Investigations of Tin(II) Halide Aqueous Solutions and Solvent Extracts by ^{119}Sn Nuclear Magnetic Resonance Spectroscopy: Characterisation of the Trihalogenostannate(II) Anions $[SnX_3]^-$, $[SnX_2Y]^-$, and $[SnX(Y)Z]^-$ (X, Y, or Z = Cl, Br, or I)

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The ^{119}Sn chemical shifts of all ten trihalogenostannate(II) anions $[SnCl_xBr_yI_z]^-$ ($x + y + z = 3$) are observed in diethyl ether extracts of tin(II) mixed-halide systems measured at −60 °C. The tin(II) nuclear shielding order I < Br < Cl is the opposite of that found in tin(IV) halide systems. At room temperature, the tin resonance signals of tin(II) complexes in aqueous HCl, HBr, and HI solutions, or their solvent extracts, are single peaks whose positions depend on the composition of the phase, showing that several species are in rapid equilibrium. The complex acids $H[SnX_3]$ exhibit ^{119}Sn chemical shifts of $\delta = -40$ (X = Cl), +135 (X = Br), and +350 (X = I) p.p.m. in ether extracts at room temperature.

The trihalogenotin group, now well known as a ligand in transition-metal compounds, was first identified in the complex acids $HSnX_3$ (X = Cl or Br) in ether extracts studied by Raman spectroscopy.[1] Subsequently, several groups investigated salts of these complexes and the corresponding mixed halides using far-i.r., Raman, and Mössbauer spectra.[2–6] *X*-Ray structural analyses are available for solids containing the $[SnCl_3]^-$ and $[SnBr_3]^-$ ions which confirm that the structures are trigonal pyramidal with a lone pair of electrons in the valence shell of tin.[7–9] The nature of tin(II) halide solutions is incompletely understood. Complex ions are formed and it is possible that the species present include solvated $SnCl_2$, $[SnCl_3]^-$, and $[SnCl_4]^{2-}$.[10,11] Although ^{119}Sn n.m.r. spectroscopy has been applied extensively to organometallic and co-ordination compounds of tin,[12–15] few tin(II) systems have been examined by this technique.[16–19] Tin(II) chloride in hydrochloric acid is an important reducing agent possibly through reactions involving $[SnCl_3]^-$. The trihalogenostannate(II) ions deserve attention as structures in which a main group element in its lower oxidation state is co-ordinatively unsaturated.

We have used the technique of solvent extraction[20] to obtain diethyl ether phases containing the complexes $[SnX_3]^-$, $[SnX_2Y]^-$, $[SnXY_2]^-$, $[SnY_3]^-$, and $[SnX(Y)Z]^-$ (where X, Y, and Z = Cl, Br, or I) and investigated the ^{119}Sn n.m.r. spectra, including low-temperature measurements which are necessary to observe the discrete species. For the $[SnX_3]^-$ complex anions we find that the chemical shift moves downfield in the order Cl < Br < I, making the iodide the system in which the tin nucleus is the least shielded. This is the opposite of the trend in the tin(IV) tetrahalides and hexahalide complexes, $[SnX_6]^{2-}$.[21]

Results and Discussion

Tin(II) *Halide Aqueous Solutions.*—In the earliest report of ^{119}Sn n.m.r. spectra, Burke and Lauterbur[16] found that the chemical shift of $SnCl_2 \cdot 2H_2O$ in aqueous solution was dependent upon the concentration of added hydrochloric acid between δ −520 in water and *ca.* −340 p.p.m. in 8—12 mol dm^{-3} HCl. Our measurements of 1—2 mol dm^{-3} $SnCl_2$ solutions confirm this trend and give a limiting value of δ −335 p.p.m. for the chemical shift of the species present in concentrated HCl. Tin(II) bromide and iodide solutions exhibit the same kind of behaviour. The limiting chemical shifts are −190 for the bromide system and −105 p.p.m. for iodide. The evidence of other techniques,[10,11,22] notably Raman spectroscopy,[1,5] suggests that the major species in these solutions are the complex ions $[SnX_4]^{2-}$ although it is possible that the chemical shift represents the average of several species in equilibrium. This must be the situation in solutions of low HX concentration where the chemical shift depends on the composition, and it is likely that aquated complexes, *e.g.* $[SnX_2(H_2O)_x]$, are important.

