Spectroscopic and structural studies of tin complexes

A. Marshall

SPECTROSCOPIC AND STRUCTURAL STUDIES OF TIN COMPLEXES

by

A. MARSHALL B.Sc.
(Hatfield College)

A thesis submitted for the degree of Doctor of Philosophy in the University of Durham.

October 1982

To Gillian, my family and friends.

"For the beaute, for the force and for the resonsunce".

(W. de Worde, 1506 - an early spectroscopist)

ACKNOWLEDGEMENTS

I would like to thank my supervisor Dr. K.B. Dillon for his full help and encouragement throughout the period of this study. Further thanks go to Dr. J.C. Halfpenny (x-ray crystallography), Mr. R. Coult (elemental analysis), Mrs. M. Cocks (microanalyses), Mr. A.J. Tate (differential scanning calorimetry) and Dr. R.S. Matthews (^{19}F n.m.r.). Dr. A. Royston deserves a special mention for his expertise in constructing and maintaining the multinuclear n.m.r. spectrometer.

The comments, suggestions and guidance of J. Lincoln, A.W.G. Platt, R.M.K. Deng and G.F. Hewitson throughout the practical work are also acknowledged. Final thanks are given to the S.R.C. for the maintenance award, and for help in producing the thesis to Mrs. E.M. Nevins, for the diagrams, and Miss J. Eccleston for the typing.

DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1979 and October 1982. This work has not been submitted completely or in part, for a degree in this or any other university and is the original work of the author except where acknowledged by reference.

ABSTRACT

Several hexachlorostannate (IV) and hexabromostannate (IV) salts have been prepared and studied by halogen n.q.r. spectroscopy. Correlations were found to exist between the ^{35}Cl or ^{79}Br n.q.r. frequencies and the respective Sn-Cl and Sn-Br bond lengths in the hexahalostannate ions. A similar correlation was also found for some trichlorostannate (II) ions. An approximate relationship between cation size and average n.q.r. frequency was deduced for the hexahalostannates. Crystal structure determinations by Dr. J.C. Halfpenny of $(pyH)_2SnBr_6$ and $(Me_2NH_2)_2SnBr_6$ are reported in this context. These two compounds were also studied by variable temperature n.q.r., together with $Me_3NHSnCl_3$ and seven hexachlorostannates, which revealed the existence of a number of structural phase changes between 77K and 300K.

^{119}Sn n.m.r. spectroscopy has been used to study the concentration behaviour of several stannous halides in solution, and a relationship between the chemical shift at infinite dilution and the dielectric constant of the solvent was noted. The effect of halide ions on the chemical shifts of some stannous halides and some preliminary investigations into tin (II) cyanide complexes are described. Pairwise interaction theory has been used extensively in the interpretation of the results of exchange reactions in solution between octahedral tin complexes containing chloride, bromide, fluoride, azide, cyanide and thiocyanate ligands, and has enabled isomeric configurations to be assigned to many of the observed species. This theory was also used in analysing the chemical shifts of exchange products between some stannic halides in carbon disulphide, methanol and ethanol. In addition, the behaviour of $SnCl_4$, $SnBr_4$ and SnF_4 individually in aqueous media has been followed by ^{119}Sn n.m.r. measurements. The solid state ^{119}Sn n.m.r.

spectra of several tin (II) and tin (IV) compounds have been recorded and these are believed to be the first reports of such measurements.

List of Abbreviations

n.q.r.	nuclear quadrupole resonance
n.m.r.	nuclear magnetic resonance
e.f.g.	electric field gradient
i.r.	infra-red
D.S.C.	differential scanning calorimetry
D.T.A.	differential thermal analysis
pyH^+	pyridinium
$lutH^+$	lutidinium
e.g. $4\text{-}ClpyH^+$	4-chloropyridinium
Me	methyl
Et	ethyl
Prop	propyl
But	butyl
Pent	pentyl
Ph	phenyl
δ	^{119}Sn chemical shift

CONTENTS

CHAPTER 1

Introduction

The most powerful tools available to the chemist are those encompassed by the broad term of spectroscopy. In this work the main probes used are those which utilise the phenomenon of resonance between radiofrequency radiation and nuclei with a non-zero spin. These techniques are namely nuclear magnetic resonance (n.m.r.) and nuclear quadrupole resonance (n.q.r.). The former is well established and extensively used throughout chemistry, and the latter, though in less common use, provides exclusive information on compounds in the solid state available from no other techniques. The aim of this thesis is to apply these methods to the study of inorganic tin complexes in the solid state and in solution. Complexes of the type M_2SnX_6 (M = various cations, X = Cl, Br, F, I, CN, N_3) and $MSnX_3$ (M = various cations, X = Cl, Br) together with some tin (II) halides in various solvents, have been studied in this work.

Hexahalometallates have been extensively studied by n.q.r.[1] Much of the early work[2,3] was aimed at obtaining quantitative data on the nature of the metal to halogen bonds utilising the Townes-Dailey equation.[4,5] Further developments have since been made on the various factors which affect the positions of resonance lines. These include investigations of the effect of temperature,[6,7] pressure,[8,9] thermal expansion,[10,11] halogen to metal bond length[12-17] and type of cation.[18,19] The number of these factors reflects the uncertainty in what governs the position of resonance lines.

The variation of n.q.r. frequencies with temperature is particularly interesting. The technique is very sensitive and many studies[20-25] have

aimed at the detection and interpretation of structural phase changes. Models have been constructed to describe the general temperature behaviour,[26] which are mainly quite successful, such as those proposed by Bayer[6] and Kushida.[7] Other workers on R_2MX_6 compounds have developed methods[23,27] of predicting phase changes and interpreting them in terms of qualitative changes in the halogen n.q.r. spectra. Several reports of temperature variation studies on hexachloro- and hexabromostannates exist in the literature. Apart from n.q.r.[22-25,27-31] other techniques have been used to detect phase changes such as infra-red (i.r.),[32,33] ultrasonics,[34] Raman,[35] optical microscopy[36] and calorimetry.[37] These are often used in a confirmatory[29-30] role to n.q.r., as it is the only one of these techniques which looks directly at the nuclei - through their electronic environments.

The magnitude of an n.q.r. frequency reflects the size of the electric field gradient (e.f.g.) at the resonant nucleus when comparing the same nuclei. In general, s-orbital electrons contribute little to the e.f.g. (unless hybridisation occurs) as they are spherically symmetrical. The main contributions come from the p- and d-orbital electrons, which are the ones mainly involved in the formation of chemical bonds. This has led to speculation of whether a relationship exists between bond length and n.q.r. frequency for chemically bonded quadrupolar nuclei. Linear relationships have been found between the ^{35}Cl n.q.r. frequency and the M-Cl bond length in chlorocyclophosphazenes,[12,13] platinum (II) chloride[14] adducts, tetrachloroiodates,[15] and adducts of stannic chloride;[17] a non-linear relationship for some mercury (II) chloride systems has also been reported.[16] The hexachlorostannates appear not to show a correlation, however;[19] indeed differences in frequencies have been attributed to

different cation size[18,19] for this class of compounds. This conclusion was based on the study of the cations: K^+, NH_4^+, Rb^+, Cs^+ and Me_4N^+, where the anions all have regular octahedral geometry[19] with Sn-Cl bond lengths varying only between 2.402 - 2.423Å. The bond length correlation found for the tetrachloroiodates[15] spanned bond lengths of 2.42 - 2.60Å, due to severe distortions of the anions. Only one attempt[38] to compare n.q.r. frequencies with Sn-Cl bond length for hexachlorostannates with distorted anions has been made, for the compound $(4\text{-ClpyH})_2SnCl_6$, where there appears to be a correlation between n.q.r. frequency and bond length.

Many hexachlorostannates have been studied by x-ray diffraction, although much of the earlier work provided data with error limits too large[39-41] to be of use for comparison of bond lengths with n.q.r. frequencies. Others quoted unit cell dimensions only.[33,42,43] More recent data, however, has produced better accuracy for the hexachlorostannates with the following cations: NH_4^+,[19,44] K^+,[19,44] Rb^+,[19] Cs^+,[19] Me_4N^+,[19,57] Et_3NH^+,[45] Et_4N^+,[80] $Me_2NH_2^+$,[79] 4Cl-pyH^+,[38] $(Me_2N)_2CH^+$,[46] $PhCH{:}NH_2^+$,[48] $Ph_2C{:}NH_2^+$,[47] $(H_9O_4)_2.H_2O^{2+}$[123] and $Ca(H_2O)_6^{2+}$.[30] Fewer hexabromostannates have been studied. The early work[49] manifests the same inaccuracies as for the chloro-compounds. The only recent structure determination in which bond lengths are quoted[37] is for K_2SnBr_6.

Several hexahalostannates containing mixed halogens have been described.[50-56] These have largely been studied by vibrational spectroscopy[50,51,53] although ESCA,[55] photoelectron[54] and Mössbauer[51,52] spectroscopy have also been applied. The compounds prepared have mainly been of the type $SnX_4Y_2^{2-}$ (X, Y = F, Cl, Br, I), and were found to have the cis-configuration of ligands. Chlorobromostannates with morpholinium and piperidinium cations have however been prepared[53] with the halogens in the trans-configuration. Russian workers[56] also claim the preparation

of some compounds containing $SnXY_5^{2-}$ and $SnX_3Y_3^{2-}$ (X, Y = Cl, Br) ions.

Halide complexes of tin (II) are in general more difficult to prepare than those of tin (IV). This is due to the existence of several different types of anions and careful control of the ratio of reactants needs to be used to synthesize the desired products. Compounds of the type $MSnX_3$,[58-71] $MX.SnX_3$,[58,65,66,70] MSn_2X_5[58,65,66,70-72] and MSn_3F_{10}[73] (X = F, Cl, Br, I; M = monopositive cation) have been reported in the literature. The susceptibility to oxidation by atmospheric oxygen of these complexes is also a problem.[62,63,78] Characterisation and investigation of the tin (II) complexes has been carried out by a variety of techniques (Mössbauer,[58,62,63] i.r.,[59,67] Raman,[62,63] x-ray diffraction[60,61,70-76] and n.q.r.[76,77]) and the compounds are now well established. Little work has been done on the n.q.r. with only the compounds $CsSnX_3$ (X = Cl, Br, I)[77] and $[SnCl_3][SnCl(OH_2)_2].H_2O$[76] studied to date.

Very little work has been published on the ^{119}Sn n.m.r. of inorganic tin complexes to date.[81] This reflects to some extent the problems in detecting the ^{119}Sn nucleus. Despite it being the most abundant (8.6% natural abundance) of the tin isotopes which have a nuclear spin of one half (the others are ^{115}Sn and ^{117}Sn), ^{119}Sn still only has about one twentieth of the sensitivity of hydrogen in the n.m.r. experiment.[81] This means that Fourier transform n.m.r. is usually necessary for the procurement of spectra of reasonable resolution, for all but the most easily observable systems. The lack of protons in inorganic systems in general precludes the use of double resonance techniques in this case, although one study[82] has been made using ^{19}F for double resonance experiments. Work in this area is therefore restricted to those who have

access to the necessary Fourier transform spectrometers.

Molecular tin (IV) chloride, bromide and iodide, and their exchange products have been investigated by Burke and Lanterbur;[83] the chemical shifts of a few other compounds were also quoted by them. This work[83] was the first to record the observation of the n.m.r. phenomenon from tin compounds. Further work[84] has been described on tin tetrachloride with hydrochloric acid in acetone and water solutions, as well as on tin tetrabromide,[84] while other workers[85] have confirmed some of the chemical shifts obtained by Burke and Lanterbur from more recent studies. The only inorganic, six-coordinate tin complexes investigated by ^{119}Sn n.m.r. to date are $Na_2Sn(OH)_6$,[83,85] $K_2Sn(OH)_6$,[83] SnF_6^{2-} [82] and $SnCl_6^{2-}$ (in 25 oleum and 100% H_2SO_4).[121]

The ^{119}Sn n.m.r. data available on tin (II) compounds is also very sparse. The chemical shifts of $SnCl_2$ in tetrahydrofuran, water and hydrochloric acid have been recorded[81,85] as well as the chemical shift of $SnBr_2$ in hydrobromic acid,[85] all at single concentrations. A recent paper,[86] however, gives information on the variation of chemical shift with solvent and concentration for SnF_2, $SnCl_2$, $SnBr_2$ and SnI_2 in dimethylsulphoxide, hexamethylphosphoramide, dimethylformamide and Me_2O. Tin (II) has also been studied, in the form of trichlorostannate as a ligand, in anions of the type $[M(SnCl_3)_5Cl]^{4-}$, (Me = Ru, Os). In these papers,[87,88] coupling constants are reported for the ^{117}Sn and ^{115}Sn isotopes with ^{119}Sn, as well as for ^{119}Sn with itself, though it should be noted that 600,000 scans of 0.3 sec. duration using a 22 mm. diameter sample were necessary to obtain some of the spectra from the Fourier transform spectrometer used.

A number of pseudohalogeno-derivatives of tin have been prepared.

$Sn(CN)_2$ has been isolated[89] from the reaction of HCN with cyclopentadienyl tin (II) compounds, while $Sn(CN)_4$ is claimed to have been observed in flame photometry experiments.[90] Compounds containing the $[Sn(N_3)_6]^{2-}$ ion have been synthesized by several workers,[91-93] from the reaction of NaN_3 with $SnCl_6^{2-}$ or $SnCl_4$ in various media. In addition, for the azides, anions of the type $[cis\ SnCl_4(N_3)_2]^{2-}$, $[Cl_4Sn(\mu\text{-}N_3)_2SnCl_4]^{2-}$ and $[SnCl_4(N_3)I]^{2-}$ have been prepared[94,95] as their tetramethylammonium salts. $[Sn(NH_2)_6]^{2-}$ has been reported to be formed from the action of KNH_2 on Ph_4Sn in liquid ammonia,[96,97] while $[Sn(IO_3)_6]^{2-}$ has been prepared[98] from K_2SnCl_6 or Li_2SnCl_6 with iodic acid in dilute nitric acid solution. $[Sn(OCN)_6]^{2-}$ has been made[99] by an exchange reaction between $(Me_4N)_2SnCl_6$ and AgOCN in acetone. Other examples of these types of complexes in the literature include $[Sn(NO_2)_6]^{2-}$,[100] $[Sn(SCN)_6]^{2-}$ [101] and $[SnCl_4(SCN)_2]^{2-}$,[102] the latter from experiments in a liquid SO_2 medium.

CHAPTER 2

Experimental

(a) Handling of Moisture- or Oxygen-Sensitive Materials

The principal technique employed in the manipulation of compounds of this type was to handle them under a dry nitrogen atmosphere. A glove box was mainly used for this purpose. This was built in the University workshops and was equipped with a large entry port (approx. 12 in. x 6 in. diameter) and a small "quick-entry" port (approx. 6 in. x 2 in. diameter). The former was purged with nitrogen gas over a period of 30 - 40 mins. before access, while the latter took only a few seconds to purge using the excess pressure caused by pushing the gloves into the box. The inert atmosphere was produced by passing nitrogen from a laboratory line through a column packed with phosphorous pentoxide into the box. A dish of phosphorous pentoxide was also kept in the box, to remove the last traces of water present, and replenished when necessary. To enable suction filtration, a water pump was connected to one of the box inlet pipes via a cold trap cooled with an acetone/solid CO_2 bath. The trap has two-fold use in preventing water diffusing into the box while at the same time stopping harmful materials getting out of the box and into the laboratory atmosphere. A recirculation pump was also placed inside the box so the atmosphere could be passed through a second cold trap overnight, and hence purged of undesirable gases and vapours. Other manipulations under nitrogen were performed in "Quickfit" apparatus using an appropriate arrangement of taps and tubes connected to the laboratory supply of the gas. In particular this was used for reactions where water, ethanol, acetone or methanol were used as solvents, these materials being undesirable in the glove box.

(b) The Vacuum Line

This was used for pumping off solvents to leave dry solids from solution, for drying damp materials, for degassing solvents and for the manipulation of volatile materials. The line was equipped with several B14 "Quickfit" sockets which allowed connection to a mercury manometer and an Edwards "Vacustat" gauge to monitor pressure, and a nitrogen line so that vessels could be let down to dry nitrogen instead of air. The vacuum was produced by an Edwards "Speedivac" high vacuum pump which was protected from the line by two traps cooled by liquid nitrogen.

(c) Chemicals and Solvents

All chemicals and solvents used were of the best available commercial grades except where cost proved prohibitive. Purification was carried out by recrystallisation for solids, and distillation for solvents, when necessary. To obtain degassed solvents for use with oxygen-sensitive compounds the liquids were pumped under vacuum, but without boiling, and let down to dry nitrogen. This cycle was repeated four of five times, the solvent then being stored under a nitrogen atmosphere. Solvents for use in the glove box were dried using a grade 4A molecular sieve. Tetraalkylammonium halides were dried by pumping under vacuum on a water bath for several hours. The dryness of the compounds was then checked by recording their i.r. spectra.

