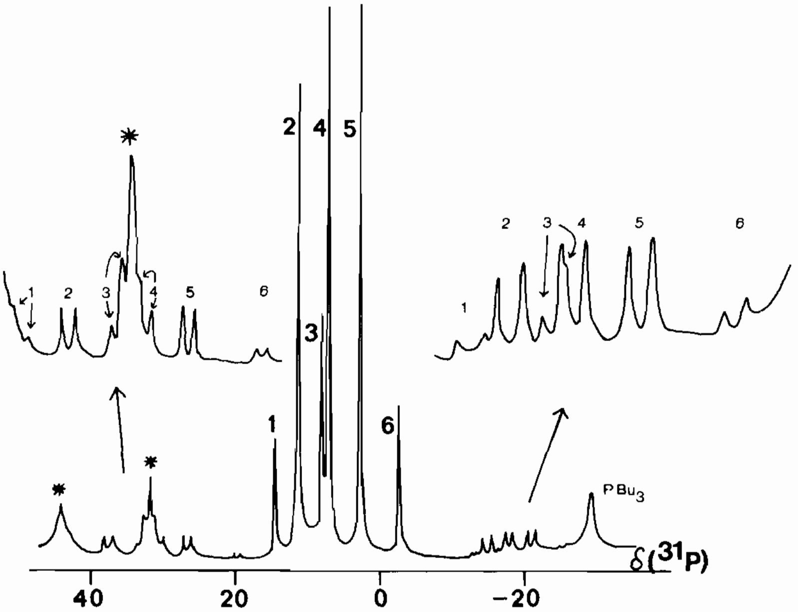

Fig. 2. The room temperature phosphorus-31 NMR spectrum of a solution obtained by treating a 1:1 mixture of $SnCl_4$ and $SnBr_4$ with excess PBu_3. The two peaks marked with asterisks are due to an impurity in the phosphine. The species are identified in Table III.

TABLE III. NMR Data for $SnCl_xBr_{4-x}(PBu_3)_2$ and $[SnCl_xBr_{5-x}(PBu_3)]^-$ Series in CH_2Cl_2 at −30 °C.[a]

			$\delta(^{119}Sn)$ (rel $SnMe_4$) (ppm)	$\delta(^{119}Sn)$ (rel $SnCl_4$)		$\delta(^{31}P)$ (ppm)	J(Sn–P) (Hz)
				Expt	Calc		
1	$SnCl_4(PBu_3)_2$		−573	−423	−430	14.3	2395
2	$SnCl_3Br(PBu_3)_2$		−658	−508	−508	11.0	2280
3	$SnCl_2Br_2(PBu_3)_2$	(t)	−738	−588	−567	7.5	2175
4	$SnCl_2Br_2(PBu_3)_2$	(c)	−750	−600	−587	6.5	2170
5	$SnClBr_3(PBu_3)_2$		−837	−687	−675	1.9	2065
6	$SnBr_4(PBu_3)_2$		−935	−785	−785	−4.0	1960
7	$[SnCl_5(PBu_3)]^-$		−652	−502	−494	14.0	2020
8	$[SnCl_4Br(PBu_3)]^-$	(Cl)	−783	−633	−621	13.5	1865
9	$[SnCl_4Br(PBu_3)]^-$	(Br)	−839	−689	−679	12.1	2010
10	$[SnCl_3Br_2(PBu_3)]^-$	(Cl, t)	−913	−763	−748	11.6	1720
11	$[SnCl_3Br_2(PBu_3)]^-$	(Cl, c)	−927	−777	−769	10.5	1710
12	$[SnCl_3Br_2(PBu_3)]^-$	(Br)	−986	−836	−827	10.0	1865
13	$[SnCl_2Br_3(PBu_3)]^-$	(Cl)	−1069	−919	−917	5.7	1565
14	$[SnCl_2Br_3(PBu_3)]^-$	(Br, t)	−1132	−982	−975	6.5	1720
15	$[SnCl_2Br_3(PBu_3)]^-$	(Br, c)	−1144	−994	−996	5.3	1720
16	$[SnClBr_4(PBu_3)]^-$	(Cl)	−1225	−1075	−1086	4.8	1405
17	$[SnClBr_4(PBu_3)]^-$	(Br)	−1301	−1151	−1164	0.1	1555
18	$[SnBr_5(PBu_3)]^-$		−1470	−1320	−1354	−6.9	1415