The ^{119}Sn n.m.r. spectra of mixed-halide solutions also consist of single sharp lines, the positions of which depend on the composition of the mixture and lie between those of the separate chloride, bromide, or iodide systems. Again it is clear that the signals are the averages of the various species present which are labile on the n.m.r. time-scale at room temperature.

Solvent Extracts of Tin(II) *Halide Solutions.*—The ^{119}Sn n.m.r. spectrum of the diethyl ether extract of 1.5 mol dm^{-3} $SnCl_2$ in 6 mol dm^{-3} HCl solution is a signal, δ −78 p.p.m., well removed from that of the aqueous solution at −336 p.p.m. Other $SnCl_2$ solutions yield solvent extracts in which the n.m.r. signal of the tin(II) species varies with the HCl concentration of the system, as shown in Table 1. The $SnBr_2$ solutions exhibit similar behaviour, and again the signal given by the extract is well removed from that of the species in aqueous solution. Previous experience[1,20] has shown that ether extraction discriminates against doubly charged complexes, such as $[SnCl_4]^{2-}$ in the present instance. We believe that the signal due to the extracted species at room temperature, whose chemical shift varies with the composition of the system (Table 1), arises from $[SnCl_3]^-$ in equilibrium with other complexes, most likely $[SnCl_2(H_2O)]$ and/or $[SnCl_3(H_2O)]^-$. The n.m.r. spectrum of an acetone solution of hydrated $SnCl_2$ crystals which contain the entity $SnCl_2(H_2O)$[22] is a signal at δ −150 p.p.m. (linewidth 1 500 Hz) which closely resembles the spectrum of the ether extract from aqueous 1 mol dm^{-3} $SnCl_2$ in 2 mol dm^{-3} HCl. The ether extract from $SnCl_2$ in 8 mol dm^{-3} HCl gives a signal at δ = −40 p.p.m., and that from $SnBr_2$ in at least 6 mol dm^{-3} HBr gives δ = +135 p.p.m. We attribute these signals, which move slightly to −29 and +140 p.p.m., when the extracts are cooled to −40 °C, to $[SnCl_3]^-$ and $[SnBr_3]^-$, respectively. The Raman spectra of these extracts agree with those of earlier work[1,4] which were attributed to these species in the form of the complex acids $H[SnX_3]$ (X = Cl or Br).

Table 1. N.m.r. spectra of tin(II) halide aqueous solutions and solvent extracts at room temperature

$SnCl_2$ solutions (1.0 mol dm^{-3})	[HCl] (mol dm^{-3})	N.m.r. data*		
		Aqueous soln.	Et_2O extract	$Bu^i(Me)CO$ extract
	2	−429 (80)	−150 (1 000)	
	4	−365 (75)	−75 (150)	−78 (65)
	6	−336 (70)	−55 (65)	
	8	−332 (70)	−40 (65)	
$SnBr_2$ solutions (0.5 mol dm^{-3})	[HBr] (mol dm^{-3})			
	2	−365 (80)	+82 (800)	
	4	−230 (80)	+118 (150)	+114 (180)
	6	−207 (80)	+136 (125)	
	8	−188 (80)	+135 (100)	

* Chemical shift, $\delta(^{119}Sn)$/p.p.m., with linewidth/Hz in parentheses.