(d) Preparation of Starting Materials

(i) Tin (II) bromide[103-106] was prepared by dissolving granulated tin in an excess of concentrated hydrobromic acid which had first been degassed from oxygen and let down to nitrogen. After complete solution of the tin and cessation of hydrogen gas evolution, the liquid was pumped off on the vacuum line to leave the anhydrous product, a pale yellow powder. The

compound was found to be dry by the absence of O-H peaks in the infra-red spectrum and characterised by elemental analyses:

Expected for $SnBr_2$ Sn 42.62% Br 57.38%

Found Sn 41.7% Br 57.5%

(ii) Tetrabutylammonium cyanide was prepared according to the method of Platt.[120] 20 mls. of 41% aqueous But_4NOH and 40 mls. MeOH were placed in a flask connected to the vacuum line, frozen to 77K and evacuated. 1.4 mls. HCN were then condensed into a graduated cold finger and further transferred to the flask. After allowing the mixture to warm to room temperature the solvent was pumped off on a water bath. The remaining solid was then redissolved in toluene which was again pumped off. The product was then pumped for 3 hrs. to leave the anhydrous product.

Analyses: Expected for But_4NCN C 76.12% H 13.43% N 10.45%

Found C 74.85% H 16.66% N 9.33%

(iii) Tetrabutylammonium azide was prepared by the action of hydrogen azide on tetrabutylammonium hydroxide. HN_3 was not isolated during the preparation due to its unpleasant nature, but instead it was made as an aqueous solution according to a method in the literature.[111] In a typical preparation 2.73 g. NaN_3, 0.7 g. NaOH and 25 mls. H_2O were placed in a distillation apparatus. When the solution was boiling, 15 mls. 40% H_2SO_4 were added in drops. The distillate was collected in a flask containing 16 mls. of 41% But_4NOH; this mixture being constantly stirred. When only about 10 mls. of mother liquor remained the distillation was stopped. The distillate was then extracted with CH_2Cl_2 and the latter was pumped off on the vacuum line to leave a reddish brown oil. This was then dried using MeOH and toluene and the resulting sludge was stirred for several hours with 30 - 40° petroleum ether, under dry nitrogen, to leave a powdery orange-pink

solid. The final product was kept and used under anhydrous conditions due to its hygroscopic nature.

Analyses: Expected for But_4NN_3 C 67.61% H 12.68% N 19.72%

Found C 67.33% H 15.09% N 18.00%

(iv) Cations for the synthesis of halostannates were prepared as the appropriate halides. Typically a base would be dissolved in an excess of hydrohalic acid and the solution pumped to dryness on the vacuum line to leave the solid product. The dryness of the products was checked by running their i.r. spectra. Cations prepared by this method included variously substituted alkylammonium and pyridinium species.

(v) Cyanogen chloride was synthesized according to the method of Jennings and Scott.[107] Typically 6 g. of powdered NaCN were stirred in a mixture of 50 mls. CCl_4 and 1 ml. of glacial acetic acid while chlorine gas was slowly passed through it. The reaction mixture was maintained between 263 and 268K. When excess chlorine had been added the mixture was warmed to 313K and all the evolved gases were collected in a trap at 196K. This was then allowed to warm to 273K to allow any HCl or Cl_2 to boil off. The product was finally distilled on the vacuum line into a container fitted with a "Rotaflo" tap for storage. The infra red spectrum showed HCN as the only contaminant.

(e) Elemental Analyses

A Perkin-Elmer 240 elemental analyser was used for determination of C, H and N by microcombustion. The machine was found to be fairly reliable for C and N but variable for H. Air- and moisture-sensitive compounds were sealed in small aluminium capsules in the glove box before analysis.

Mr. Coult performed the analyses for all other elements. Phosphorous

was determined by sodium peroxide fusion in a nickel Parr bomb followed by dissolving in concentrated nitric acid. The sample was then estimated colorimetrically on formation of a yellow molybdovanado-complex. Halogens were combusted in an oxygen flask (Schoniger's method) while allowing the vapours to absorb into dilute aqueous peroxide solution. The halide was then estimated by potentiometric titration with aqueous $^{N}/_{100}$ $AgNO_3$. Tin samples were usually treated with .880 ammonia solution and warmed on an infra-red heater. Further treatment was carried out with concentrated nitric acid, followed by evaporation with the lamp, then concentrated sulphuric acid and finally by combustion in a silica crucible. The tin was then determined gravimetrically as SnO_2. Unfortunately the presence of halogens often causes loss of tin, no matter how carefully the evaporations are carried out. For this reason where compounds gave good C, H and N analyses the tin content was sometimes not determined. Other metals (e.g. Ag, K) were determined in aqueous media using a Perkin-Elmer 403 Atomic Absorption Spectrophotometer.

(f) Vibrational Spectra

Infra red spectra were obtained from Perkin Elmer 577 or 597 spectrophotometers. Solids were run as Nujol mulls between CsI plates; these plates were protected by thin polythene discs in cases where the compounds would attack the caesium iodide. Occasionally solution spectra were run using a 0.05 mm. solution cell with KBr windows, as well as gaseous spectra using a 10 cm. cell also with KBr windows.

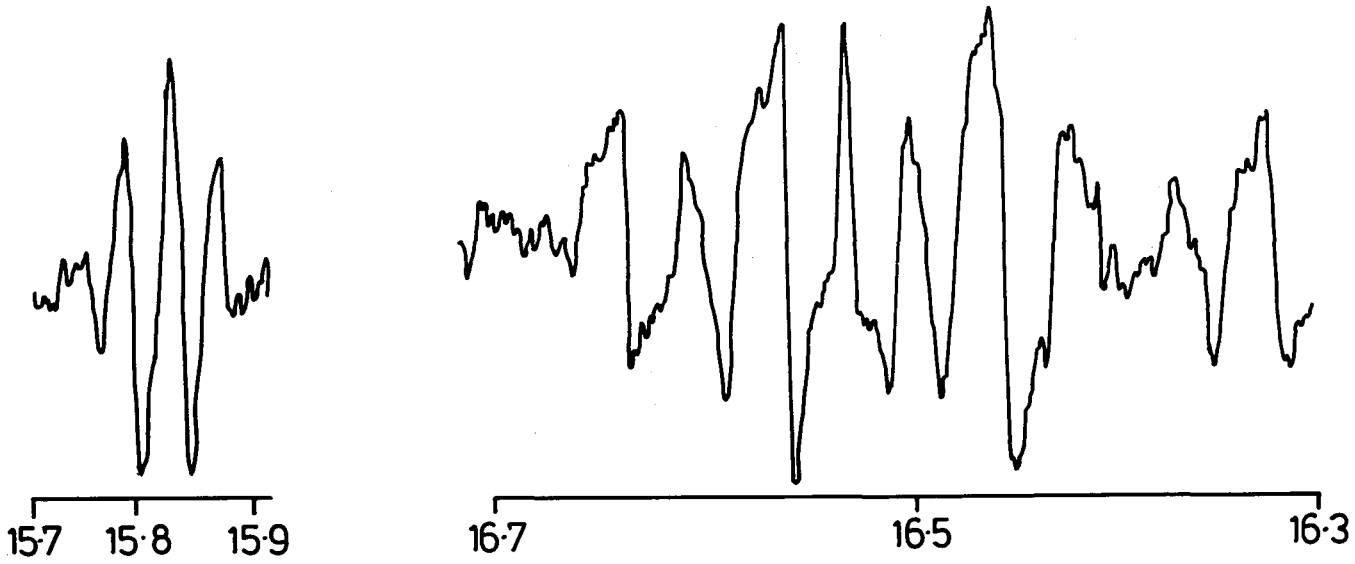
Raman spectra were recorded by Mrs. J. Šlegrová using a Cary 82 spectrometer operating with an argon laser.

(g) N.q.r. Spectrometers

^{35}Cl n.q.r. spectra were obtained from a commercial mid-range Decca

Sample ^{35}Cl n.q.r. Spectra Fig. 2.1

i) $(SCl_3)_2SnCl_6$ at 210·2K ii) $(Et_2NH_2)_2SnCl_6$ at 77K



spectrometer operating between 5 and 55 MHz. The frequency range scanned was determined by selection of the appropriate radiofrequency coil, into which a 13 mm. sample container was placed. The frequencies were measured at the start and finish of each run using an Advance Instruments TC16 frequency counter and intermediately by the frequency markers of the instrument. These were set to mark at every 25 kHz and every 1 MHz respectively. Positions of the resonance frequencies were determined manually from the marker scales. The spectrometer was of a super-regenerative oscillator type operating with a 1 MHz crystal oscillator and was used in the Zeeman modulation mode with a quench frequency of 25 kHz. A home built external time constant box was fitted to extend the time constant of the machine to 20 secs. and enhance weak signal detection. A glass Dewar vessel was situated round the sample enabling spectra to be recorded at low temperatures. Liquid nitrogen (77K) and solid carbon dioxide (196K) were used as the coolants. Scan speeds were usually set so that the full frequency range of a coil could be traversed overnight when searching for unknown signals; at these speeds and with sufficient lagging the coolants survived the period of the run.

On locating a signal the spectrum was rerun to check that the result was reproducible. This was necessary as spurious signals were sometimes generated by the equipment. In particular, spurious signals were produced by various coils, without samples, at $\sim$ 14.2 MHz and between 9.2 and 9.7 MHz.

Where closely overlapping signals were detected, that small region of the spectrum would be run at very slow scan speeds to enable maximum resolution to be obtained. An example of this is shown in Figure 2.1(ii). for $(Et_2NH_2)_2SnCl_6$ at 77K. There are thought to be four overlapping signals

of intensities 1:2:2:1 in this spectrum. This was deduced by comparing it with spectra showing single signals, an example of which is shown for $(SCl_3)_2SnCl_6$ at 210.2K (Figure 2.1(i).). This problem is an illustration of the difficulties associated with interpreting the lineshapes produced by the superregenerative oscillator type of spectrometer. These lineshapes are a mixture of dispersion and absorption curves and have sidebands separated by the quench frequency used. The Decca machine has facilities for sideband suppression but the signals detected for the halostannates were not sufficiently strong to enable this to be used. Furthermore, for each signal, it has to be decided which of the absorption or dispersion modes predominates. The signal shown for $(SCl_3)_2SnCl_6$ in Figure 2.1. is quite symmetrical and is assumed to show its centre at the absorption maximum. A less symmetrical signal however, might be measured as a dispersion signal in the middle of the line between the two largest peaks of the pattern.

In principle the relative intensities of lines within a single ion should be directly proportional to the number of quadrupolar nuclei causing each line. During a wide sweep of frequency, however, sufficient changes in lineshape, gain and saturation behaviour can occur to make intensities only reliable for signals closer than 1 MHz, and then only to about 10%. This again is a function of the spectrometer.[108] The relative intensities quoted later are therefore visual guesstimates based on the knowledge that there must be integral numbers of discrete environments for nuclei in regular crystal lattices. Where single lines were followed over a series of temperatures, the intensity of these was estimated from their signal heights. Signal height is defined as the perpendicular distance between the two largest, adjacent (but opposite in direction) peaks of the

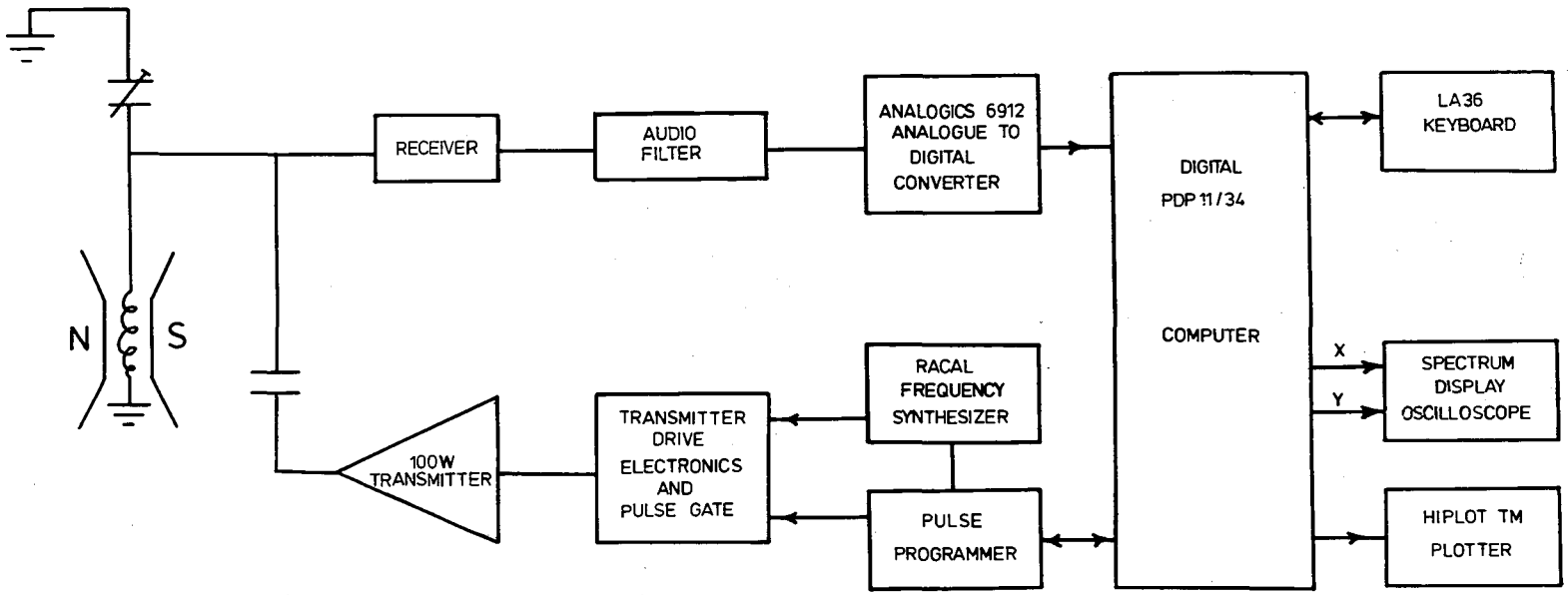
signal lineshape. This empirical guide to intensity was considered sufficient for the purpose used, especially since full integration of the lines is impossible without knowledge of the exact contribution from each of the dispersion and absorption curves.

The form of the sample to be analysed by n.q.r. is often important. Ideally this should be in a crystalline form and should be a reasonably pure compound, not a physical mixture of several species. The sample bottles should also be filled as fully as possible but without too much grinding or packing down of the compound since strains in the crystals can broaden the signals. This last point necessitates the synthesis of compounds on a 4 - 5 gm. scale with relatively small crystals, not powders if at all possible. Even when the above criteria were satisfied, however, signals were not always detected.

For the bromine measurements a Decca spectrometer fitted with a high frequency head was used. The principal difference in this machine from that previously described was that it was operated from a 5 MHz crystal oscillator with a quench frequency of 50 kHz and with a 10 sec. time constant. The electronics of the head meant that it had to be of a more bulky design than the mid-range machine which made cooling more difficult. If liquid nitrogen was used as the coolant, for example, only about 2 hours elapsed before the Dewar round the sample needed refilling, for a constant temperature of 77K to be maintained. Furthermore the inside of the sample can had to have an atmosphere of dry helium to keep water from condensing on a variable capacitor (used for varying the frequency) inside it. This was supplied from a cylinder via tubing fitted with an outlet for excess pressure. This equipment was successfully used in the 110 - 145 MHz region. Attempts to detect signals between 50 and 100 MHz failed and it was not

Figure 2.2.

Multinuclear n.m.r. Spectrometer.



established whether the equipment was functioning properly in this region or whether the compounds used (various tribromostannates) were at fault.

(h) N.m.r. Spectrometers

^{119}Sn n.m.r. spectra were recorded on the home built Fourier transform multinuclear spectrometer shown diagramatically in Figure 2.2. This instrument was constructed at Durham University by Dr. A. Royston. A 1.4T magnet from a Perkin-Elmer R10 instrument was utilised, and was fitted with a special tin probe taking n.m.r. tubes of 8.4 mm. external diameter. A thermostat kept the probe at 307.2K. The ^{119}Sn resonances were sought on and around 22.376 MHz which was set using the frequency synthesizer. By using different probes and different set frequencies other nuclei could be studied. Spectra were displayed on an oscilloscope and could be printed on a plotter as required. The whole system was driven by a PDP11/34 computer controlled from a keyboard. The computer program included facilities for free induction decay manipulation, phase correction of spectra, measurement and tabulation of peaks, variation of pulse lengths and the time between pulses, and storage of spectra. Peaks were measured, relative to an external tetramethyltin reference, in p.p.m. with the downfield direction taken as positive. Due to the low natural abundance (8.6%) ^{109} and low magnetic moment (-1.046 nuclear magnetons) ^{109} of ^{119}Sn, several thousand scans often had to be accumulated for reasonable spectra to be obtained.

