Tin-119 Nuclear Magnetic Resonance Studies of Some Mixed Halogeno-complexes of Tin(IV)

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Several chlorofluorostannates $[SnCl_nF_{6-n}]^{2-}$, and all the bromochlorostannates $[SnCl_nBr_{6-n}]^{2-}$, have been identified in solution by means of ^{119}Sn n.m.r. spectroscopy. Isomeric configurations where $n = 2$, 3, or 4 have been assigned by the method of pairwise interactions.

Mixed hexahalogenostannates(IV) are well established, and may be prepared in solution by various methods, including ligand exchange between different ions $[SnX_6]^{2-}$ and $[SnY_6]^{2-}$, substitution, for example of another halide by fluoride, and sometimes by addition of different halide ions to the tin(IV) halide SnX_4. The fluoro-complexes in particular have been investigated in MeOH, $CHCl_3$ or dimethyl sulphoxide (dmso) solution by ^{19}F n.m.r. spectroscopy.[1] Complete identification of species containing one kind of fluorine environment only was sometimes difficult, however, and several $^1J(^{19}F-^{119}Sn)$ values could not be determined.[1] The increased availability of multinuclear Fourier-transform (F.t.) spectrometers provides an alternative method, ^{119}Sn n.m.r. spectroscopy, for investigating these complexes.

We report the results from such a study of the chlorofluorostannates $[SnCl_nF_{6-n}]^{2-}$ in CH_2Cl_2 solution with $NBu^n{}_4{}^+$, $N(C_5H_{11})_4{}^+$ (C_5H_{11} = n-pentyl), or $PBu^n{}_4{}^+$ as counter ions, which gives information complementary to the data obtained previously.[1] We also give the shift values for the bromochlorostannates $[SnCl_nBr_{6-n}]^{2-}$ (as their $PBu_4{}^+$ salts) at 307.2 K where all the possible isomers were detected. While this work was in progress, the results of a similar study at a lower temperature (243 K) were reported; [2] the shift values are somewhat to higher field at the higher temperature. Isomeric configurations in both series have been assigned by the method of pairwise interactions, originally proposed for ^{13}C chemical shifts in tetrahedral species by Vladimiroff and Malinowski [3] and since applied extensively to octahedral complexes of niobium,[4] antimony,[5] and phosphorus,[6-10] as well as from the signal multiplicities of the fluoro-complexes.

Experimental

All manipulations involving hydrolysable compounds were carried out either *in vacuo* or under an atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, in general without further purification apart from tetra-alkylammonium chlorides which were dried as described previously,[9] and SnI_4 which was recrystallised from $CHCl_3$. Tetra-n-butylammonium fluoride was obtained from Dr. C. J. Ludman of this Department as a water clathrate containing between 27 and 33 mol of water. The exact fluoride content was determined by elemental analysis. This compound was used, together with $SnCl_4$, SnF_4, PBu_4Cl and $N(C_5H_{11})_4Cl$, to prepare the $[SnCl_nF_{6-n}]^{2-}$ ions by mixing the appropriate quantities of the reagents in CH_2Cl_2. Once the NBu_4F had dissolved in CH_2Cl_2, the water separated out and could be removed by pipette. Little or no evidence of hydrolysis was found as a result of this procedure.

Tetrabutylphosphonium Hexachlorostannate, $[PBu_4]_2[SnCl_6]$. -This was prepared by stirring PBu_4Cl and $SnCl_4$ in a 2 : 1 ratio in concentrated aqueous HCl for 1 h. The resulting solid was filtered off, dried *in vacuo*, and recrystallised from Me_2CO to give white needles (Found: C, 45.3; H, 8.9. $C_{32}H_{72}Cl_6P_2Sn$ requires C, 45.2; H, 8.5%).