Table 2. Tin-119 n.m.r. data for tin(II) mixed-halide complexes in diethyl ether extracts

(*a*) At + 22 to −60 °C

Temperature/°C	Chloride + bromide[a]		Bromide + iodide[b]		Chloride + iodide[c]	
	δ/p.p.m.	Linewidth/Hz	δ/p.p.m.	Linewidth/Hz	δ/p.p.m.	Linewidth/Hz
22	22	180	169	550	70	3 000
0	25	550	178	1 500	(v br)	
−20	28	1 700	*ca.* 180	(br)	(v br)	
−40	*ca.* 5	(br)	*ca.* 180	(br)	Four peaks[d]	
−60[e]	Four peaks		Four peaks		Four peaks	

(*b*) Trihalogenostannate(II) ions at −60 °C

Anion	δ/p.p.m.	Linewidth/Hz
(**1**) $[SnCl_3]^-$	−26	2 400
(**2**) $[SnCl_2Br]^-$	33	2 400
(**3**) $[SnClBr_2]^-$	87	1 750
(**4**) $[SnBr_3]^-$	142	1 200
(**5**) $[SnBr_2I]^-$	226	1 100
(**6**) $[SnBrI_2]^-$	301	700
(**7**) $[SnI_3]^-$	362	400
(**8**) $[SnCl_2I]^-$	118	2 700
(**9**) $[SnClI_2]^-$	252	1 200
(**10**) $[SnCl(Br)I]^-$	176	2 500

[a] Extract of 1.5 mol dm^{-3} $SnCl_2$ aqueous solution in 3 mol dm^{-3} HCl + 2 mol dm^{-3} HBr. [b] Extract of 1 mol dm^{-3} $SnBr_2$ aqueous solution in 2 mol dm^{-3} HBr + 1 mol dm^{-3} LiI. [c] Extract of 1 mol dm^{-3} $SnCl_2$ aqueous solution in 5 mol dm^{-3} HCl + 1 mol dm^{-3} LiI. [d] Broad peaks at 360, 250, *ca.* 100, and −25 p.p.m. [e] The spectra are shown in Figure 1 and the chemical shifts of the species are listed in part (*b*).

Vibrational spectra have shown the occurrence in tin(II) mixed-halide systems of the trihalogenostannate(II) anions $[SnCl_2Br]^-$ and $[SnClBr_2]^-$ which are recognised by their individual Raman and i.r. frequencies.[3,4] We examined the ^{119}Sn n.m.r. spectrum of the ether extract of a tin(II) solution in 3 mol dm^{-3} HCl and 2 mol dm^{-3} HBr in anticipation of finding the mixed-halide complexes but instead observed only a single line, δ +60 p.p.m. (linewidth 320 Hz). The result of mixing the separate ether extracts from HCl and HBr solutions was similar; in this instance a line at δ +40 p.p.m. (linewidth 225 Hz). Investigations of bromide and iodide, or chloride and iodide, mixtures gave analogous results, but in the Cl/I case the signal from the ether extract was a broad resonance. This suggested slower exchange, implying that the discrete signals of the constituent species should appear in the spectra of samples at low temperature.

Table 2 gives the ^{119}Sn n.m.r spectra of ether extracts of tin(II) mixed-halide solutions at a series of temperatures. For each mixture, the initially sharp signals became very broad on cooling, before dividing into four separate peaks at −60 °C (Figure 1). At this temperature the signals are evidently those of the complexes $[SnX_3]^-$, $[SnX_2Y]^-$, $[SnXY_2]^-$, and $[SnY_3]^-$ (for each pair of Cl, Br, and I). Several points deserve attention. If random mixing prevails in the equilibrium mixture the species $[SnX_2Y]^-$ and $[SnXY_2]^-$ should outweigh their progenators by 3 to 1. When the areas of the peaks in Figure 1 are compared, this ratio is found to hold almost exactly for the Cl/Br system. However, in the Cl/I system the amounts of all four species are about equal. In this respect the behaviour of the present trihalogenostannate(II) complexes parallels that of several other systems which have been investigated by n.m.r. spectroscopy, particularly those of boron halides[23] and gallium halide complex anions, $[GaX_4]^-$.[24,25] The chemical shifts of the trihalogenostannate(II) anions are given in Table 2(*b*). The list includes $[SnCl(Br)I]^-$ which was identified by an additional peak, between those of $[SnBr_3]^-$ and $[SnBr_2I]^-$, in the spectrum of a sample prepared by combining Sn/Br/I and Sn/Cl/Br ether extracts. This spectrum contained the resonances of all ten complex anions; the chemical shifts were the same as those of the binary mixtures of halides although the peaks were somewhat broader and only small amounts of $[SnCl_3]^-$, $[SnBr_3]^-$, and $[SnI_3]^-$ were present. For completely random reorganisation