^{31}P n.m.r. spectra were run on another Fourier transform machine also constructed by Dr. A. Royston and described elsewhere.[110] This was controlled by a Varian 620/L computer and used the same type of magnet as the previous machine, with a similarly set thermostat, but operating at 24.29 MHz. Chemical shifts were measured relative to an external 85% H_3PO_4

reference with the downfield direction taken as positive.

^{19}F n.m.r. spectra were recorded by Dr. R. Matthews on a Bruker HX90E Fourier transform spectrometer operating at 84.658 MHz. 5 mm. spinning sample tubes were used containing capillaries of D_2O as an external lock. Shifts were measured with the downfield direction taken as positive, relative to C_6F_6 or SnF_6^{2-} references.

(i) Sealed Tubes

For storing volatile materials or when using volatile reactants in n.m.r. experiments, sealed tubes were used. These were silica tubes of the appropriate diameter fitted with B14 cones which could be connected to the vacuum line. Compounds were transferred to the tubes by distillation on the vacuum line if volatile, or manually (often under nitrogen in the glove box) if otherwise. Once filled they were frozen to 77K, evacuated and sealed with a strong flame.

(j) Differential Scanning Calorimetry

The instrument used in these measurements was a Perkin Elmer DSC2 Differential Scanning Calorimeter operated by Mr. A.J. Tate. Samples were encapsulated in aluminium containers and introduced via a dry box to the sample pans of the calorimeter. Scrupulous dryness was found to be necessary in the sample area as condensation below about 200K destroyed the baseline of the spectrum. For this reason the dry box was equipped with P_2O_5 drying dishes and the immediate sample area was subjected to a purge of dry helium gas. An indium standard which melted sharply at 429.78K was used to calibrate the instrument.

CHAPTER 3

The N.q.r. Frequencies of Various Halostannates and Some of the Factors Affecting Them

(a) Introduction

The n.q.r. frequencies of many elements in co-ordination complexes have been recorded,[1] and the halostannates are no exception. Octahedral complexes have received particular attention via the study of their halogen n.q.r. frequencies, and attempts have been made to account for the quantitative differences between frequencies for different complex ions. In particular the Townes-Dailey relationship has been implemented to relate the ionic character to the electronegativity difference for metal-halogen bonds in several hexahalometallates.[2] The reason for the variation of n.q.r. frequencies within the hexachlorostannates, however, has not been fully elucidated. Brill et al[19] concluded that the repulsive forces between the anions produce a dominant effect on their halogen n.q.r. frequencies, and found a good correlation between the interionic halogen-halogen distances and the ^{35}Cl n.q.r. frequencies, using the Born repulsive potential, $\exp(-r/\rho)$. They deduced that there was no correlation between frequency and Sn-Cl bond length, as has been found for other metal-halogen complexes,[14,16,17] but instead that a relationship of frequency with cation size existed. No systematic study of the variation of n.q.r. frequencies within the hexabromostannates or any of the tin (II) halo-complexes has been carried out to date; in fact little n.q.r. data[75,76] is available on these compounds.

Since the publication of Brill et al[19] more structural data has been obtained. The crystal structures of a large number of hexachlorostannates are known, the unit cell dimensions of which are listed in Table 3.1. Fewer

Table 3.1.

The Unit Cell Dimensions of Some Hexachlorostannates at Room Temperature

Cation	Cell Dimensions/Å	Unit cell type	Z	Reference
Tl^+	a=9.990	Cubic	4	43
K^+	a=9.9818	Cubic	4	19
Rb^+	a=10.0961	Cubic	4	19
Cs^+	a=10.3552	Cubic	4	19
NH_4^+	a=10.0442	Cubic	4	19
$MeNH_3^+$	a=8.42, α=50.23°	Rhombohedral	1	31
$Me_2NH_2^+$	a=8.593, b=12.649, c=7.571	Orthorhombic	2	79
Me_3NH^+	a=12.21	Cubic	4	39
Me_4N^+	a=12.835	Cubic	4	19
$EtNH_3^+$	a=7.24, c=8.41	Hexagonal	1	43
Et_3NH^+	a=9.950, b=10.698, c=10.767, β=100.22°	Monoclinic	2	45
Et_4N^+	a=14.024, b=14.331, c=13.284, β=90.6°	Monoclinic	4	80
$EtMe_3N^+$	a=13.20	Cubic	4	43
$Et_2Me_2N^+$	a=9.065, c=14.12	Tetragonal	2	43
Et_3MeN^+	a=13.51	Cubic	4	43
Me_3S^+	a=12.41	Cubic	4	43
$EtMe_2S^+$	a=12.80	Cubic	4	43
Et_3MeP^+	a=13.93	Cubic	4	43
$4ClpyH^+$	a=8.555, b=16.692, c=7.122, β=113.15°	Monoclinic	2	38
$PhCH{=}NH_2^+$	a=7.41, b=10.45, c=7.39, α=90.72°, β=116.03°, γ=85.00°	Anorthic	1	48
$Ph_2C{=}NH_2^+$	a=8.616, b=16.826, c=10.483, β=112.22°	Monoclinic	2	47
$(Me_2N)_2CH^+$	a=11.286, b=13.437, c=14.341, β=93.89°	Monoclinic	4	46
$NH_2NH_3^+$	a=11.8, b=8.2, c=11.8	Orthorhombic	4	112

Table 3.2.

The Unit Cell Dimensions of Some Hexabromostannates at Room Temperature

Cation	Cell Dimensions/Å	Unit Cell Type	Z	Reference
K^+	a=10.621, b=7.427, c=7.442, β=90.18°	Monoclinic	2	37
Rb^+	a=10.58	Cubic	4	49
Cs^+	a=10.77	Cubic	4	49
NH_4^+	a=10.57	Cubic	4	49
$MeNH_3^+$	a=8.61, α=52.22°	Rhombohedral	1	31
$Me_2NH_2^+$	a=14.88, b=7.61, c=7.60	Orthorhombic	2	This work
pyH^+	a=13.02, b=8.660, c=8.249, β=96°	Monoclinic	2	This work

hexabromostannate structures have been elucidated; all these are shown in Table 3.2. These tables are a survey of the literature to the present date and are intended to cover all compounds of the type M_2SnX_6 (X = Cl, Br). Each structure quoted is from the most recent reference available, based on the assumption that the more recent the work, the more likely its accuracy, since equipment is improving all the time. Few structures have been fully determined for the tribromo- and trichlorostannates (II). The compounds which have had their structures determined include: $KCl.KSnCl_3.H_2O$,[75] $[SnCl_3][SnCl(OH_2)_2].H_2O$,[76] $CsSnCl_3$,[119] $Me_4N^+SnCl_3^-$,[122] $[Co(diphos)_2Cl]SnCl_3$,[122] $[Co(diphos)_2Cl]SnCl_3.nC_6H_5Cl$,[122] $[Co^{III}(NH_3)_6](SnCl_3)Cl_2$,[122] $[Co^{II}(en)_3](SnCl_3)Cl$,[122] $NH_4SnBr_3.H_2O$,[74] $MeNH_3^+SnBr_3^-$ [122] and $CsSnBr_3$ [122] (compounds containing the trihalostannate (II) groups as ligands are not included).

It is the lack of accurate structural data which has prevented full investigation of these complexes from the n.q.r. standpoint. In the complexes where a relationship between bond length and frequency has been found, small changes in bond length resulted in large changes in n.q.r. frequency

(e.g. for the tetrachloroiodates[15] an increase of about 8% in the I-Cl bond length produced a doubling of ^{35}Cl n.q.r. frequency). For the hexachlorostannates therefore, where the n.q.r. frequencies range from around 15 to 18 MHz,[1] it is possible that changes of the order of 0.001Å might be important if a similar relationship existed. Because of this, the necessity for accurate crystallographic data is paramount. An example of the difficulties in the refinement of x-ray diffraction data is given by considering the crystal structure of K_2SnCl_6. Brill et al[19] found the Sn-Cl bond length in this compound to be 2.411Å, whereas Lerbscher and Trotter[44] calculated a value of 2.428Å, after thermal libration had been considered. Clearly such disagreement is large in the current context. The n.q.r. measurements in the literature, on the other hand, are more consistent, e.g. values of 15.063[19] and 15.065 $\pm$ 0.002 MHz[2] have been quoted by different workers for K_2SnCl_6 at room temperature.

(b) The Hexachlorostannates

(i) Frequency Measurements

The search for ^{35}Cl n.q.r. signals from many of the hexachlorostannates prepared in this work (see section 3(e)(i)) proved successful. The results obtained are shown in Table 3.3. for measurements at each of three temperatures: liquid nitrogen (77K), solid carbon dioxide (196K) and room temperature (300K); all compounds which did not produce signals were run at these temperatures also. As a general trend it was found that the signal intensities (i.e. signal to noise ratios) increased on going to the lower temperatures. The actual signal to noise figures have not, however, been quoted as they have no primary bearing on the following discussion (rather the relative intensities within single compounds being of importance). This trend is to be expected from consideration of the

Table 3.3.

The ^{35}Cl N.q.r. Frequencies of Some Hexachlorostannates

Cation	^{35}Cl n.q.r. frequencies of $SnCl_6^{2-}$ ions at various temperatures/ ± 0.003 MHz					
	77K		196K		300K	
$MeNH_3^+$	15.928(2)[a]	15.983(1)	15.838		15.811	
$Me_2NH_2^+$	16.041(2)	16.846(1)	16.060(1)	16.515(2)	-	
Me_3NH^+	16.828(2)	16.882(1)	16.728(2)	16.788(1)	16.625	
Me_4N^+	16.678(2)	16.755(1)	16.770		16.680	
Me_3S^+	16.42[b](2)	16.51(1)	16.410(2)	16.450(1)	16.395	
$Et_2NH_2^+$	16.41(1)	16.54(2)	16.220(1)	16.387(2)	16.120	
	16.65(2)	16.75(1)	16.412(3)			
Et_3NH^+	-		14.987		14.925	
Et_4N^+	16.360(1)	16.575(1)	16.335(1)	16.54(1)	-	
	16.660(1)	16.975(1)	16.865(1)	16.987(1)		
	17.010(1)	17.205(1)	17.412(2)	17.480(2)		
	17.285(1)	17.555(1)				
	17.635(1)					
pyH^+	15.207(1)	15.288(2)			17.360	
	15.365(1)	17.107(1)				
	17.210(2)	17.290(1)	15.312(1)	17.075(1)		
	17.545(2)	17.600(1)	17.492(1)			
2-$ClpyH^+$	15.61(2)	17.12(1)	15.660(1)	17.448(2)	-	
	17.65(3)					
3-$ClpyH^+$	15.92(1)	16.25(2)	15.907(2)	17.482(1)	16.230(1)	16.735(1)
	16.91(1)	17.14(1)			16.780(1)	
	17.56(1)					
3,5-$ClpyH^+$	16.148(2)	16.280(3)	16.068(2)	16.138(3)	16.395	
	17.180(1)		16.905(1)			
3,5-$lutH^+$	18.73(1)	18.80(1)	18.56(1)	18.66(1)	18.405	
SCl_3^+	-		15.84		15.703	
But_4P^+	-		-		17.02	17.30(very weak)
3-$IpyH^+$	-		-		-	
Ph_2I^+	-		-		-	
PCl_4^+	-		-		-	
$Ph_2PCl_2^+$	-		-		-	
Ph_3PCl^+	-		-		-	
Ph_4P^+	-		-		-	
$Prop_4N^+$	-		-		-	

(a) Values in brackets indicate estimates of the relative intensities of the signals; (b) error = ± 0.05 MHz in all figures quoted to two decimal places.

Boltzmann distribution of the energy levels: the lower the temperature, the greater the population difference between the energy levels within the nuclei responsible for the resonances and hence the stronger the signals,[109] except if saturation occurs.

One of the dilemmas in n.q.r. spectroscopy is the question of why some compounds exhibit signals where others, containing quadrupolar nuclei, do not. It was found for the hexachlorostannates that in a number of cases no signals were obtained (see Table 3.3.). This is certainly due in part to the insensitivity of the spectrometer used, but it is still apparent that the signals from some quadrupolar nuclei are inherently harder to detect than others. The quality of the samples used was found to be of importance. Those prepared in powder form consistently gave weaker (if any) signals than samples of crystalline form. This is illustrated in Table 3.4. The elemental analyses of these compounds can be found in section 3(e)(i) and from these figures in most instances, there appears to be little difference in the purity of the samples. The increase in signal strengths for the crystalline species must therefore be due to their more ordered structures. All the successful frequency measurements in Table 3.3. are from experiments on crystalline samples.

Despite good crystalline form, some samples did not produce n.q.r. signals. These compounds were without exception hexachlorostannates with large cations e.g. of the tetra-alkylammonium salts $(Me_4N)_2SnCl_6$ and $(Et_4N)_2SnCl_6$ gave signals whereas $(Prop_4N)_2SnCl_6$ did not. Another example of a sample with a large cation is $(But_4P)_2SnCl_6$. This compound gave very weak signals at 300K, but it is not clear why, with such a large cation it should produce stronger resonances than say $(Prop_4N)_2SnCl_6$ which has a smaller cation. The reason might be in its sample form i.e. purity and

Table 3.4.

The Dependence of Sample Form on Obtaining ^{35}Cl N.q.r. Signals From Hexachlorostannates

Compound	Sample Form	
	Powder	Crystalline
$(MeNH_3)_2SnCl_6$	✓	✓
$(Me_4N)_2SnCl_6$	✓	✓
$(Et_2NH_2)_2SnCl_6$	x	✓
$(3\text{-ClpyH})_2SnCl_6$	x	✓
$(3,5\text{-ClpyH})_2SnCl_6$	?	✓
$(3,5\text{-lutH})_2SnCl_6$	?	✓
$(pyH)_2SnCl_6$	✓	✓
$(3\text{-IpyH})_2SnCl_6$	x	x

Key: ✓ n.q.r. signals easily seen;

? n.q.r. signals very weak;

x no n.q.r. signals detected.

crystallinity. The weakening of signals by large cations probably occurs via the physical dilution of active ^{35}Cl nuclei, so that fewer of these nuclei are available within similar sized samples for detection by the spectrometer, and hence the signal intensities are lower. This reason might also account to some extent for the failure to observe resonances for the series of hexachlorostannates with substituted tetrachlorophosphonium cations (PCl_4^+, $Ph_2PCl_2^+$, Ph_3PCl^+, Ph_4P^+), although these compounds were never prepared in a fully satisfactory form (see section 3(e)(i)). The phosphonium salts have relatively large cations but were not produced in

crystalline form since their insolubility in a variety of solvents precluded recrystallisation. The only signals detected were from $(PCl_4)_2SnCl_6$, with resonances at 32.105 and 32.725 MHz, and several weaker ones in between these two values, at 77K. These correspond to the chlorines of the PCl_4^+ ion (cf. 32.274, 32.388, 32.424 and 32.958 MHz at 77K[116] for PCl_4^+ in $PCl_4^+PCl_6^-$). It is curious that one set of resonances were observed for the cation but none for the anion, within the same sample. This behaviour is not unknown: for $PCl_4^+ICl_4^-$ and $Ph_3PCl^+ICl_4^-$, signals have been detected for the cations at 77K but not the anions.[117] One possible explanation might be the broadening of ^{35}Cl signals from the $SnCl_6^{2-}$ ions by interaction with chlorines of the PCl_4^+ ions, although no evidence for coupling between quadrupolar nuclei exists in the literature; though against this is the fact that any interaction might be expected to broaden the cation resonances as well. Another possibility would be the averaging of e.f.g.'s, and hence broadening of signals, by molecular motion i.e. with the $SnCl_6^{2-}$ ions experiencing more movement than the cations. Against this however, is the fact that there were no ^{35}Cl n.q.r. frequencies detected for the anions at 77K, at which temperature little vibration would be expected. In contrast, for $(SCl_3)_2SnCl_6$, ^{35}Cl n.q.r. signals were detected for the anion at 196K and 300K, but no signals could be found for the cation at 77K, 196K or 300K. The region searched for the ^{35}Cl resonances of the SCl_3^+ ion was 32 - 46 MHz since SCl_3^+ signals have been detected in this region for $SCl_3^+SbCl_6^-$ previously[118] (42.185 and 42.932 MHz at 77K).

Table 3.4. shows that $(3\text{-IpyH})_2SnCl_6$ produced no n.q.r. signals even when in crystalline form. This is surprising in view of the fact that all the other hexachlorostannates with variously substituted pyridinium cations

produce n.q.r. signals and the size of these cations should be comparable to the 3-IpyH$^+$ ion. The only difference for 3-IpyH$^+$ is the presence of the quadrupolar iodine nucleus in the ion. Again it is conceivable that some interaction between the chlorine and iodine is taking place. The iodine possibly aids relaxation of the nuclei, thus shortening relaxation times and causing broadening of the ^{35}Cl n.q.r. signals of the $SnCl_6^{2-}$ ions, leading to the failure to detect signals.