Tetrabutylphosphonium Hexabromostannate, $[PBu_4]_2[SnBr_6]$. —This was prepared by stirring a 2 : 1 mixture of PBu_4Cl and $SnBr_4$ in a large excess of concentrated aqueous HBr for several hours. The solid product was filtered off, dried *in vacuo*, and recrystallised from Me_2CO to give yellow needles (Found: C, 34.6; H, 7.3; Br, 40.4; P, 4.6; Sn, 12.0. $C_{32}H_{72}Br_6P_2Sn$ requires C, 34.4; H, 6.5; Br, 42.9; P, 5.5; Sn, 10.6%). The ^{119}Sn n.m.r. spectrum of the product in CH_2Cl_2 showed a small peak due to $[SnClBr_5]^{2-}$ (δ −1 815 p.p.m.) as well as the $[SnBr_6]^{2-}$ signal (δ −2 075 p.p.m.), but from the relative intensities the impurity appeared to be present only in *ca.* 1% abundance.

Trimethylsulphonium Hexaiodostannate, $[SMe_3]_2[SnI_6]$.—This was obtained by dissolving recrystallised SnI_4 in $CHCl_3$ and adding the stoicheiometric quantity of SMe_3I in acetone. The mixture was stirred for 30 min, but the product showed evidence of incomplete reaction. It was stirred in concentrated aqueous HI–acetone (1 : 1) for 2 h, filtered off, washed with EtOH and Et_2O, and dried in a desiccator (Found: C, 7.1; H, 1.7; I, 70.1; S, 6.3; Sn, 11.9. $C_6H_{18}I_6S_2Sn$ requires C, 7.0; H, 1.8; I, 73.6; S, 6.2; Sn, 11.5%).

Tetrapropylammonium Hexaiodostannate, $[NPr^n{}_4]_2[SnI_6]$.—This was similarly prepared by mixing stoicheiometric quantities of SnI_4 and NPr_4I, each dissolved in $CHCl_3$. The instant black precipitate was filtered off and washed with Et_2O (Found: C, 22.3; H, 4.7; I, 60.6; N, 2.6; Sn, 7.5. $C_{24}H_{56}I_6N_2Sn$ requires C, 23.0; H, 4.5; I, 60.8; N, 2.2; Sn, 9.5%).

^{119}Sn N.m.r. spectra were recorded at 307.2 K on a Fourier-transform multinuclear spectrometer constructed by Dr. A. Royston, which utilises the permanent magnet (1.4 T) from a Perkin-Elmer R10 spectrometer, a Racal 9061/2 frequency synthesiser as the frequency source, a Dec pdp 11/34 computer, and a HIPLOT digital plotter. Samples were contained in stationary sample tubes (outside diameter 8.4 mm). Chemical shifts were measured relative to external $SnMe_4$, with the downfield direction taken as positive.

Results and Discussion

(*a*) *Chlorofluorostannates*(IV).—Mixtures of chlorofluorostannate(IV) ions were prepared in CH_2Cl_2 solution as described above; the proportions of species present were altered by varying the quantities of reagents used. The ^{119}Sn n.m.r. spectra were complex because of spin–spin coupling and overlap of the resultant multiplets, particularly for Cl : F ratios close to 1 : 1 where many species coexist in solution. The best

Table 1. $\delta(^{119}Sn)$ for $[SnCl_nF_{6-n}]^{2-}$ in CH_2Cl_2

Ion	Multiplicity	$\delta(^{119}Sn)$/p.p.m. Observed [a]	Calculated	$^1J(^{19}F-^{119}Sn)$/Hz
$[SnCl_6]^{2-}$	Singlet	−733.0	−733.0	—
$[SnCl_5F]^{2-}$	Doublet	−695.5	−698.4	2 430
trans-$[SnCl_4F_2]^{2-}$	Triplet	−666.7 [b](?)	−663.9	1 943 [b](?)
cis-$[SnCl_4F_2]^{2-}$	Triplet	−685.5	−687.7	2 263
mer-$[SnCl_3F_3]^{2-}$	Doublet of triplets	—	−676.9	—
fac-$[SnCl_3F_3]^{2-}$	Quartet	−697.0	−700.6	2 056
trans-$[SnCl_2F_4]^{2-}$	Pentet	−688.5 [b](?)	−689.9	—
cis-$[SnCl_2F_4]^{2-}$	Triplet of triplets	−716.8	−713.6	1 821, 2 132
$[SnClF_5]^{2-}$	Doublet of pentets	−755.3	−750.4	1 528, 1 875
$[SnF_6]^{2-}$	Septet	−810.8	−810.8	1 579

[a] ±2 p.p.m. [b] Poorly resolved, weak peak.