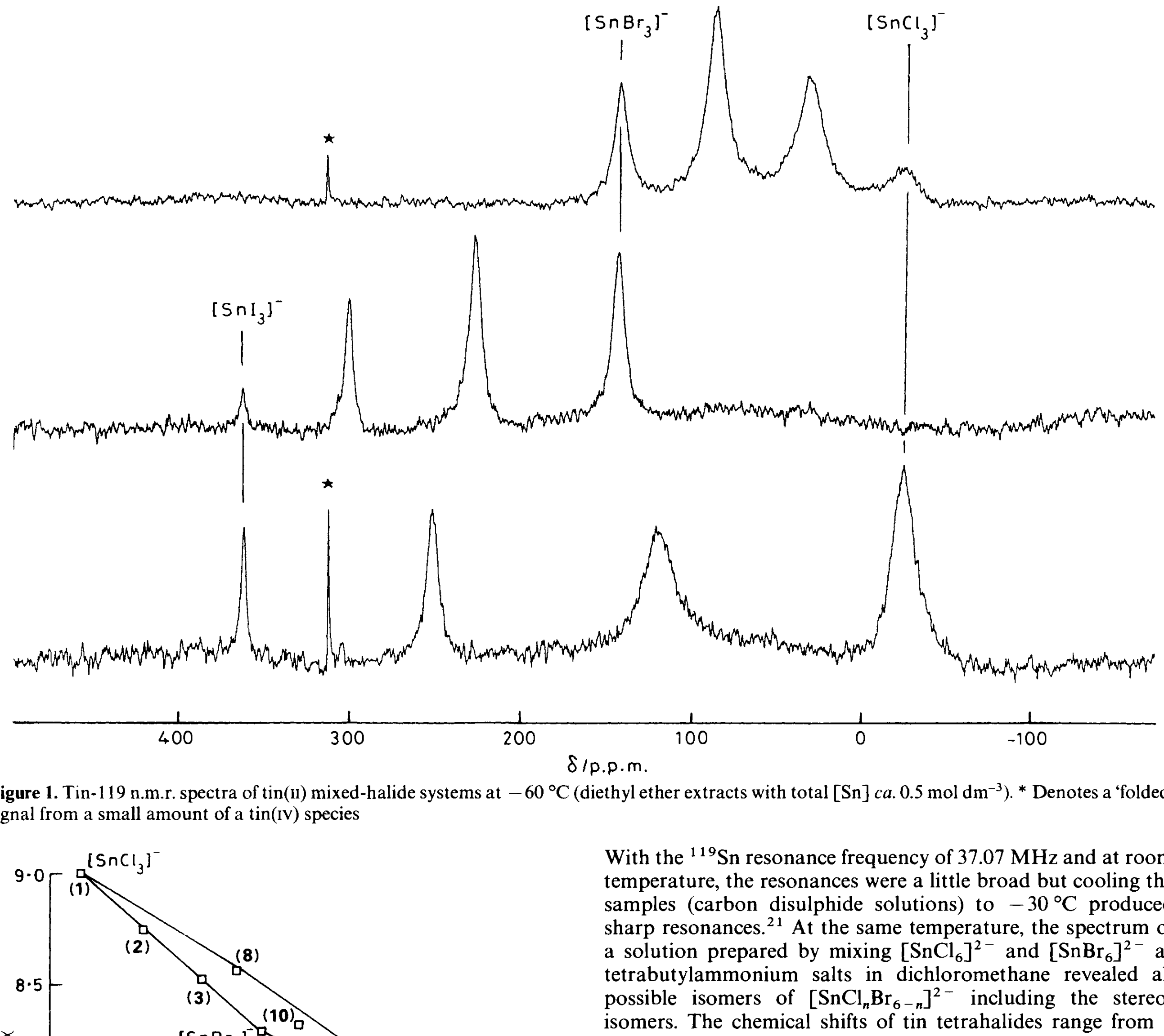

Figure 1. Tin-119 n.m.r. spectra of tin(II) mixed-halide systems at -60 °C (diethyl ether extracts with total [Sn] *ca.* 0.5 mol dm^{-3}). * Denotes a 'folded' signal from a small amount of a tin(IV) species

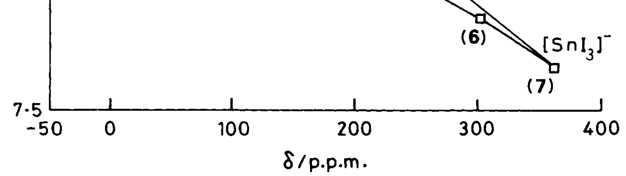

Figure 2. Tin-119 chemical shift–Mulliken electronegativity correlation for the $[SnCl_xBr_yI_z]^-$ ($x + y + z = 3$) ions. Key numbers refer to the entries in Table 2

the three unmixed species should be present in amounts of 3.7% in the 1 : 1 : 1 mixture at equilibrium. There should be 11.1 mol % of each of the species of the type SnX_2Y, and 22.2 mol % of SnX(Y)Z, and our spectrum gave peaks in approximately these proportions.

The tin halides, mixed halides, and halogeno-complex ions of the tin(IV) oxidation state have been studied extensively by n.m.r. spectroscopy.[12,16,21] For the tetrahalides, pairwise mixtures gave all five resonances of the species SnX_nY_{4-n} in the amounts expected for random distribution of the halogens. With the ^{119}Sn resonance frequency of 37.07 MHz and at room temperature, the resonances were a little broad but cooling the samples (carbon disulphide solutions) to -30 °C produced sharp resonances.[21] At the same temperature, the spectrum of a solution prepared by mixing $[SnCl_6]^{2-}$ and $[SnBr_6]^{2-}$ as tetrabutylammonium salts in dichloromethane revealed all possible isomers of $[SnCl_nBr_{6-n}]^{2-}$ including the stereoisomers. The chemical shifts of tin tetrahalides range from δ -150 ($SnCl_4$) to $-1\,679$ p.p.m. (SnI_4), and of the tin(IV) complex anions from δ -732 ($[SnCl_6]^{2-}$) to $-2\,064$ p.p.m. ($[SnBr_6]^{2-}$).