Diphenyliodonium hexachlorostannate also produced no signals. Though this compound was not produced in crystalline form due to its insolubility, it nevertheless furnished good elemental analyses. The fairly large cation would detract from the observation of signals, although $(Ph_2CNH_2)_2SnCl_6$ has had its ^{35}Cl n.q.r. signals detected,[17] and this compound might be expected to have a similar sized cation. Once more the iodine atoms might broaden the signals by interaction with the anions. Possible evidence of interaction between cation and anion is afforded by the pronounced lowering of site symmetry of the hexachlorostannate ion reported from a vibrational study of $(Ph_2I)_2SnCl_6$.[113] The distortion of the $SnCl_6^{2-}$ ion for this compound is most likely to occur through interaction between chlorines and the positively charged iodine.

The publication of the crystal structures of $(PhCHNH_2)_2SnCl_6$[48] and $[(Me_2N)_2CH]_2SnCl_6$ prompted a search for the ^{35}Cl n.q.r. signals from these compounds. Both compounds were shown to contain $SnCl_6^{2-}$ ions with several different Sn-Cl bond lengths and data for a possible ^{35}Cl n.q.r. frequency/Sn-Cl bond length correlation was sought. Unfortunately the preparations of both proved to be unsatisfactory, if not unreproducible. The crude products from the reported preparative methods gave no ^{35}Cl n.q.r. signals in the region expected for hexachlorostannates (i.e. 12 - 20 MHz). Details

of the preparations are given in section 3(e)(i).

Another compound with a cation capable of distorting the $SnCl_6^{2-}$ ion is 4-methyl-1,2,3,5-dithiadiazolium hexachlorostannate.[114] This compound was synthesized at Durham by Dr. N.R.M. Smith[114] and was hoped to prove useful for ^{35}Cl n.q.r. frequency/Sn-Cl bond length correlation. Regrettably no n.q.r. signals could be detected from it.

Several of the compounds in Table 3.3. have already been studied by ^{35}Cl n.q.r., although not at all the temperatures used in this work. Virtually all the literature values agree well (within about 0.1% or better) with Table 3.3. and are shown in Table 3.5. for comparison.

Table 3.5.

The ^{35}Cl N.q.r. Frequencies of Some Hexachlorostannates from Literature Sources

Compound	^{35}Cl n.q.r. frequency at various temperatures MHz			Reference
	77K	196K	300K	
$(MeNH_3)_2SnCl_6$	15.932	15.857	15.815	31
			15.811[a]	115
$(Me_3NH)_2SnCl_6$			16.635[a]	115
$(Me_4N)_2SnCl_6$			16.663[a]	115
$(Et_3NH)_2SnCl_6$			14.94[b]	18
$(pyH)_2SnCl_6$			17.37[b]	18

(a) 296K; (b) 298K.

The only difference found was for $(MeNH_3)_2SnCl_6$, which in this work was found to exhibit two closely spaced resonances at 77K at 15.983 and 15.928 MHz. The former resonance is weaker than the latter and was perhaps

not observed in the previous work.[31] The latter frequency, however, agrees well with the literature value of 15.932 MHz.

From Table 3.3. it can be seen that most of the hexachlorostannates produce only one line at 300K. This implies that the anions are in symmetrical environments such that each chlorine nucleus experiences an identical e.f.g.. Indeed the unit cell symmetries of several of the compounds have been determined by x-ray diffraction and confirm this: $(Me_4N)_2SnCl_6$,[19] $(Me_3NH)_2SnCl_6$[39] and $(Me_3S)_2SnCl_6$[43] have cubic unit cells, and $(MeNH_3)_2SnCl_6$[31] has a rhombohedral unit cell. For $(Et_3NH)_2SnCl_6$ however, the $SnCl_6^{2-}$ ion was shown to be distorted,[45] so this n.q.r. result is misleading. The structure of this compound shows that the anion contains three pairs of chlorines, each with different Sn-Cl bond lengths; thus three different electronic environments for the chlorines would be expected, and hence there should be three n.q.r. frequencies. One explanation for the observation of only one signal would be if the other chlorines, whose resonances were not seen, were subject to different relaxation times which could broaden their resonances sufficiently to make their detection difficult. Similarly care must be taken before any conclusions are drawn about the symmetries of the $SnCl_6^{2-}$ ions in those compounds with pyridinium or substituted pyridinium cations. The compound $(4\text{-ClpyH})_2SnCl_6$ has been found to contain distorted $SnCl_6^{2-}$ ions;[38] each contains 3 pairs of non-equivalent chlorines, the distortion being caused by N-H...Cl-Sn hydrogen bonds. It would seem reasonable for such hydrogen bonding to exist in other similar salts. The variable temperature behaviour confirms this for $(pyH)_2SnCl_6$ (see section 4(c)(vii)); here one line is shown to be hydrogen bonded by its positive temperature coefficient. Furthermore for $(pyH)_2SnCl_6$ the n.q.r. values at various temperatures (Table 4.6.) show that the compound gives

three resonances until just below 300K, when two of them fade out. There is no sign of an impending phase change at this temperature (Figure 4.7.) so it is probable that there are three pairs of non-equivalent chlorines in this compound also, at 300K, but that two of them give no n.q.r. lines due to their relaxation times. Thus it is concluded that the anion in $(pyH)_2SnCl_6$ is not as symmetrical as might be thought from the observation of the single frequency at 300K. A similar system might be present for $(3,5\text{-lutH})_2SnCl_6$ and $(3,5\text{-ClpyH})_2SnCl_6$ since the possibility of N-H...Cl-Sn hydrogen bonding exists in these compounds. This remains speculative, however, as there is no evidence to support it, i.e. there may be unseen n.q.r. lines at 300K in addition to the single ones observed for each compound.

The compound $(3\text{-ClpyH})_2SnCl_6$ shows three ^{35}Cl n.q.r. lines at 300K between 16.23 and 16.78 MHz, which indicates the presence of three discrete electronic environments for the chlorines of the $SnCl_6^{2-}$ ions. In addition, since the signals are of roughly the same intensity, the n.q.r. spectrum suggests that each type of environment is as equally as populated as the others. The most probable structure is one with each $SnCl_6^{2-}$ ion containing three inequivalent pairs of chlorines in a similar way to $(4\text{-ClpyH})_2SnCl_6$, although the distortion from regular octahedral geometry here would be much less marked since the ^{35}Cl n.q.r. frequencies are much closer together than for this compound [at 300K, $(4\text{-ClpyH})_2SnCl_6$ gives ^{35}Cl n.q.r. resonances at 14.97, 17.32 and 17.52 MHz[38]].

Below 300K, many of the hexachlorostannates under study show an increase in the number of ^{35}Cl n.q.r. resonance lines. This is usually indicative of the occurrence of a structural phase change, which causes distortion of the anions, and hence produces electronically inequivalent chlorine sites which were previously equivalent. Measurements at the three different

temperatures in Table 3.3. give an indication of whether phase changes occur at temperatures intermediate to those of the actual measurements i.e. where more lines are observed at one temperature than for another. For many of the cases where phase changes were suspected, fuller temperature dependence studies were carried out, and these are detailed in Chapter 4 for methyl-, dimethyl-, trimethyl- and tetramethylammonium, trimethylsulphonium, trichlorosulphonium and pyridinium hexachlorostannates. The remaining compounds from Table 3.3. were not subjected to fuller temperature study for one of two reasons: either the signals were too weak, or else too close together to enable rapid scanning of the resonances. Without rapid scanning (i.e. up to a maximum period of about one hour for the acquisition of each signal) inordinate lengths of time and quantities of coolants would have had to be used to obtain the results, and this was considered impracticable.

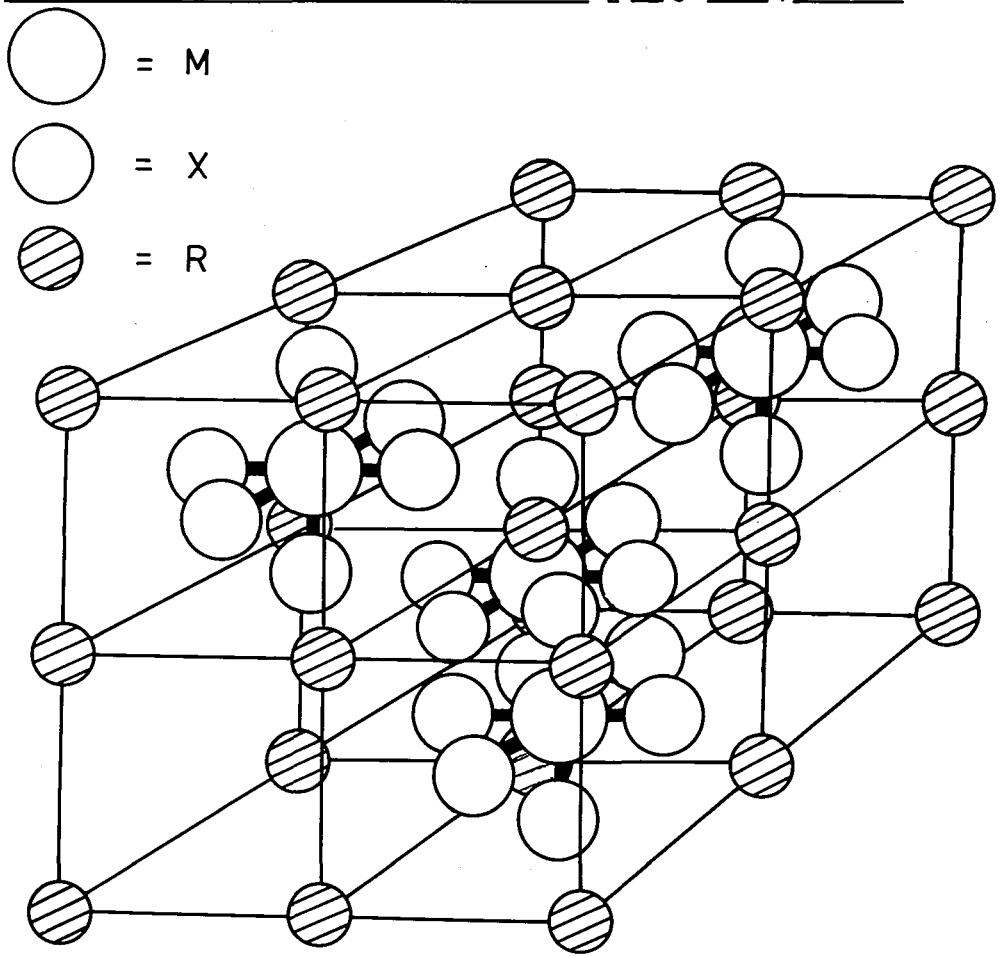
It seems clear from Table 3.3. that most of the hexachlorostannates studied experience phase changes between 77 and 300K. $(Et_2NH_2)_2SnCl_6$ appears to undergo at least two changes, between 77 and 196K, and between 196 and 300K, as its number of resonances goes from four to three, and three to one respectively. $(Et_3NH)_2SnCl_6$ shows the disappearance of all signals at 77K; this could be due either to a phase change between 77 and 196K creating several, weaker undetected resonances, or simply a change in the relaxation behaviour of the compound, broadening the signal to obscurity. $(Et_4N)_2SnCl_6$ shows the remarkable transition of six lines at 196K going into nine at 77K, indicating the presence of at least nine different electronic environments (i.e. e.f.g.'s) for the ^{35}Cl nuclei in the low temperature structure; this compound also loses all its signals at 300K. $(2\text{-ClpyH})_2SnCl_6$ similarly shows no resonances at 300K but undergoes a phase transition

between 77K and 196K with three lines going to two for the higher temperature. $(3\text{-ClpyH})_2SnCl_6$ appears to pass through at least two crystal phases between 77K and 300K; unusually it decreases its number of resonances from three to two on going from 300K to 196K, these two then split into five more by the time it has been cooled to 77K. $(3,5\text{-ClpyH})_2SnCl_6$ only shows evidence of one phase transition as its single resonance at 300K changes to three for 196K and 77K. $(3,5\text{-lutH})_2SnCl_6$ also shows evidence of only one transition; this is again between 300K and 196K as its single line at the higher temperature splits into two.

Little can be deduced as to the nature of each of the above phase changes from the information available. The only possible conclusions are gained by consideration of the relative intensities of the signals together with the actual number of lines. However without further data, all that can be said is that the relative intensities of the lines correspond to the relative populations of each of the ^{35}Cl nuclei responsible for the particular resonances. Even then some of the data does not make sense: e.g. for $(Et_4N)_2SnCl_6$ at 196K the total number of chlorines turns out to be a multiple of eight from the relative intensities, when it should be a multiple of six for hexachlorostannate ions (a unit cell with 4 different $SnCl_6^{2-}$ ions and hence 24 possible different Cl might account for this). Another question is how an intensity pattern of 3:2:1 can arise for signals from $(3,5\text{-ClpyH})_2SnCl_6$ and $(2\text{-ClpyH})_2SnCl_6$: are there three different environments in this ratio for the chlorines in each anion, or is there more than one type of anion within the structure? These questions can only be answered when more detailed n.q.r. measurements are available, or when complementary information from other techniques such as x-ray crystallography is obtained.

Figure 3.1.

The Cubic Antifluorite Lattice of R_2MX_6 Compounds



The chloropyridinium cations in the hexachlorostannate salts also gave ^{35}Cl n.q.r. signals. These were at 37.625 and 38.075 MHz for (3,5-ClpyH)$_2SnCl_6$, 37.455 MHz for (3-ClpyH)$_2SnCl_6$; and 37.945 MHz for (2-ClpyH)$_2SnCl_6$. All the frequencies quoted were measured at 77K.

(ii) The Relationship Between Cation Size and ^{35}Cl N.q.r. Frequency for the Hexachlorostannates

The compounds with the general formula M_2SnCl_6 (M = unipositive cation) are known to crystallise in the cubic antifluorite structure, or slight distortions of it, for the majority of cases. This structure consists essentially of a cubic array of cations with anions situated in alternate cube centres, as illustrated in Figure 3.1.. If the size of the anions is considered to be constant (since the Sn-Cl bond lengths only vary between 2.407 and 2.463Å for all the hexachlorostannates with known structures, this is reasonable - see Table 3.7.) then it would be expected that the size of the cation (M) would be the controlling factor for the overall size of the lattice. Thus, if from the unit cell dimensions of the hexachlorostannates, the volumes of single M_2SnCl_6 units are calculated (i.e. total unit cell volume divided by Z, which is the number of formula units per unit cell) for each compound, then these values should give an estimate of the volumes which the cations occupy in the lattices i.e. their sizes. The volumes of M_2SnCl_6 units have been calculated and are shown in Table 3.6. together with the average ^{35}Cl n.q.r. frequencies of the corresponding salts; these values are plotted in Figure 3.2. The n.q.r. figures in Table 3.6. were calculated as weighted averages of the frequencies shown in Table 3.3., each weighting depending on the relative intensities of the resonances. The frequency for $(Me_2NH_2)_2SnCl_6$ was calculated, after extrapolation to 300K, of the two frequencies seen for that compound in

Figure 3.2.

Variation of n.q.r. Frequency with Cation Size for the Hexachlorostannates

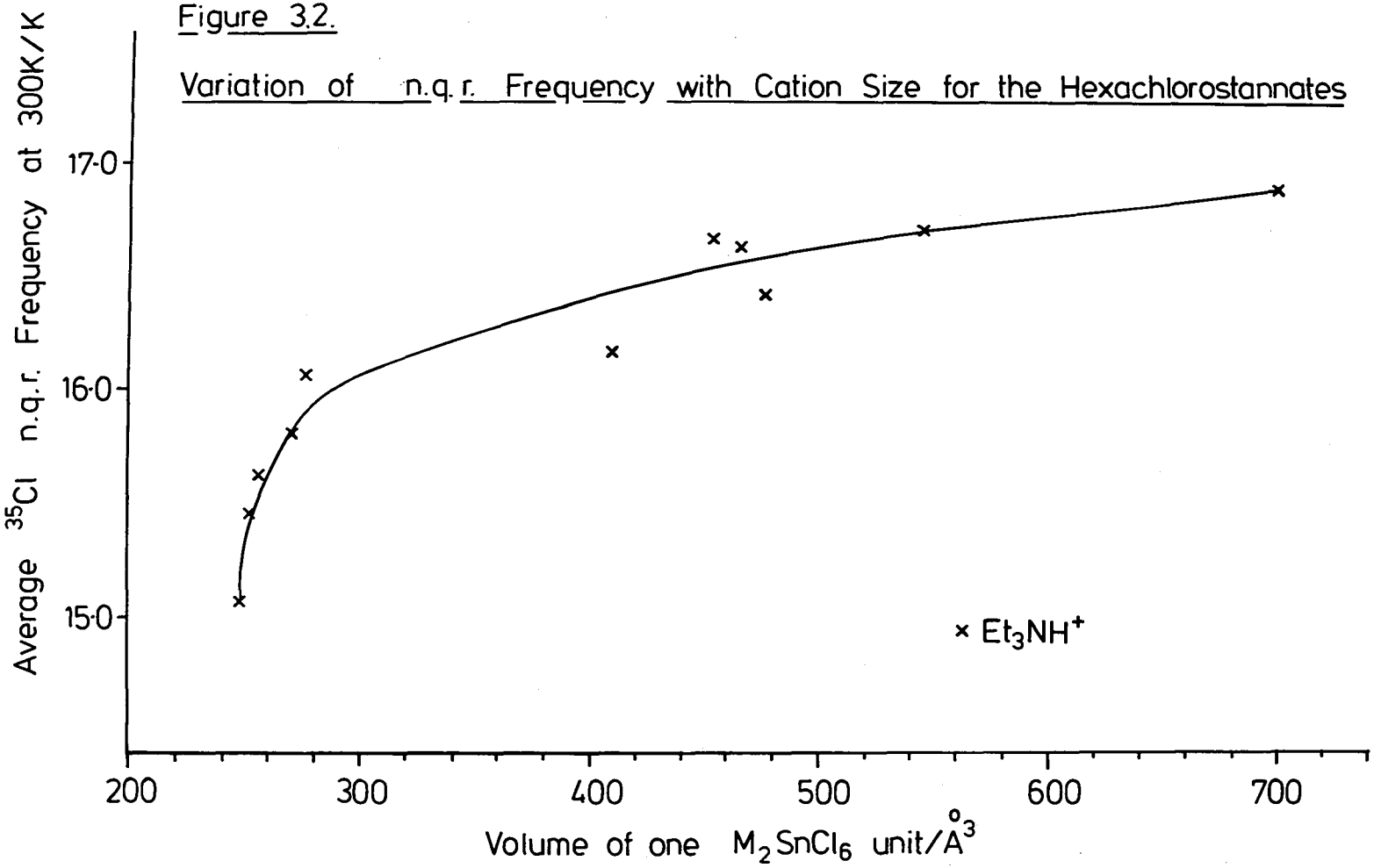


Table 3.6.