Table 2. $\delta(^{119}Sn)$ for $[SnCl_nBr_{6-n}]^{2-}$ in CH_2Cl_2 at 307.2 K

Ion	$\delta(^{119}Sn)$/p.p.m. Observed *	Calculated
$[SnCl_6]^{2-}$	−729.3	−729.3
$[SnCl_5Br]^{2-}$	−916.1	−917.4
trans-$[SnCl_4Br_2]^{2-}$	−1 106.6	−1 105.4
cis-$[SnCl_4Br_2]^{2-}$	−1 120.5	−1 123.4
mer-$[SnCl_3Br_3]^{2-}$	−1 330.1	−1 329.5
fac-$[SnCl_3Br_3]^{2-}$	−1 344.0	−1 347.6
trans-$[SnCl_2Br_4]^{2-}$	−1 560.6	−1 553.6
cis-$[SnCl_2Br_4]^{2-}$	−1 571.0	−1 571.7
$[SnClBr_5]^{2-}$	−1 815.5	−1 813.8
$[SnBr_6]^{2-}$	−2 074.0	−2 074.0

* ±2 p.p.m.

method for identification of individual ions was to prepare initially mixtures rich in either Cl or F, so that certain species ($[SnCl_6]^{2-}$, $[SnCl_5F]^{2-}$, $[SnClF_5]^{2-}$, $[SnF_6]^{2-}$) could readily be detected. This was facilitated to some extent by a knowledge of some of the coupling constants from a previous ^{19}F n.m.r. study,[1] although these had been determined in different solvents. In the spectra of the more complex mixtures seven of the ten possible ions were successfully identified from their characteristic splitting patterns; the results are shown in Table 1. This enabled the pairwise interaction terms [3-10] to be evaluated. The F–F and Cl–Cl terms were taken as −67.57 and −61.08 p.p.m. respectively from the shifts of $[SnF_6]^{2-}$ and $[SnCl_6]^{2-}$, while the average value of −52.45 p.p.m. found from several ions was used for the F–Cl term. The calculated chemical shifts, including those for the other three possible species, are included in Table 1.

Possible resonances from *trans*-$[SnCl_4F_2]^{2-}$ and *trans*-$[SnCl_2F_4]^{2-}$ were then tentatively identified from the spectra, although these ions gave only poorly resolved, weak signals even after *ca.* 70 000 pulses. One surprising feature was that the *mer* isomer of $[SnCl_3F_3]^{2-}$ could not be located; on statistical grounds it should be more abundant than *fac*-$[SnCl_3F_3]^{2-}$, and its strongest peaks would then be readily observable in spectra of mixtures with a Cl : F ratio close to 1 : 1. The failure to detect this species, together with the weakness of the resonances assigned to *trans*-$[SnCl_4F_2]^{2-}$ and *trans*-$[SnCl_2F_4]^{2-}$, strongly suggests that a *cis* configuration for two (or more) fluorines in chlorofluorostannates may be more stable than a *trans* arrangement. Similar directing effects have been observed in other systems, for example in azidochlorophosphates(v) where an exclusively *cis–fac–cis* pattern of substitution was found to operate.[6,7]

Table 1 shows that the pairwise method gives very reasonable agreement (within 5 p.p.m.) with the observed values of the ^{119}Sn chemical shifts, and successfully predicts that the resonance at lowest field will be that of *trans*-$[SnCl_4F_2]^{2-}$. It was noticed, however, that the Cl–F interaction terms calculated from the experimental shifts of individual isomers increased systematically with the number of fluorines present, before the average was evaluated. This trend suggests that additional fluorines complement each other in shielding the tin nucleus, and that the simple pairwise-additivity model is not sophisticated enough to cope with this detail. The model assumes a constant (O_h) geometry and deviations from this idealised structure may account in part for the observed variation in the interaction terms.