[21] The tin(II) complex anions display chemical shifts ranging from δ $+362$ ($[SnI_3]^-$) to $+142$ ($[SnBr_3]^-$) and -26 p.p.m. ($[SnCl_3]^-$). The shielding of the tin nucleus is considerably less in the tin(II) species than it is in the tin(IV) systems, perhaps because a lower co-ordination number is involved. Whereas the tin(IV) compounds have the shielding order Cl < Br < I, which is regarded as normal halogen dependence,[26] the tin(II) halides show the opposite order. Within the present series $[SnCl_xBr_yI_z]^-$ ($x + y + z = 3$) the chemical shift of tin in the environment of a lone pair of electrons and trigonal co-ordination of the halide ligands is a function of the ligand electronegativity. As shown in Figure 2, the dependence of δ on the total ligand electronegativity is almost linear for a given pair of halides. This parallels the correlation of the Mössbauer isomer shift with electronegativity found by Clark *et al.*[3]

The shielding order I < Br < Cl is found among compounds of the transition metals in which the valence shell is either half-filled or complete.[26] Among main group systems, boron shows the order Cl < Br < I in both BX_3 and $[BX_4]^-$ species.[23] The antimony trihalides SbX_3, which are isoelectronic with the $[SnX_3]^-$ ions, have not been characterised by n.m.r.