[a]The compound numbers refer to the resonances in Figs. 2, 3 and 4. Interaction parameters: Cl–Cl = 0, Br–Br = −113.3, Cl–Br = −46.2, P–Cl = −53.0, P–Br = −41.5 ppm. δ_{charge} = −282 ppm. For compounds 8–17 the halide *trans* to the phosphine is indicated after the formula. c and t refer to halides in the equatorial plane.

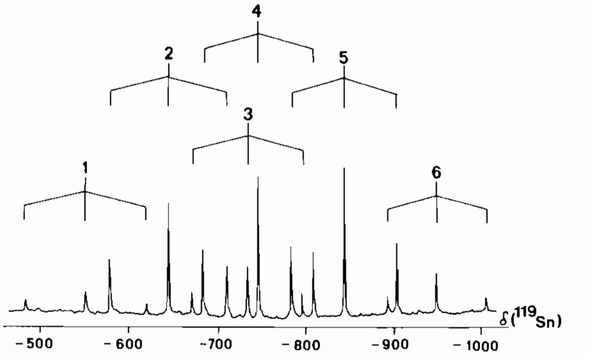

Fig. 3. The tin-119 NMR spectrum at −30 °C of a solution obtained by treating a 1:1 mixture of $SnCl_4$ and $SnBr_4$ with excess PBu_3. The species are identified in Table III.

at −30 °C the free phosphine resonance was sharp. The tin-119 NMR spectrum, shown in Fig. 3, consisted of six triplets whose coupling constants agreed with those derived from the phosphorus spectrum. The six species present are the *trans* isomers of $SnCl_xBr_{4-x}(PBu_3)_2$; chemical shifts and coupling constants are given in Table III.

The compounds $NBu_4[SnCl_5(PBu_3)]$ and $NBu_4[SnBr_5(PBu_3)]$ were prepared in solution by interacting $NBu_4[SnX_5]$ with one mole of phosphine. In each case the phosphorus-31 resonance consisted of a strong singlet flanked by tin satellites together with a weak resonance identified as due to $SnX_4(PBu_3)_2$. The tin-119 spectrum consisted of a strong doublet, whose coupling constant was equal to that observed in the phosphorus spectrum, and a weak singlet due to a SnX_6^{2-}. Thus solutions containing $[SnX_5(PBu_3)]^-$ undergo a small amount of disproportionation of the type

$$2[SnX_5(PBu_3)]^- \rightleftharpoons SnX_4(PBu_3)_2 + SnX_6^{2-}$$

with the bromo complex showing more disproportionation than the chloro one. This reaction has been reported previously [9] for the chloro system, but in that case the tetraethylammonium cation was used and the insoluble $[NEt_4]_2SnCl_6$ was precipitated driving the equilibrium to the right and thus $[SnCl_5(PBu_3)]^-$ was not observed.