The Correlation of Cation Size with ^{35}Cl N.q.r. Frequency for Hexachlorostannates

Cation (M)	Volume[c] of One M_2SnCl_6 Unit/Å^3	Average ^{35}Cl n.q.r. Frequency at 300K/MHz	n.q.r. Reference
K^+	248.6	15.063	19
NH_4^+	253.3	15.453	19
Rb^+	257.3	15.60	19
Cs^+	277.6	16.057	1
$MeNH_3^+$	271.1	15.811	b
$Me_2NH_2^+$	411.4	16.145[a]	b
Me_3NH^+	455.1	16.625	b
Me_4N^+	528.6	16.680	b
Me_3S^+	477.8	16.395	b
4-ClpyH$^+$	467.6	16.603	38
Et_3NH^+	563.9	14.925	b
$Ph_2C{=}NH_2^+$	703.4	16.86	17

(a) Calculated from extrapolation of lower temperature measurements;
(b) this work; (c) calculated from Table 3.1.

Figure 4.3.

Figure 3.2. shows a general trend for the average ^{35}Cl n.q.r. frequency to increase with increasing cation size. This can be rationalised if the electrosatic repulsion between the anions is considered. Increasing repulsive forces between the $SnCl_6^{2-}$ ions would diminish the core electron polarisations around the ^{35}Cl nuclei, hence diminishing the e.f.g.'s at these nuclei, and therefore decreasing their observed n.q.r. frequencies.

The larger the cations therefore, the greater the separation of the anions, and the higher their n.q.r. frequencies become. From the figure, as the cations increase in size, the average n.q.r. frequency appears to approach a limit i.e. the frequency becomes independent of cation size. This limit is around 17.0 MHz at 300K and presumably represents the n.q.r. frequency of isolated $SnCl_6^{2-}$ ions. Extrapolation to this limit cannot be carried out too accurately though, because of the spread of the points.

There is also a second limit since as the n.q.r. frequency decreases, a point is reached where the volume of the M_2SnCl_6 units remains constant at about 240Å.[3] This is likely to be the point at which the anions are in the closest possible contact with each other, with the cations fitting in the holes in between them, such that the anion size governs the overall unit cell size. This is confirmed by the crystal structures[19] of K_2SnCl_6, $(NH_4)_2SnCl_6$, Rb_2SnCl_6 and Cs_2SnCl_6 which have relatively constant distances between the anions (3.648, 3.678, 3.713 and 3.896Å respectively) indicating that the size of the cations has little effect on the contact distances between the anions c.f. 5.681Å for the anion-anion contact distance in $(Me_4N)_2SnCl_6$. The ionic radii of K^+, NH_4^+, Rb^+ and Cs^+ are, for comparison, 1.33, 1.43, 1.47 and 1.67Å respectively.[109] From these figures, a 20% increase in ionic radius produces a 6% increase in the distance between the anions, so in this region the effect of cation size is negligible.

This plot of M_2SnCl_6 volume versus ^{35}Cl n.q.r. frequency therefore gives a way of predicting the average n.q.r. frequencies at room temperature from the unit cell dimensions of hexachlorostannates. All the points in Figure 3.2. lie within 0.2 MHz of the plotted line except the one for $(Et_3NH)_2SnCl_6$ which is considerably lower. This anomaly can be reconciled, however, by recourse to the crystal structure of the compound,[45] which shows the anion to contain three different Sn-Cl bond lengths. The

compound is thus expected to show at least three different n.q.r. frequencies, whereas only one resonance is seen. In this instance these 'missing' frequencies are expected to be higher than the one seen, so that the average ^{35}Cl n.q.r. frequency at 300K of $(Et_3NH)_2SnCl_6$ would be close to 16.665 MHz, in accordance with the plot in Figure 3.2.

The correlation outlined in the preceding discussion is essentially the same as that proposed by Brill et al,[19] that is to say with anionic repulsions responsible for the changes in ^{35}Cl n.q.r. frequencies. The difference in this work is that it uses unit cell dimensions to predict frequencies, and seems to be applicable to non-cubic structures. The model of Brill et al correlates interionic Cl...Cl distances with the n.q.r. results and these distances can only be found after full crystal structures have been determined: unit cell dimensions are much easier to obtain. Furthermore, Brill et al considered only cubic systems, and their model has not been tested with compounds where different Cl...Cl contact distances exist within the crystal lattice e.g. $(4\text{-ClpyH})_2SnCl_6$[38] or $(Me_2NH_2)_2SnCl_6$,[79] compounds which correlate reasonably well in Figure 3.2.

In conclusion it must be stated that this method must be treated with some caution. The assumption in it is that cation size can be calculated by subtracting the same fixed amount from the unit volume of each M_2SnCl_6 group. This is only intended as an approximation since firstly, from a purely geometrical standpoint this has shortcomings, and secondly, if any chemical bonding (such as hydrogen bonding) occurs between cation and anion, the ions would approach each other somewhat more closely than would normally be possible and the overall unit cell volume would be smaller. Even with these limitations, however, a relationship between cation size and average ^{35}Cl n.q.r. frequency certainly does exist for the

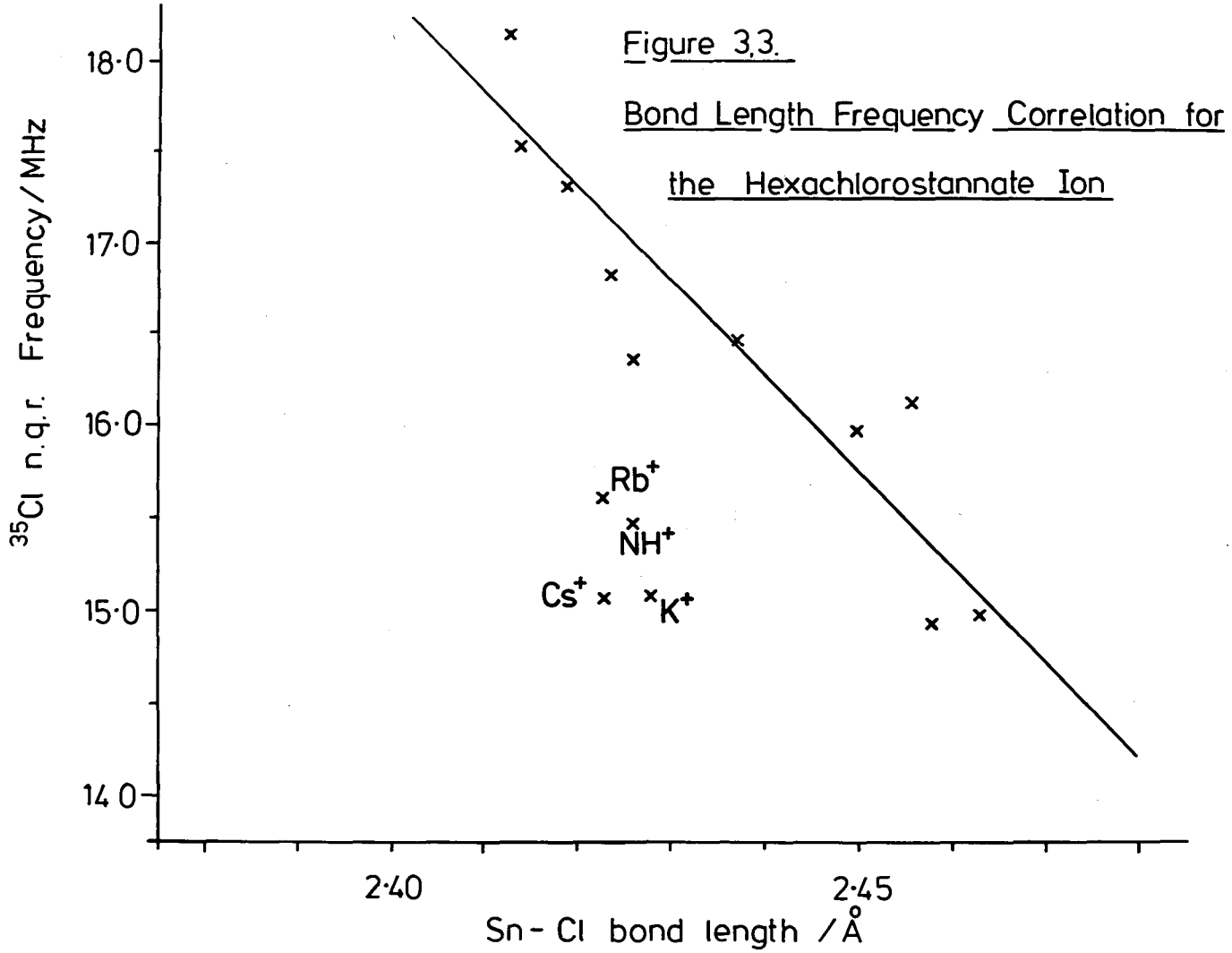


Figure 3.3.

Bond Length Frequency Correlation for the Hexachlorostannate Ion

hexachlorostannates.

(iii) The Relationship Between Sn-Cl Bond Length and ^{35}Cl N.q.r. Frequency for the Hexachlorostannates

The Sn-Cl bond lengths and their associated ^{35}Cl n.q.r. frequencies for several hexachlorostannates are shown in Table 3.7. and the same values are plotted in Figure 3.3. Assignment of frequencies to bond lengths for compounds having more than one Sn-Cl bond distance (and hence more than one ^{35}Cl n.q.r. frequency) is made on the assumption that the longer bond lengths correspond to the lower frequencies. This should be true if there is little π-bonding present in the Sn-Cl bonds, since the longer the bond, the greater the ionic character of the chlorine, and hence the lower its e.f.g. and n.q.r. frequency. Similar assignments have been made elsewhere.[15,17]

Figure 3.3. shows that, with the exception of the hexachlorostannates with K^+, Rb^+, Cs^+ and NH_4^+ cations, there appears to be a reasonably linear relationship between the ^{35}Cl n.q.r. frequencies and the Sn-Cl bond lengths from these compounds. The solid line in the figure is the least squares fit of all the points barring the ones for the four cations mentioned above. This line can be represented by the equation:

$$^{35}\text{Cl n.q.r. frequency/MHz} = 137.33 - 49.63 \times (\text{Sn-Cl bond length}/\text{Å}) \qquad \text{(eq.3.1.)}$$

The reason that these four hexachlorostannates are excluded from the fit is almost certainly connected with the effects of interanionic repulsion. All of these compounds have relatively small cations which enable the anions to come into close contact with each other. In this limit, it is probable that the repulsive potential between the ions given by e^{-r}/ρ (r = interionic distance, ρ = constant) is the dominant factor in

Table 3.7.

Correlation of ^{35}Cl N.q.r. Frequencies with Sn-Cl Bond Lengths for the Hexachlorostannates at 300K

Compound	d(Sn-Cl)/Å at 300K	Structure reference	^{35}Cl n.q.r. frequency at 300K/MHz	n.q.r. reference
K_2SnCl_6	2.428[a]	44	15.063	19
Rb_2SnCl_6	2.423	19	15.60	19
Cs_2SnCl_6	2.423	19	16.057	1
$(NH_4)_2SnCl_6$	2.426[a]	44	15.453	19
$(Me_2NH_2)_2SnCl_6$	2.437[a]	79	16.440[c]	
	2.450[a]		15.945[c]	b
$(Me_4N)_2SnCl_6$	2.424	57	16.680	b
$(Et_3NH)_2SnCl_6$	2.458	45	14.925	b
	2.427		-	
	2.407		-	
$(4\text{-ClpyH})_2SnCl_6$	2.463	38	14.97	18
	2.419		17.32	
	2.414		17.52	
$(Ph_2{=}NH_2)_2SnCl_6$	2.456	17	16.10	17
	2.426		16.35	
	2.413		18.14	

(a) Bond lengths corrected for thermal librations; (b) this work;

(c) calculated by extrapolation of low temperature data.

the variation of n.q.r. frequencies, as shown by Brill et al.[19] As r becomes larger, however, this effect becomes much less important, since these repulsive forces obey an exponential behaviour. The principal influence on the n.q.r. frequencies for the larger cations is therefore expected to be the Sn-Cl bond length as the repulsive forces assume a progressively smaller role. The conclusion of Brill et al that ^{35}Cl n.q.r. frequencies do not correlate with Sn-Cl bond length was therefore somewhat myopic. Their work was based primarily on five compounds: hexachlorostannates with the cations K^+, NH_4^+, Rb^+, Cs^+ and Me_4N^+. The first four of these, however, show different behaviour to the majority, and should perhaps be considered exceptions with respect to discussion of bond length-frequency relationships.

Equation 3.1. gives a method of predicting frequencies from bond lengths (and vice versa), with the constraint that the hexachlorostannate considered must have cations large enough to separate the anions from their distance of closest approach. The two unseen ^{35}Cl n.q.r. frequencies of $(Et_3NH)_2SnCl_6$ corresponding to the Sn-Cl bond lengths of 2.427 and 2.407Å would therefore, from equation 3.1., be expected to come at 16.89 and 17.87 MHz respectively at 300K. This would given an average frequency of 16.56 MHz at 300K, which would move the eroneous point shown in Figure 3.2. to within reasonable agreement for the relationship between cation size and frequency. Conversely the values of ^{35}Cl n.q.r. frequencies in Table 3.3. might be used to predict Sn-Cl bond lengths, e.g. for $(SCl_3)_2SnCl_6$ the observed frequency at 300K of 15.703 MHz corresponds to a bond length of 2.451Å.

(c) The Hexabromostannates

(i) Frequency Measurements

The Br n.q.r. frequencies for the hexabromostannates prepared in this work which gave signals are shown in Table 3.8. Of these, only $(MeNH_3)_2SnBr_6$

has been studied before, and shows good agreement with the values in the literature; ^{79}Br resonances at 131.75 ± 0.05 MHz at 77K, 131.11 ± 0.05 MHz at 190K and 130.79 ± 0.05 MHz at 300K.[31] No evidence was found in this compound for the splitting of the resonance at 77K which was seen for the corresponding hexachlorostannate (section 3(b)(i)). The agreement of values was encouraging since the high frequency n.q.r. spectrometer was a prototype machine from Decca Radar Ltd., and was at times temperamental in behaviour.

Table 3.8.

The Br N.q.r. Frequencies of Some Hexabromostannates

Cation	Br n.q.r. frequencies at various temperatures/±0.005 MHz		
	77K	175 - 195K[a]	300K
$MeNH_3^+$	131.726		
$Me_2NH_2^+$	130.575(1) 130.730(1) 135.020(4)	131.715(1)[b] 134.798(2) [187.0K]	131.205(1) 135.150(2)
Me_3NH^+	138.871	137.991 [186.0K]	137.170
Me_4N^+	140.30(1)[d] 140.60(1)[d]	138.670 [178.0K]	137.736
Me_3S^+	141.37(2)[d]	-	138.10[d]
pyH^+	119.034(2)[c] 120.910(2)[c] 122.595(1)	118.764(2)[c] 119.583(2)[c] 122.822(1) [190.6K]	116.565(1)[c] 118.000(2)[c] 123.660(1)
Et_4N^+	-	-	-
$Prop_4N^+$	-	-	-
Ph_2I^+	-	-	-

(a) Measurement temperatures shown in square brackets; (b) approximate relative intensities are shown in round brackets; (c) ^{81}Br frequencies (all others are ^{79}Br frequencies); (d) ±0.05 MHz.