Comparison of the coupling constants (Table 1) with those obtained from ^{19}F n.m.r.[1] shows reasonable agreement, in view of the different solvents used. The ^1J value for $[SnF_6]^{2-}$ of 1 579 Hz lies well within the reported range from 1 557 Hz in water to 1 603 Hz in dmso.[1] ^1J Values have been measured for the first time for $[SnCl_5F]^{2-}$, *cis*-$[SnCl_4F_2]^{2-}$, and (possibly) *trans*-$[SnCl_4F_2]^{2-}$.

(*b*) *Bromochlorostannates*(IV).—Exchange between $[SnCl_6]^{2-}$ and $[SnBr_6]^{2-}$ was studied *via* their tetrabutylphosphonium salts in CH_2Cl_2 solution. Both compounds and their exchange products were found to be very soluble in this solvent. All ten possible bromochlorostannates $[SnCl_nBr_{6-n}]^{2-}$ ($0 \leqslant n \leqslant 6$) were observed (Table 2); their signal intensities were as expected from statistical considerations, and no directing influence on substitution seemed to occur, unlike the chlorofluorostannates. The pairwise-interaction terms were readily evaluated. The Cl–Cl term was taken as −60.78 p.p.m. and the Br–Br term as −172.83 p.p.m. from the shifts of $[SnCl_6]^{2-}$ and $[SnBr_6]^{2-}$ respectively, while the Cl–Br term was taken as the mean value (−107.79 p.p.m.) from all other possible isomers. (Initially the Cl–Br term was found from the experimental shift of $[SnCl_5Br]^{2-}$, and this value was used to assign isomeric configurations to all the other ions; the Cl–Br terms were then evaluated for each ion and the mean value determined.) Table 2 shows that the overall agreement between observed and calculated values is very good in this series.

While this work was in progress the results of a similar study at 243 K, using the tetrabutylammonium salts, were reported.[2] Comparison of the chemical shifts shows that, with the exception of $[SnCl_6]^{2-}$, the values are to higher field at 307.2 K by between 4.1 and 15.5 p.p.m. Without a more detailed investigation it is not possible to say whether this effect is due solely to temperature variation, or whether the change of counter ion also makes a contribution. ^{119}Sn N.m.r.

shifts are often markedly dependent on temperature, solvent, and concentration,[11] and although the effects may well be smaller for six- than four-co-ordinate species, they could account for the observed differences.

(*c*) *Exchange Reactions involving Iodostannates*(IV).—No ^{119}Sn n.m.r. signals could be obtained from solutions of either trimethylsulphonium or tetrapropylammonium hexaiodostannates, and the main effect of adding $[SnI_6]^{2-}$ to a solution containing $[SnX_6]^{2-}$ ($X = Cl$ or Br) was the fading out of the $[SnX_6]^{2-}$ signal when sufficient hexaiodostannate had been added. Similar behaviour was observed by Colton *et al.*[2] The reasons for this are not clear; the presence of iodine substituents may induce rapid relaxation of the tin nuclei, possibly because of quadrupolar effects, or there could be fast exchange between the various species in the mixtures, giving rise to one or more very broad peaks which could be difficult to detect, but the latter process would not account for the failure to observe signals from $[SnI_6]^{2-}$ salts alone. The only (presumed) evidence for iodo-complexes came from addition of iodine ions (as tetra-n-alkylammonium salts) to $[SnX_6]^{2-}$ ($X = Cl$ or Br) solutions in CH_2Cl_2. For $[SnCl_6]^{2-} + N(C_5H_{11})_4I$ two signals were observed at -729.9 ($[SnCl_6]^{2-}$) and -813.7 p.p.m., while for $[SnBr_6]^{2-} + NPr_4I$ two peaks were found at $-2\,074.8$ ($[SnBr_6]^{2-}$) and $-2\,179.6$ p.p.m. These signals cannot be assigned to individual ions in the absence of other information, and may well arise from exchanging species, since a higher-field shift than that found for $[SnCl_5Br]^{2-}$ may reasonably be expected for $[SnCl_5I]^{2-}$.

The results show that ^{119}Sn n.m.r. spectroscopy is a valuable technique for detecting the formation of mixed halogeno-complexes of tin(IV), particularly when used in conjunction with the method of pairwise interactions which enables isomeric configurations to be assigned.

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