An equimolar mixture of $[SnCl_5(PBu_3)]^-$ and $[SnBr_5(PBu_3)]^-$ gave complex phosphorus and tin

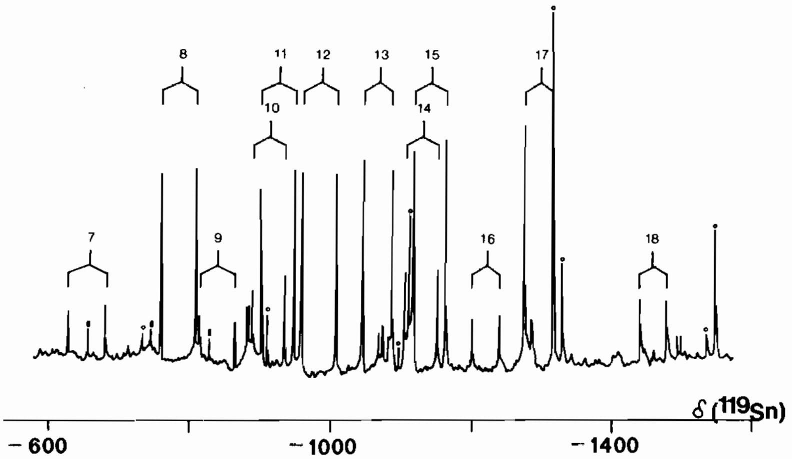

Fig. 4. The tin-119 NMR spectrum at −30 °C of a solution containing $[SnCl_5(PBu_3)]^-$ and $[SnBr_5(PBu_3)]^-$ prepared as described in the text. The species are identified in Table III. Resonances marked ● are due to $SnCl_xBr_{6-x}^{2-}$ and those marked ■ are due to $SnCl_xBr_{4-x}(PBu_3)_2$ species. Three small doublets are unidentified, but are probably tributylphosphine oxide complexes.

NMR spectra. The phosphorus-31 spectrum consisted of twelve moderate to strong resonances together with some weaker signals and a complex set of tin satellites. The phosphorus spectrum did not lead to an unambiguous identification of the species present in solution. However, the tin-119 NMR spectrum is extremely informative concerning the species in solution. As shown in Fig. 4, it consists of twelve doublets together with resonances for all the mixed halides $[SnCl_xBr_{6-x}]^{2-}$ ($SnClBr_5^{2-}$ and $SnBr_6^{2-}$ are present but occur at lower frequencies than covered by the Figure). Weak resonances due to $SnCl_xBr_{4-x}$-$(PBu_3)_2$ species can also be identified. The twelve doublets are clearly due to the twelve possible species (including isomers) in the series $[SnCl_xBr_{5-x}(PBu_3)]^-$ and indeed the two outermost doublets do correspond to the positions observed for $[SnCl_5(PBu_3)]^-$ and $[SnBr_5(PBu_3)]^-$. The spectrum observed by mixing exactly 1:1 proportions of the components gave relative abundances of $[SnCl_xBr_{5-x}(PBu_3)]^-$ species which were weighted towards the chloride rich species, whilst resonances due to $[SnCl_xBr_{6-x}]^{2-}$ were weighted towards the bromide rich species. The spectrum shown in Fig. 4 is that for a solution in which the abundances of $[SnCl_5(PBu_3)]^-$ and $[SnBr_5$-$(PBu_3)]^-$ were made equal by adding some excess of bromo compound whilst monitoring the phosphorus spectrum. This procedure, which was adopted to ensure identification of all the mixed halo monophosphine derivatives, meant that bromide rich species dominate the mixed hexahalo anion species in solution. Table III lists the chemical shifts and coupling constants for all these species.

Discussion

The interpretation of the results for the simple tetrahalides is straightforward. The identification of the various species is simplified by considering first the mixtures of two components and all chemical shifts can be rationalised by the well known pairwise additivity model introduced by Vladimiroff and Malinowski [10]. Pairwise additivity, which was first introduced to discuss carbon-13 shifts, recognises the change caused by a substituent on the wave functions of neighbouring substituents and allows calculation of the chemical shift by summing the pairwise interactions of all the substituents taken as adjacent pairs. In tetrahedral complexes the chemical shift of the central atom is calculated by summing pairwise interactions along the six edges of the tetrahedron. Thus, in the $SnCl_4/SnBr_4$ system the Cl–Cl and Br–Br interaction parameters are obtained from the parent compounds (1/6 the chemical shift) and a mean value for the Cl–Br interaction is obtained from $SnCl_3Br$ and $SnClBr_3$. It is important to note that the actual values of the parameters depend upon the choice of reference for the chemical shifts, but the additivity is independent of that choice. The tin halide system is unique among those studied by metal NMR because it gives well defined series of complexes with two stereochemistries in the same oxidation state, and the situation arises to investigate whether the same interaction parameters can be used in both systems. It quickly became apparent that for this purpose it is simpler to use $SnCl_4$ as the reference against which all calculations are performed, and the comparison between calculated and experimental chemical shifts for the tetrahalides is given in Table I.