$(Me_2NH_2)_2SnBr_6$ shows interesting behaviour in going from 77K to 300K and a fuller study has been performed. This is described in Chapter 4 (section 4(d)(ii)). The existence of several ^{79}Br frequencies at each of

the temperatures indicates that the anion is distorted in this compound. This was shown to be the actual case by an x-ray diffraction study (see the following section). In contrast, $(Me_3NH)_2SnBr_6$ shows a single ^{79}Br n.q.r. frequency at all temperatures studied. This infers a regular octahedral structure for the $SnBr_6^{2-}$ ions, i.e. all the bromine atoms are in equivalent positions in the structure. $(Me_3S)_2SnBr_6$ also shows a single frequency at 300K, which indicates the presence of a regular octahedral anion. This signal, however, was very weak (hence the larger error bounds) and if other signals were present, weaker than this one, they would not have been detected.

$(Me_4N)_2SnBr_6$ also exhibits a single resonance at 178K and 300K, but shows three at 77K. This implies that there is a structural phase change between 77K and 178K during which the anion distorts from a regular octahedral configuration for high temperatures to one of lower symmetry. The exact nature of the low temperature phase is difficult to predict from the three signals observed since the sum of their relative intensities is not a factor of six, as might be expected for the six bromines per anion. One explanation could be wrong estimation of the intensities (these signals were quite weak), while another could be the failure to observe other resonances also present. Unfortunately experimental difficulties in attaining steady temperatures between 77K and 178K precluded a more detailed study of the phase change.

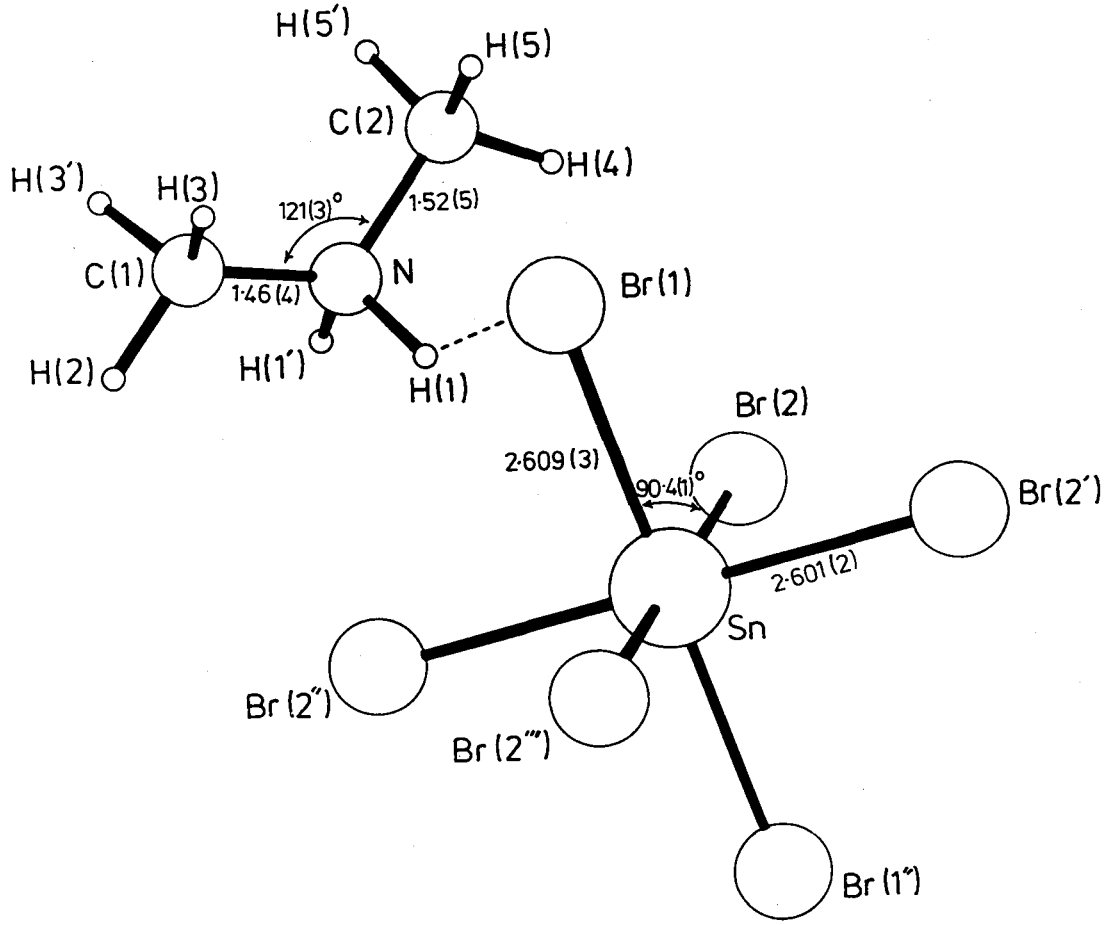
The study of $(pyH)_2SnBr_6$ brought to light one of the deficiencies of the prototype spectrometer used in this research. The machine could be made to operate consistently only between 110 and 142 MHz, while there were blank spots in the range from 100 to 110 MHz, and the region from 142 to 149 MHz could only be scanned on intermittent occasions (the reason for this behaviour was not elucidated). This meant that it was necessary to study $(pyH)_2SnBr_6$ in the 110 - 142 MHz region where the three signals,

shown in Table 3.8., were found. These were assigned as two from ^{81}Br nuclei, and one from ^{79}Br nuclei, since two strong signals were found at around 143 and 145 MHz, at 77K, on one occasion when the spectrometer was functioning in this region. The observed frequencies at 119.034 and 120.910 MHz when multiplied by the factor of 1.19707 (this is the ratio of the ^{79}Br to ^{81}Br frequencies from theory[108]) give predicted ^{79}Br frequencies of 142.5 and 144.7 MHz, thus assigning these as ^{81}Br resonances. A ^{79}Br resonance at 146.8 MHz corresponding to an ^{81}Br resonance of 122.595 was not detected, indicating that the resonance at 122.595 MHz was due to ^{79}Br nuclei in the first instance. This was confirmed by the observation of signals at 103.385 and 102.423 MHz at 300K and 77K respectively, after a careful search: the ^{79}Br resonance at 123.660 MHz predicts a frequency of 103.30 MHz for the ^{81}Br isotope at 300K. The observed intensities of these low frequency lines were somewhat larger than their corresponding ^{81}Br lines and indicates different relaxation behaviour for the two nuclei. Indeed the relative intensity of the low frequency line at 300K was about three times that of its ^{79}Br counterpart. The n.q.r. spectrum of $(pyH)_2SnBr_6$ therefore shows the existence of 3 different electronic environments for the bromine atoms, probably in a 3:2:1 intensity ratio. A fuller temperature dependence study and further discussion is detailed in section 4(d)(ii).

Several hexabromostannates did not produce n.q.r. resonances in the 110 - 142 MHz region at 77K, ∿ 190K and 300K despite repeated searches. These compounds were $(Ph_2I)_2SnBr_6$, $(Et_4N)_2SnBr_6$ and $(Prop_4N)_2SnBr_6$. The reason for this failure could be due to the size of the cations, or, for the diphenyliodonium case, to broadening of the lines by the iodine atom, as discussed for the hexachlorostannates. A second possibility for the lack of observed resonance could be spectrometer insensitivity.

Figure 3.4

The Crystal Structure of Dimethylammonium Hexabromostannate



(ii) The Crystal Structures of $(Me_2NH_2)_2SnBr_6$ and $(pyH)_2SnBr_6$

The crystal structures of $(Me_2NH_2)_2SnBr_6$ and $(pyH)_2SnBr_6$ (using the same crystals from the n.q.r. experiments) were determined via an x-ray diffraction study by Dr. J.C. Halfpenny whilst at Durham University. Full details of these structures are not included here, however, rather only that data which has particular relevance to the discussion of the n.q.r. results.

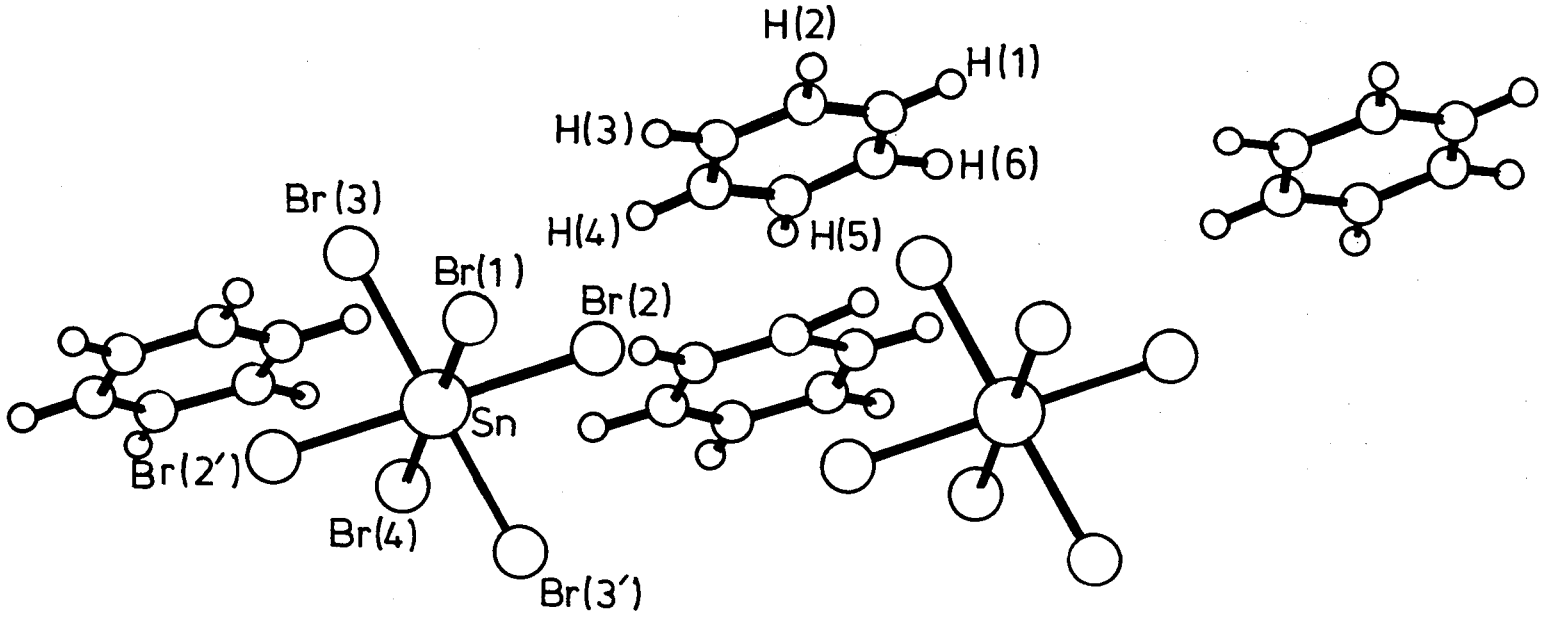
$(Me_2NH_2)_2SnBr_6$ was found to crystallise into an orthorhombic unit cell with dimensions: a = 14.88(1), b = 7.61(1) and c = 7.60(1)Å. The structure essentially consists of slightly distorted $SnBr_6^{2-}$ octahedron, hydrogen bonded to $Me_2NH_2^+$ ions via the N-H hydrogens. Figure 3.4. shows the structures and mutual arrangement of the ions, as well as the various bond lengths with their standard deviations in brackets (only one $Me_2NH_2^+$ ion is shown for clarity). Evidence for the proposed hydrogen bonding is afforded by the closeness of approach between Br 1 and the calculated H 1 position, 3.01Å, which is less than the sum of their Van der Waals radii (lit.[109] 1.2Å for H and 1.95Å for Br). Similarly, hydrogen bonding is indicated by an H 1 - Br 2 distance of 2.76Å between cations and anions in neighbouring unit cells.

$(pyH)_2SnBr_6$ crystallises into a monoclinic unit cell with dimensions of: a = 13.02(1), b = 8.660(1), c = 8.249(1)Å and $\beta = 96(1)^\circ$. The structure is shown in Figure 3.5. and illustrates the mutual arrangements of 4 pyH^+ and 2 $SnBr_6^{2-}$ ions. Unfortunately it proved impossible to locate the N atoms in the pyridinium rings so these were treated as benzene. The ring may possibly be statistically disordered to account for this. The $SnBr_6^{2-}$ proved to be distorted with 4 different Sn-Br bond lengths, though Sn-Br(1) and Sn-Br(3) have the same length within experimental error (see the figure). Br(1) and Br(4) are both partially occupied sites. Several

Figure 3.5

The Crystal Structure of Pyridinium Hexabromostannate

Sn-Br(1) = 2·624(6) Å
Sn-Br(2) = 2·582(1) Å
Sn-Br(3) = 2·622(1) Å
Sn-Br(4) = 2·565(6) Å



H-Br distances are less than the sum of the Van der Waals radii of H and Br which implies that the structure contains interionic hydrogen bonds. The H(1)-Br(4) and H(3)-Br(4) distances are 2.84 and 2.83Å respectively, while H(4)-Br(1) = 2.98Å and H(4)-Br(2) = 3.04Å. It is likely that the strongest hydrogen bonds would occur between bromines and hydrogens bonded to the nitrogen atoms on the pyridinium ring, but the observed H-Br lengths do not help in determining the nitrogen positions.

(iii) The Relationship Between Cation Size and ^{79}Br N.q.r. Frequency for the Hexabromostannates

Similar assumptions are made in this section to those in section 3(b)(ii) for estimation of the size of the cations in compounds of the type M_2SnBr_6 (M = unipositive cation), i.e. that the volume of the unit cells of these compounds gives a measure of the respective sizes of each cation. The justification for this is the relatively constant size of the $SnBr_6^{2-}$ ions as adjudged by very small changes in Sn-Br bond lengths over a series of hexabromostannates (for all the known M_2SnBr_6 structures d(Sn-Br) ranges from 2.565 to 2.622Å - see Table 3.9.). The data for the hexabromostannates is shown in Table 3.8. and plotted in Figure 3.6.

Figure 3.6. reveals a similar type of relationship between cation size and ^{79}Br n.q.r. frequency as found for the hexachlorostannates (c.f. Figure 3.2.) though there is less data for the bromo-compounds. It should also be noted that the dimensions for the rubidium, caesium and ammonium hexabromostannates were obtained in 1937,[49] hence the accuracy of these results is not expected to be as good as for those obtained for the other compounds, which were determined more recently, mainly due to improvements in instrumentation. The plot, however, reveals the trend of a general increase in average ^{79}Br n.q.r. frequency with increasing cation size which

Figure 3.6

Correlation of Cation Size with ^{79}Br n.q.r. Frequency for Hexabromostannates

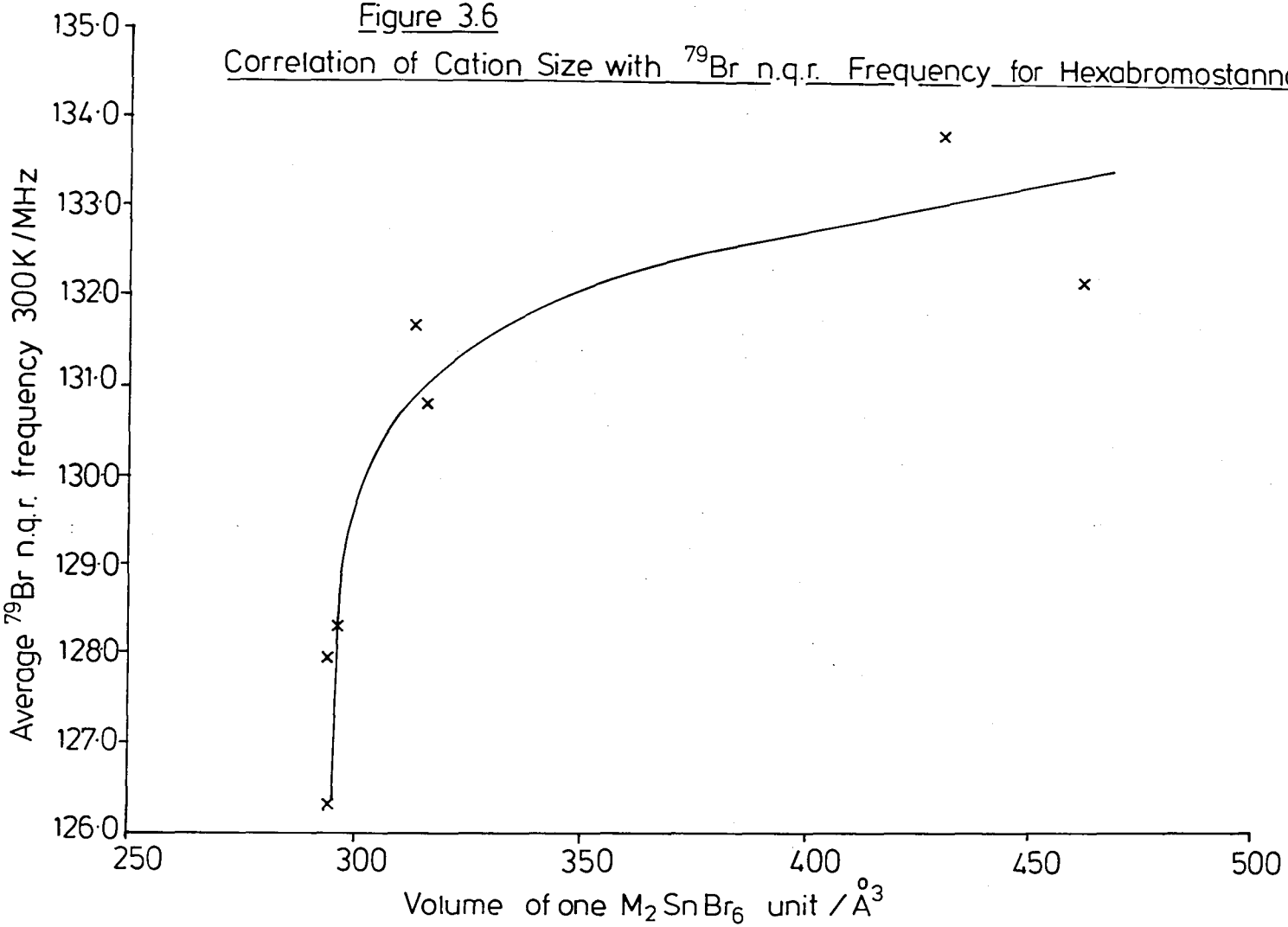


Table 3.9.