spectroscopy due to the fact that the quadrupole moment of ^{121}Sb makes this a difficult nucleus for systems of other than cubic symmetry. A failure to observe ^{121}Sb resonances from $SbCl_3$ in HCl, or $SbBr_3$ in HBr, has been reported.[27] In the case of phosphorus trihalides, mixed halides are readily observed at room temperature by ^{31}P n.m.r. spectroscopy, and their exchange reactions take some minutes to reach equilibrium.[28,29] The order of phosphorus nuclear shielding by the halogen ligands is an irregular one, Br < Cl < I, which reflects the influences of π bonding as well as trends in the ionic character of the P–X bond with the change of ligand electronegativity.[29] The present data for the trihalogenostannate(II) ions are supplemented by those for $[SnF_3]^-$, for which the ^{119}Sn chemical shift is -700 p.p.m.[19] It appears that the increase in the ionic character of the tin–halogen bond from Sn–I to Sn–F is accompanied by a marked increase in the shielding of the tin nucleus which can be attributed to the influence of the non-bonding electron pair.

Investigations of the SnF_2–F^-–H_2O system by ^{19}F and ^{119}Sn n.m.r. and Mössbauer spectroscopy provide evidence of rapid ligand exchange between several solution species, including $[SnF_2(H_2O)]$, $[SnF_3]^-$, and possibly $[Sn_2F_5]^-$.[19] It is likely that similar equilibria occur in the chloride, bromide, and iodide solutions of the present study, and that alterations in these equilibria explain the large changes in the tin resonance as a function of the composition of the solution. However, the chemical shift of a particular tin complex species is unlikely to alter much with a change of solvent.[14–16] Thus we can conclude that $[SnCl_3]^-$, with δ -40 p.p.m. in ether extracts at room temperature, is not present in other than small amounts in aqueous or hydrochloric acid solutions of $SnCl_2$, for which the tin resonance is a signal within the range δ -520 to -335 p.p.m. The increase in shielding which characterises the aqueous solution species, compared with the $[SnX_3]^-$ ions, suggests an environment of higher co-ordination number than three, and the complexes $[SnCl_2(H_2O)_2]$, $[SnCl_3(H_2O)]^-$, and $[SnCl_4]^{2-}$ may be the principal species in aqueous chloride media.

For comparison with the aqueous and solvent extract phases, we measured the n.m.r. spectra of solutions of $SnCl_2 \cdot 2H_2O$ in dimethylformamide (dmf), and in dimethyl sulphoxide (dmso). The resonances, *ca.* -300 p.p.m. in dmf and *ca.* -400 p.p.m. in dmso, depend on the solvent and on the concentration of the solution (as already found for anhydrous solutions of $SnCl_2$ or $SnBr_2$ in these donor solvents[18]). This behaviour, which can be ascribed to co-ordination to the tin(II) centre, is also manifest in a dependence of the tin chemical shifts of the $[SnCl_3]^-$ and $[SnBr_3]^-$ ions on the nature of the solvent. For several combinations of tin(II) complex and solvent we find the following $\delta(^{119}Sn)$ values: $AsPh_4SnCl_3$, -51 p.p.m. in CH_2Cl_2; $NBu^n_4SnCl_3$, -52 p.p.m. in CH_2Cl_2, -42 p.p.m. in MeCN, -28 p.p.m. in dmf; $NBu^n_4SnBr_3$, 117 p.p.m. in CH_2Cl_2, 113 p.p.m. in dmf, 122 p.p.m. in MeCN. An additional value, that of $PBu^t_3HSnCl_3$, -30 p.p.m. in CH_2Cl_2,[17] suggests that the chemical shift is influenced by the counter ion, at least in a case where the cation ($[PBu^t_3H]^+$) might be expected to interact with the tin(II) complex anion. The major point, however, is that the chemical shifts of tin(II) species in donor solvents or in solutions with a co-ordinating ligand are consistent with the well established property of tin in the tin(II) state to expand the valence shell beyond an octet.[22] The capacity of tin(II) to attain co-ordination numbers above three provides the means to explain another aspect of the behaviour of the present systems, which is the rapid exchange of ligands in mixed-halide systems, not only the aqueous solutions but also the ether extracts. We envisage that ligand exchange by reaction (1) can proceed *via* species of the type $[X_2Sn(\mu\text{-}X)(\mu\text{-}Y)SnY_2]^{2-}$ in which tin becomes four-co-ordinate. We note that, although such doubly bridged species have not been reported for tin, there are reports of halogen-bridged tin(II) anions such as $[Sn_2Cl_5]^-$ and $[Sn_2Br_5]^-$ in molten salt systems of $SnX_2 + MX$, and of crystalline pentahalogenodistannate(II) salts $M[Sn_2X_5]$.[6,22] An alternative mechanism is one involving the initial dissociation of $[SnX_3]^-$ to solvated SnX_2 and X^- but this seems a less likely route, particularly for reaction in a solvent of low polarity such as ether.