For octahedral systems the method of application is exactly the same as for tetrahedral except that there are now twelve pairwise interactions for each species [11] and direct application of the method gives good agreement between experimental and calculated chemical shifts for the hexahalo anions.

However, we will calculate the shifts for octahedral complexes using the parameters derived from the tetrahedral species.

In the tetrahedron each halide has three neighbours and in the octahedron each has four, so that on a simple model the interaction parameters may be taken to increase by a factor 4/3 in the octahedron. Also there are twice as many edgewise interactions in the octahedron so the factor 8/3 may be used to convert chemical shift ranges from tetrahedral to octahedral systems. The observed chemical shift range from $SnCl_4$ to $SnBr_4$ is 473 ppm, so the expected range from $SnCl_6^{2-}$ to $SnBr_6^{2-}$ using the same interaction parameters is 473 X 8/3 = 1261 ppm. This is within 5% of the experimental value of 1332 ppm, so this geometrical approach does give acceptable predictions of the chemical shift range.

The model can be refined by allowing for the different bond lengths in tetrahedral and octahedral complexes. It appears that the crystal structure of $SnCl_4$ has not been determined, but electron diffraction [12] gives the Sn–Cl distance as 2.281 Å (Cl–Cl = 3.717 Å). X-ray diffraction gives a Sn–Br bond length of 2.40 Å for $SnBr_4$ [13]. Recent investigations of $SnCl_6^{2-}$ salts give a mean Sn–Cl bond length of 2.428 Å (Cl–Cl = 3.423 Å) [14, 15]. Only one recent report of the crystal structure of a $SnBr_6^{2-}$ salt has appeared [16] which reported a Sn–Br distance of 2.593 Å. Fortunately, the percentage increase in bond length in changing from $SnCl_4$ to $SnCl_6^{2-}$ is almost the same as for changing from $SnBr_4$ to $SnBr_6^{2-}$, so the same correction can be applied in each case.

Allowing for the different halogen–halogen contact distances in the anions compared to the tetrahalides, and assuming that interaction is inversely proportional to the halogen–halogen separation, the predicted chemical shift range for the hexahalo anions is

$$473 \times 8/3 \times \frac{3.717}{3.423} = 1369 \text{ ppm}$$

compared with the experimental value of 1332 ppm. This is an error *overall* of some 3% which is comparable with the accuracy of empirical approaches to carbon chemical shifts over much smaller chemical shift ranges.

The only remaining problem is how to allow for the difference in chemical shift of the two types of compound due to charge. The relationship is of the form

$$\delta_{oct} = \delta_{tet} + \delta_{charge}$$

We have selected that value of δ_{charge} (= –569 ppm) which gives the minimum in the algebraic sum of the differences between calculated and observed chemical shifts over all the species. Calculated and experimental results are given in Table II and it can be seen that the agreement is excellent. This is the first time that the same interaction parameters, corrected for geometrical factors, have been used for two series of complexes of different stereochemistries.

The relative intensities of the resonances are confirmatory evidence for the assignments as they are those expected for a random distribution of the halide anions, so there can be no doubt as to not only the stoichiometry, but also the geometrical identity, of each of the mixed halide anions.