The Correlation of Cation Size with ^{79}Br N.q.r. for Hexabromostannates at 300K

Cation (M)	Volume of one M_2SnBr_6 unit[a]/Å^3	Average ^{79}Br n.q.r. frequency at 300K/MHz	N.q.r. reference
K^+	293.5	127.95	124
Rb^+	296.1	128.34	2
Cs^+	312.3	131.69[b]	1
NH_4^+	295.2	126.53	1
$MeNH_3^+$	315.1	130.820	c
$Me_2NH_2^+$	430.3	133.835	c
pyH^+	462.5	132.202[b]	c

(a) Calculated using the data in Table 3.2.; (b) calculated from the ^{81}Br frequencies (ratio of ^{79}Br: ^{81}Br = 1.19707:1.00000[108]); (c) this work.

can be rationalised in terms of interanionic repulsion, as for the hexachlorostannates (section 3(b)(ii)). Similarly there seems to be a limit where the n.q.r. frequency changes very rapidly for only small changes in M_2SnBr_6 volume. This is almost certainly the point at which the $SnBr_6^{2-}$ ions are in the closest possible contact so that it is the anions which determine the overall unit cell volume and not the cations (which fit into the spaces between the anions). This limit occurs at approximately 295Å^3. The opposite limit (i.e. where the average n.q.r. frequency becomes independent of cation size), corresponding to $SnBr_6^{2-}$ ions free from the effects of interanionic repulsions, is not easy to measure owing to insufficient data, though it would appear to lie between 134 and 135 MHz.

(iv) The Relationship Between Sn-Br Bond Length and ^{79}Br N.q.r. Frequency for the Hexabromostannates

The Sn-Br bond lengths together with their associated ^{79}Br n.q.r. frequencies are listed in Table 3.9. The frequencies were assigned on the basis of their relative intensities for $(Me_2NH_2)_2SnBr_6$ and $(pyH)_2SnBr_6$ since the former showed two signals in a 2:1 intensity ratio and the latter showed three signals in a 1:2:3 intensity ratio. The structures of these compounds (section 3(c)(ii)) show the hexabromostannate ions to contain four Sn-Br bonds of one length and two of another for $(Me_2NH_2)_2SnBr_6$, while $(pyH)_2SnBr_6$ has three Sn-Br bonds of one length (the x-ray diffraction study shows one at 2.624(6)Å and two at 2.622(1)Å which are the same within the error limits), two of another, and one more different to these two.

Table 3.10.

Correlation of ^{79}Br N.q.r. Frequencies with Sn-Br Bond Lengths for the Hexabromostannates at 300K

Compound	d(Sn-Br)[a]/Å at 300K	Structure reference	^{79}Br n.q.r. frequency at 300K/MHz	N.q.r. reference
K_2SnBr_6	2.590	37	128.71	124
	2.591		128.02	
	2.597		127.12	
$(Me_2NH_2)_2SnBr_6$	2.601	b	135.15	b
	2.609		131.205	
$(pyH)_2SnBr_6$	2.565	b	139.656[c]	b
	2.582		141.288[c]	
	2.622		123.660	

(a) see text for assignments of bond lengths to n.q.r. frequencies;

(b) this work; (c) calculated from the ^{81}Br values.

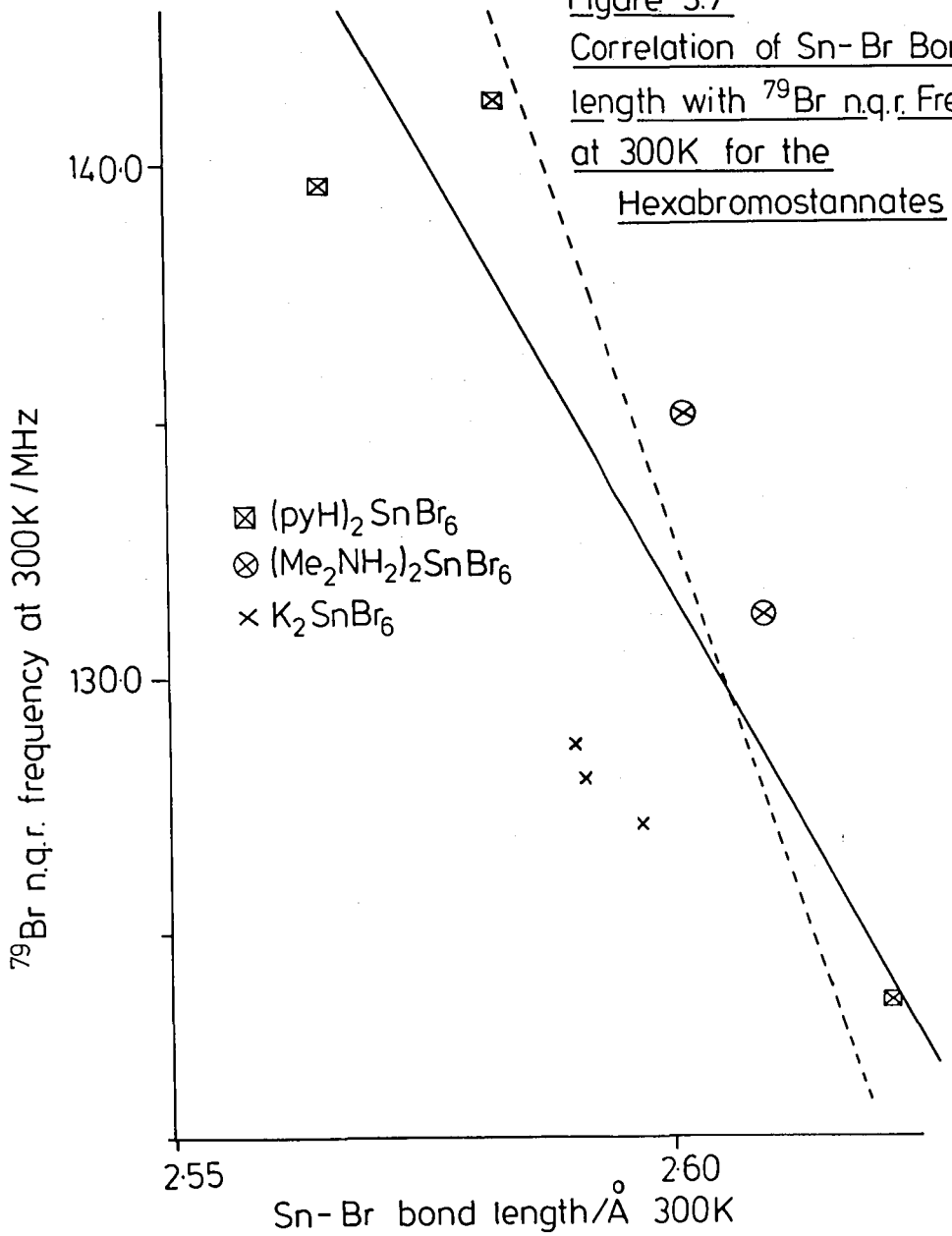


Figure 3.7
Correlation of Sn-Br Bond length with ^{79}Br n.q.r. Frequency at 300K for the Hexabromostannates

The assignment of which bromine atom gives rise to each resonance is therefore unambiguous for these two compounds. K_2SnBr_6, on the other hand, shows three n.q.r. frequencies of equal intensity corresponding to the three inequivalent pairs of bromine atoms per anion in this compound.[37] The assignment of bond lengths to frequencies for this compound, therefore, is made on the assumption that the longer the bond, the lower the n.q.r. frequency. The reason for this assumption has been discussed previously in section 3(b)(iii).

Figure 3.7. shows the plot of the points. The two lines shown represent two least squares calculations: for the solid line the sum of the squares of the frequencies were minimised, whereas for the broken line, the sum of the squares of the bond lengths were minimised. In each calculation the data from K_2SnBr_6 was neglected. These lines can be represented by the following equations:

Solid line:

$$\text{Sn-Br bond length/}\mathring{A} = 2.9780 - 2.8694 \times 10^{-3} \times (^{79}\text{Br n.q.r. frequency/MHz}) \quad \text{(eq. 3.2.)}$$

Broken line:

$$^{79}\text{Br n.q.r. frequency/MHz} = 873.05 - 284.63 \times (\text{Sn-Br bond length/}\mathring{A}) \quad \text{(eq. 3.3.)}$$

The difference in the results obtained from the two different approaches to the calculations reflects the caution which should be exercised in statistical treatment of data, especially when so few points are used in the analysis. The figures from K_2SnBr_6 were not included in the calculations since the bromines in this compound are probably under considerable influence from interanionic repulsion, as the $SnBr_6^{2-}$ ions are in close contact with each other (see previous section). Some of the hexachlorostannates were also discounted from bond length/frequency correlations for similar reasons (section 3(b)(iii)). When repulsions are important, bond length appears to

be a secondary influence on n.q.r. frequencies for the hexachlorostannates, due to core electron polarisations.[19] Such core electron polarisation is expected for the hexabromostannates also, but might have a less marked effect in this case since the data for K_2SnBr_6 are not so far removed from other points as they are for the corresponding hexachlorostannates, where strong interanionic repulsion is occurring (i.e. the deviation from the bond length/frequency linear correlation is less for the hexabromostannates). The presence of an extra shell of eighteen electrons for the bromine atoms over the chlorine atoms may act to soften the effects of repulsion on the core electrons around the bromine nuclei, and so decrease the influence on the n.q.r. frequencies.

In conclusion, the existing data points towards a relationship between ^{79}Br n.q.r. frequencies and Sn-Br bond length, although more results would be desirable before this is firmly established.

(d) Halogeno-complexes of Tin (II)

(i) Frequency Measurements

Several halogeno-complexes of tin (II) were successfully prepared (section 3(e)(iii)), but only three of these produced any n.q.r. signals. The results for these compounds are shown in Table 3.10.

As can be seen all the results are for trichlorostannates, and none of the tribromostannates ($Me_3NH^+SnBr_3^-$, $Me_4N^+SnBr_3^-$ and $pyH^+SnBr_3^-$) gave any signals. The region in which the Br resonances were sought was 40 - 100 MHz since the only compound of this type in the literature, $CsSnBr_3$, gives an ^{81}Br resonance at 63.073 MHz at 298K.[77] All of these tribromostannates were in good crystalline form, and reasonably pure to judge from their experimental analyses (section 3(e)(iii)). It seems unlikely that the Br nuclei should be present in the structures of these compounds as discrete

Table 3.11.

The N.q.r. Frequencies of Some Trihalostannates

Compound	^{35}Cl n.q.r. frequencies at various temperatures/±0.003 MHz					
	77K		190K		300K	
$KCl.KSnCl_3.H_2O$	-		-		-	
$RbSn_2Cl_5$	-		-		-	
$MeNH_3^+SnCl_3^-$	-		-		-	
$Me_2NH_2^+SnCl_3^-$						
$Me_2NH_2^+SnCl_3^-$	10.5[b](1)[a]	11.3[b](2)	10.42[c](2)	10.99[c](1)	10.322(3)	
					10.831(2)	
$Me_3NH^+SnCl_3^-$	11.332(1)	11.560(1)	11.201(1)	11.364(1)	11.004(1)	11.177(2)
	11.859(1)		11.644(1)			
$Me_4N^+SnCl_3^-$	11.98[c]		11.743(1)	11.758(2)	11.418(1)	11.428(2)
$pyH^+SnCl_3^-$	-		-		-	
$Et_4N^+SnCl_3^-$	-		-		-	
	Br n.q.r. frequencies between 40 and 100 MHz					
	77K		190K		300K	
$Me_3NH^+SnBr_3^-$	-		-		-	
$Me_4N^+SnBr_3^-$	-		-		-	
$pyH^+SnBr_3^-$	-		-		-	

(a) Relative intensity estimates; (b) ±0.05 MHz: approximate centres of complex lineshapes; (c) ±0.03 MHz: weak signals.

ions (i.e. surrounded by a spherically symmetrical configuration of electrons) resulting in a zero e.f.g. and hence a zero n.q.r. frequency. Even $CsSnBr_3$, which is fairly ionic to judge from its high electrical conductivity,[58] gives n.q.r. frequencies,[77] indicating the presence of $SnBr_3^-$ ions and not separate Br^- ions. If an alkali metal ion does not produce a perovskite

type structure, composed essentially of mononuclear ions, the cations Me_3NH^+, Me_4N^+ and pyH^+ certainly seem unlikely to do so. The reason, therefore, for the dearth of n.q.r. signals probably lies with the failure of the spectrometer to detect them in the region scanned - the prototype high frequency machine from Decca Radar was used in these searches and this instrument has to date not registered any signals in the region from 50 - 100 MHz, for any compound.

$Me_2NH_2^+SnCl_3^-$ shows the unusual behaviour of exhibiting more n.q.r. resonances at 300K than at lower temperatures. Normally the higher the temperature, the more motion within the crystal lattice, and the greater the averaging of e.f.g.'s which creates equivalence in electronic environments and hence fewer n.q.r. frequencies. At lower temperatures, however, vibrations tend to be reduced, and for many compounds points are reached where averaging effects are removed to give two or more discrete, different environments, and more n.q.r. frequencies are observed. Many examples of this type of behaviour can be seen earlier in this chapter as well as in Chapter 4. The reason for the decrease in the number of signals on going to lower temperature in this instance is probably the close overlapping of signals at the temperatures measured. This would make individual measurement of the resonances impossible. Evidence for this is afforded by the existence at 300K of two very close resonances at 10.747 and 10.831 MHz, and by the fact that the signals at 77K produced lineshapes which indicated that there might have been more than one resonance present at each location - in these cases only the centres of the lineshapes were quoted to allow for this uncertainty. The signals at 190K were barely observable making any resolution of fine structure impossible. The presence of three lines of relative intensities of 3:1:2 at 300K is

interesting. If the structure contains discrete, single anions, this implies the existence of more than one type of anion, possibly two, with one containing three equivalent chlorines and the other with two chlorines in a different environment to the third. It must be stated, however, that the values of relative intensities are only visual estimates, and the conclusions drawn from them must be necessarily guarded, though a crystal structure determination might be interesting.

$Me_3NH^+SnCl_3^-$ shows an increase in the number of signals on going from 300K to 190K, which indicates an intermediate phase change. The existence of this change was confirmed by a fuller temperature dependence study (section 4(e)) and detailed discussion of the compound is included there.