$$[SnX_3]^- + [SnY_3]^- \rightleftharpoons [SnX_2Y]^- + [SnXY_2]^- \qquad (1)$$

In previous investigations of the trihalogenostannate(II) complexes by means of vibrational spectra[3,4] it was shown that salts of the discrete anions $[SnX_2Y]^-$ and $[SnX(Y)Z]^-$ could be prepared, and the spectra of solutions were attributed to a single complex. For example, the i.r. and Raman spectra of $NBu^n_4[SnCl(Br)I]$ in acetone consist of bands at 276, 190, and 155 cm^{-1}, assigned to $\nu(SnCl)$, $\nu(SnBr)$, and $\nu(SnI)$ stretching modes, respectively, of the $[SnCl(Br)I]^-$ complex ion. While these assignments are likely to be correct, the evidence of rapid reorganisation of ligands among tin(II) halide complexes, which the present study provides, means that the solution samples of the previous work almost certainly consisted of mixtures in which the assigned bands are those of the major component. The inference of the earlier vibrational spectroscopic studies[3,4] was that the various $[SnCl_xBr_yI_z]^-$ ions existed as kinetically stable entities in solutions of their salts, whereas these ions are now shown to be among the most labile of all mixed halides.

Experimental

Crystalline $SnCl_2 \cdot 2H_2O$ and $SnBr_2 \cdot 2H_2O$ were used to prepare aqueous HCl or HBr solutions to which small amounts of tin powder were added to prevent oxidation, $SnI_2 \cdot 2H_2O$ was synthesised[3,11] and used to prepare a solution in 3 mol dm^{-3} HI. Mixed-halide solutions were made by combining these samples, or by adding LiI to Sn^{II}–HCl or –HBr solutions. Organic solvent extracts were obtained by shaking equal volumes of the chosen aqueous phase with either diethyl ether or isobutyl methyl ketone. The identity of the extracted species $HSnX_3$ (X = Cl, Br, or I)[1,4] was checked by observing the Raman spectra of the organic solvent phase using instruments and techniques described previously.[30] The salt $NBu^n_4SnCl_3$[4] was obtained as a crystalline solid by adding NBu^n_4Cl to a solution of $SnCl_2$ in 6 mol dm^{-3} HCl; $AsPh_4SnCl_3$ and $NBu^n_4SnBr_3$ were prepared similarly.

Tin-119 n.m.r. spectra at 149.215 MHz were obtained using a 10-mm broad-band probe in a Bruker AM400 spectrometer operating at 295 K. Low-temperature spectra were measured using a nitrogen-flushed Dewar system controlled by a Bruker B-VT 1000 unit. Spectra were collected with 16 K data points over 100 000 Hz using a 90° pulse (14 μs). Typically the pulse repetition rate was 0.2 s and the data were processed using a line broadening of 50 Hz. Internal locking signals were provided by the addition of small amounts of D_2O to aqueous solutions or $CDCl_3$ to organic solvent samples. Spectra were referenced against external $SnMe_4$. The high-frequency positive convention is used.

Acknowledgements

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