Tin tetrahalides form a large number of complexes of the type SnX_4L_2 which can have either *cis* or *trans* stereochemistry, but on the basis of vibrational and Mössbauer spectroscopy most authors [17–22] agree that phosphine adducts are *trans*. This stereochemistry has been confirmed for $SnCl_4(PEt_3)_2$ by X-ray diffraction [23]. The NMR spectra of either $SnCl_4(PBu_3)_2$ or $SnBr_4(PBu_3)_2$ alone would not give information on the stereochemistry since the tin signal would be a triplet for both isomers. However, the NMR spectrum for a mixture of these two compounds for either phosphorus-31 or tin-119 indicates that for all the mixed compounds $SnCl_xBr_{4-x}(PBu_3)_2$ the two phosphorus atoms are equivalent. For several of the species this can only be true if the phosphines are mutually *trans*, or if rapid intramolecular exchange between *cis* and *trans* isomers were occurring. The abundances of the various isomers are exactly those predicted for a random distribution of the halides with the phosphines *trans*. If both *cis* and *trans* isomers were present in solution but undergoing exchange which was rapid on the NMR time scale, the relative abundances of the various species would be very different. We conclude, therefore, that only *trans* phosphine species are present in the solution.

Tin chemical shifts of the $SnCl_xBr_{4-x}(PBu_3)_2$ series were calculated using the same halogen-halogen interaction parameters as for the hexahalo anion series, but two additional parameters are required. The P–Br interaction parameter was determined from $SnBr_4(PBu_3)_2$ and that for P–Cl from $SnCl_3Br(PBu_3)_2$*. The calculated and experimental chemical shifts are given in Table III and the excellent agreement provides confirmatory evidence of the identity of the species.

Similarly, the chemical shifts of all the members of the $[SnCl_xBr_{5-x}(PBu_3)]^-$ system can be calculated using the interaction parameters derived from the $SnCl_xBr_{4-x}(PBu_3)_2$ series provided a correction is made for charge as before. This correction was first

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*It was noticed that the chemical shift of $SnCl_4(PBu_3)_2$ was slightly variable for reasons which are not clear, but no other member of the series showed this behaviour.

determined approximately by calculating the chemical shift for $[SnCl_5(PBu_3)]^-$ and comparing it with the experimental value. The chemical shifts of all the species were then calculated with this initial value of δ_{charge} and the final value was selected, as before, by minimising the sum of positive and negative errors over all the isomers. This final value (= –282 ppm) was then used to calculate the values given in Table III. Not only are the calculated chemical shifts in excellent agreement with the experimental values – thus providing a very useful guide to assignment of the spectrum – but the charge correction in this case for a single negative charge is almost exactly half the value found, quite independently, for the double charge correction for the hexahalo anions. As mentioned earlier, the spectrum in Fig. 4 is for a solution in which the proportions of $[SnCl_5(PBu_3)]^-$ and $[SnBr_5(PBu_3)]^-$ were adjusted to be equal, thus allowing for the greater disproportionation of the bromo complex. As a result, all the other $[SnCl_xBr_{5-x}(PBu_3)]^-$ species are present in the statistical distribution (1:4:1:2:4:4:4:2:4:1:4:1) which gives strong confirmation of the assignments made in Table III.

The tin-phosphorus coupling constants for the $[SnCl_xBr_{5-x}(PBu_3)]^-$ series also show interesting and unexpected properties. The value of J(Sn–P) depends entirely upon the identity of the four halides *cis* to the phosphine in the equatorial plane of the anion. Thus, both complexes with four chlorines in the plane have the same coupling constant within experimental error. All four complexes with two chlorines and two bromines in the plane (compounds 10, 11, 14, 15) have the same coupling constant and similar relationships occur throughout the series. Although there is little opportunity to make such observations for the $SnCl_xBr_{4-x}(PBu_3)_2$ series, the coupling constants for the two compounds with two chlorines and two bromines in the equatorial plane are equal.

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