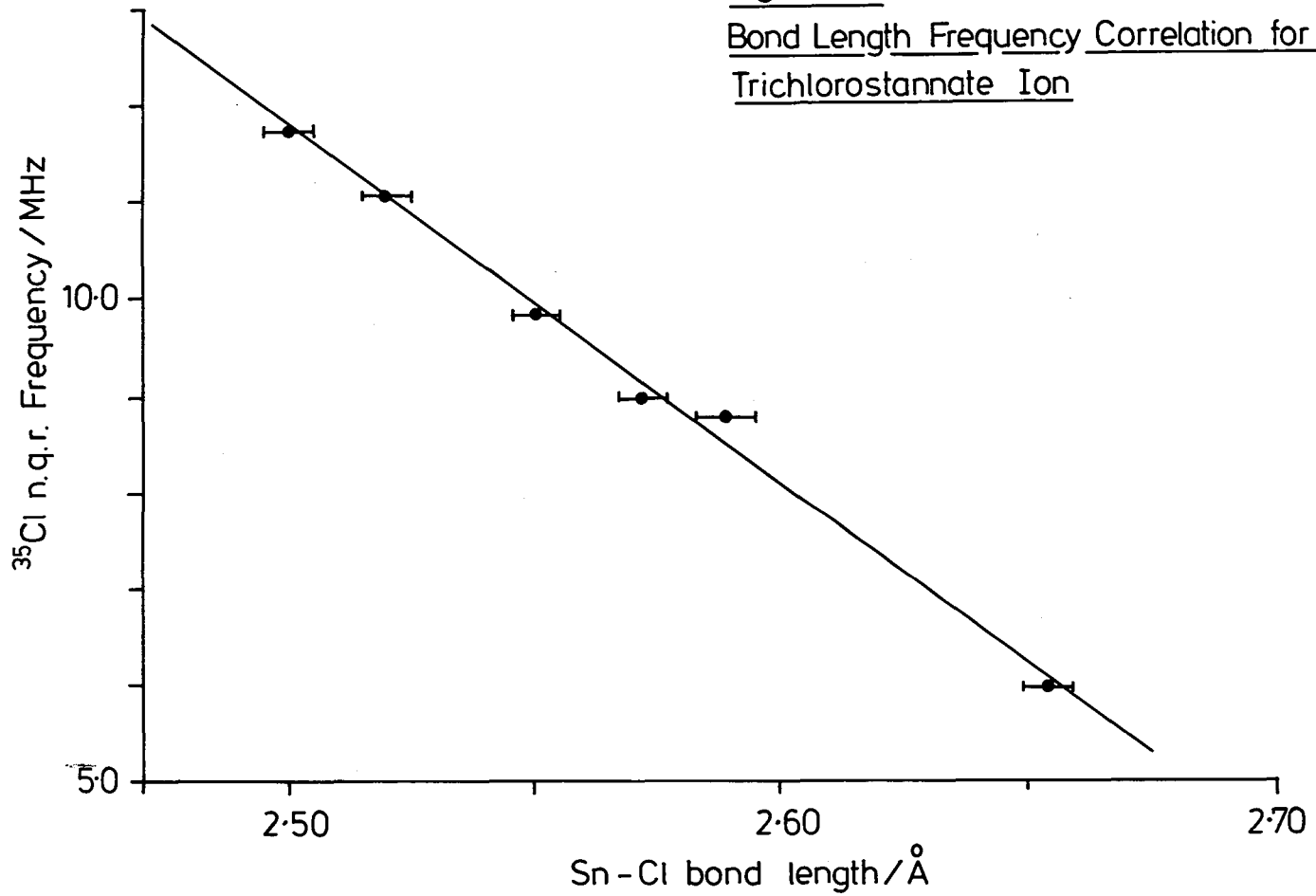
$Me_4N^+SnCl_3^-$ appears to show evidence of a phase transition between 77K and 190K since, unusually, its two signals for the higher temperature go to one for the lower. The signal at 77K was extremely weak, however, and if two signals as closely spaced as those at 190K and 300K were present, then they would not have been resolved. Indeed at both 190K and 300K the resonances were only able to be resolved from each other since the linewidths of the signals were very narrow. It was generally found that the linewidths of the trichlorostannates were less than those of the hexachlorostannates. The observation of two lines of 2:1 intensity leads to the conclusion that the anion has two chlorines in a different environment to the third, although this difference is expected to be slight since the n.q.r. frequencies are so similar.

For a number of trichlorostannates, no ^{35}Cl n.q.r. signals could be found at 77K, 190K or 300K, despite the compounds being in good crystalline form (a factor found to be important for observing signals from hexachlorostannate salts, see Table 3.4.). Several of the compounds

were difficult to synthesise, and good elemental analyses were not obtained for NH_4SnCl_3, $KSnCl_3$ and $RbSnCl_3$, (see sect. 3(e)(iii)) despite the products being in crystalline form. The problem here is thought to be the possible presence of several different compounds such as $MSnCl_3$, MSn_2Cl_5, $MCl.MSnCl_3$, and $MCl.MSnCl_3.H_2O$ (M = cation). Indeed the elemental analyses for the compound obtained in the attempted preparation of $RbSnCl_3$ suggest that $RbSn_2Cl_5$ was formed instead, while for the others, mixtures of several species are indicated. Now if a sample for n.q.r. study contains several different species, the total number of potential, observable resonances is greater, but the intensity of each one is reduced due to its physical dilution within the sample. Furthermore the random distribution of species within the sample may well help to average e.f.g.'s and reduce the intensities of the corresponding chlorine n.q.r. signals, or broaden the linewidth of each resonance. The combination of these factors make detection of n.q.r. samples from mixtures difficult, so the failure to observe signals for the ammonium, potassium and rubidium compounds is perhaps not surprising. For $pyH^+SnCl_3^-$, $MeNH_3^+SnCl_3^-$ and $Et_4N^+SnCl_3^-$, however, fairly good elemental analyses were obtained, together with good crystals, but still no signals were detected. The cause of this is not obvious. If physical dilution of the resonant nuclei by large cations was responsible, then it would be expected that $MeNH_3^+SnCl_3^-$ should give stronger signals than any of the other methyl-substituted ammonium trichlorostannates. In reality the compound with the smallest cation in the series $Me_nNH_{4-n}^+$ (n = 1, 2, 3) is the only one not to produce ^{35}Cl n.q.r. signals.

Figure 3.8.

Bond Length Frequency Correlation for the Trichlorostannate Ion



(ii) The Relationship Between Sn-Cl Bond Length and ^{35}Cl N.q.r. Frequency for the Trichlorostannates

There are two compounds in the literature for which both Sn-Cl bond length and ^{35}Cl n.q.r. data is available, though no attempt to correlate the two quantities has yet been made for the trihalostannates. The values for these compounds, $CsSnCl_3$ and $[SnCl(H_2O)_2]SnCl_3.H_2O$, and the relevant references, are shown in Table 3.11.. The assignment of the longest bond to the lowest n.q.r. frequency is made on the assumptions detailed earlier for the hexachlorostannates (section 3(b)(iii)). Figure 3.8. contains a plot of the data and reveals a good linear correlation for bond length with n.q.r. frequency for these trichlorostannates. The solid line shown in the figure is the least squares fit which can be represented by the equation:

$$^{35}Cl \text{ n.q.r. frequency/MHz} = 103.95-36.89 \times (\text{Sn-Cl bond length/}\mathring{A}) \quad \text{(eq. 3.4.)}$$

From equation 3.4. it should therefore be possible to predict some of the Sn-Cl bond lengths for the compounds in this work. It is therefore expected that at 300K $Me_2NH_2^+SnCl_3^-$ will have three different Sn-Cl bonds of

Table 3.12.

Correlation of ^{35}Cl N.q.r. Frequencies with Sn-Cl Bond Lengths for the Trichlorostannates at 300K

Compound	d(Sn-Cl)/$\mathring{A}$	Structure reference	^{35}Cl n.q.r. frequency at 300K/MHz	N.q.r. reference
$CsSnCl_3$	2.55 ± 0.01		9.799	77
	2.52 ± 0.01	119	11.005	
	2.50 ± 0.01		11.695	
$[SnCl(H_2O)_2]SnCl_3.H_2O$	2.654 ± 0.005	76	5.94	76
	2.589 ± 0.006		8.76	
	2.572 ± 0.005		8.95	

lengths 2.538, 2.527 and 2.524Å; $Me_3NH^+SnCl_3^-$ will have two different Sn-Cl bonds of lengths 2.520 and 2.515Å; and $Me_4N^+SnCl_3^-$ will have two slightly different bonds of length around 2.508Å. Furthermore, from the structure of $KCl.KSnCl_3.H_2O$,[75] which has two Sn-Cl bonds of lengths 2.54 and 2.63Å (the former twice as abundant as the latter), two ^{35}Cl n.q.r. frequencies, at 300K, at 10.25 and 6.93 MHz would be expected with respective intensities 2:1. A product, obtained from the method of preparation detailed in the crystal structure reference[75] was synthesised, but unfortunately it gave no n.q.r. signals.

(e) Preparation of Compounds

(i) Hexachlorostannates

The infra-red (i.r.) spectra of the hexachlorostannates detailed in this section were recorded for several reasons: to check the dryness of the compounds, to characterise them with respect to their cations and to check that $SnCl_6^{2-}$ rather than $SnCl_5^-$ ions were formed. Only observations in the Sn-Cl stretching region (from about 350 - 250 $cm.^{-1}$) are included in the following discussions, except where particular points are to be made. It may be inferred that the compounds were dry, and that the cations showed similar bands to those in other compounds, where i.r. data in those regions is not quoted. For the data in the Sn-Cl stretching region, assignments to $SnCl_6^{2-}$ vibrations are made where it seems fairly certain that these are correct, otherwise the bands observed are quoted without assignment. As a reference point in this context the i.r. vibrational frequencies of typical $SnCl_5^-$ and $SnCl_6^{2-}$ species are shown below:

$Et_4N^+SnCl_5^-$[126] 351(vs) 330(vs) 299(m) cm^{-1}

$(Et_4N)_2SnCl_6$[126] 303(vs) cm^{-1}

Bands below 200 cm.$^{-1}$ are not quoted above since these were not observable on the spectrometer used for the measurements (operating range 4000 - 200 cm.$^{-1}$). The $SnCl_6^{2-}$ ions may show more than a single absorption in cases where the anion is distorted.

$(MeNH_3)_2SnCl_6$ was prepared by two methods. Firstly to a suspension of 24.2 mmoles $MeNH_3^+Cl^-$ (dried previously using methanol and benzene) was added 11.9 mmoles of $SnCl_4$ in 10 mls. CH_2Cl_2, and the mixture was stirred overnight to yield a white powdery, solid product. This was filtered off and washed with CH_2Cl_2 and 30 - 40° petroleum ether. The preparation was performed under a dry nitrogen atmosphere.

Analysis:

$(MeNH_3)_2SnCl_6$ requires C 6.07% H 3.03% N 7.08% Cl 53.83% Sn 30.00%

found: C 6.19% H 3.62% N 6.99% Cl 53.6% Sn 31.3%

In a second preparation, $Me_3NH^+Cl^-$ and $SnCl_4.5H_2O$ were mixed together in a 2:1 ratio in an excess of concentrated aqueous hydrochloric acid (cHCl) to yield a white powder. This was then filtered off, recrystallised from cHCl, washed with CH_2Cl_2 and Et_2O, and finally dried in a desiccator.

Analysis of crystalline product: C 6.18% H 3.27% N 6.90%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 310 cm.$^{-1}$ (lit.[65] 317 cm.$^{-1}$).

$(Me_2NH_2)_2SnCl_6$ was obtained by adding together a 2:1 ratio of $Me_2NH_2^+Cl^-$ and $SnCl_4$ in an excess of cHCl to yield a white precipitate. This was redissolved by heating the reaction mixture, which upon slow cooling yielded fine, white needles of the product. These were then filtered off, washed with CH_2Cl_2 and dried under vacuum.

Analysis:

$(Me_2NH_2)_2SnCl_6$ requires C 11.33% H 3.77% N 6.61%

found C 11.36% H 3.52% N 6.51%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 309 cm.$^{-1}$.

$(Me_3NH)_2SnCl_6$ was prepared in a similar manner to the previous compound, except that an ethanol solution of Me_3N (33% w.w.) was used instead of $Me_2NH_2^+Cl^-$, thus preparing $Me_3NH^+Cl^-$ "in situ". Cubic, white crystals were obtained.

Analysis:

$(Me_3NH)_2SnCl_6$ requires C 15.94% H 4.43% N 6.20%

found C 15.70% H 4.17% N 6.07%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 310(sh) and 301 $cm.^{-1}$.

$(Me_4N)_2SnCl_6$ was prepared by the addition of the stoichiometric quantities of Me_4NCl and $SnCl_4$, in cHCl solution, to give a white, powdery precipitate, which was subsequently filtered off, washed with CH_2Cl_2, and dried under vacuum. The powder was recrystallised from cHCl at a later date for n.q.r. studies.

Analysis of powder:

$(Me_4N)_2SnCl_6$ requires C 20.01% H 5.00% N 5.84% Sn 24.74% Cl 44.40%

found C 19.65% H 5.73% N 7.05% Sn 24.15% Cl 44.04%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 298 $cm.^{-1}$ (literature values 298[127] or 309[126] $cm.^{-1}$).

$(Et_2NH_2)_2SnCl_6$ was prepared by two methods. In the first, sufficient $Et_2NH_2^+Cl^-$ (dried using methanol and benzene) was dissolved in 200 mls. of CH_2Cl_2 to form a 2:1 molar ratio when reacted with 17.1 mmoles of $SnCl_4$ in 20 mls. of CH_2Cl_2. The addition of $SnCl_4$ produced an instant white precipitate which was filtered off and washed with 30 - 40° petroleum ether. This preparation was performed under a dry nitrogen atmosphere.

Analysis:

$(Et_2NH_2)_2SnCl_6$ requires C 20.01% H 5.00% N 5.84% Sn 24.74% Cl 44.40%

found C 19.77% H 5.22% N 5.51% Sn 23.7% Cl 43.3%

The second preparative method used was similar to that for $(Me_2NH_2)_2SnCl_6$ except that $Et_2NH_2^+Cl^-$ was used instead of $Me_2NH_2^+Cl^-$. The product in this case was obtained in a white, crystalline form.

Analysis of crystals: C 19.98% H 5.94% N 5.53%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 300 $cm.^{-1}$.

$(Et_3NH)_2SnCl_6$ was prepared by dissolving a 2:1 ratio of $Et_3NH^+Cl^-$ and $SnCl_4.5H_2O$ in hot water, slightly acidified with cHCl, and then allowing the solution to cool slowly. The white crystals thereby produced were filtered off and dried by successive washings with CH_2Cl_2 and Et_2O.

Analysis:

$(Et_3NH)_2SnCl_6$ requires C 26.68% H 5.97% N 5.23% Cl 39.76%

found C 26.50% H 6.61% N 5.07% Cl 37.85%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 318, 305 and 287 $cm.^{-1}$.

$(Et_4N)_2SnCl_6$ was prepared by a similar method to $(Me_2NH_2)_2SnCl_6$ except that $Et_4N^+Cl^-$ was substituted for $Me_2NH_2^+Cl^-$. White crystals were obtained.

Analysis:

$(Et_4N)_2SnCl_6$ requires C 32.45% H 6.76% N 4.73%

found C 32.86% H 7.38% N 4.64%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 299 $cm.^{-1}$ (literature values: 318 and 276;[126] 303;[127] or 306 and 291 [65] $cm.^{-1}$).

$(Prop_4N)_2SnCl_6$ was prepared by dissolving $Prop_4N^+I^-$ and $SnCl_4.5H_2O$, in a 2:1 ratio, in cHCl. The solution was reduced in volume, filtered when hot (to remove some iodine which was precipitated) and allowed to cool slowly. The white crystals obtained were recrystallised a second time, filtered off, washed with Et_2O to remove the last traces of iodine, and dried in vacuo.

Analysis:

$(Prop_4N)_2SnCl_6$ requires C 40.93% H 7.96% N 3.98%

found C 41.44% H 8.84% N 3.84%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 310(sh) and 295 $cm.^{-1}$.

$(But_4P)_2SnCl_6$ was prepared by stirring $But_4P^+Cl^-$ with $SnCl_4.5H_2O$ in a 2:1 ratio, in cHCl, for 4 hours. The white powder thus obtained was filtered off and dried in vacuo. The compound was finally recrystallised from acetone.

Analysis:

$(But_4P)_2SnCl_6$ requires C 45.19% H 8.47%

found C 45.32% H 8.90%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 298 $cm.^{-1}$.

^{31}P n.m.r.: in CH_2Cl_2, one peak at 34.0 ppm.

$(Me_3S)_2SnCl_6$ was obtained by adding a solution of $Me_3S^+I^-$ in cHCl to a solution of $SnCl_4.5H_2O$ in cHCl, in a 2:1 ratio; a yellowish precipitate formed after a few seconds. The solid was filtered off and washed with acetone to remove any traces of iodine, before it was recrystallised from fresh cHCl to yield off-white cubic crystals.

Analysis:

$(Me_3S)_2SnCl_6$ requires C 14.82% H 3.71% S 13.1% Sn 24.44% Cl 43.85%

found C 14.75% H 4.01% S 12.8% Sn 23.1% Cl 43.35%

i.r. spectrum: strong $SnCl_6^{2-}$ absorption at 305 $cm.^{-1}$.

$(2\text{-ClpyH})_2SnCl_6$ was prepared by dissolving a 2:1 ratio of 2-Clpy and $SnCl_4.5H_2O$ in excess cHCl; after a few seconds a white precipitate appeared. The solid was redissolved by heating the solution, which on slow cooling gave white crystals of the product, which were dried under vacuum.

Analysis:

$(2\text{-ClpyH})_2SnCl_6$ requires C 21.40% H 1.78% N 4.99% Sn 21.17% Cl 50.65%

found C 21.55% H 1.76% N 4.17% Sn 21.26% Cl 50.45%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 308 and 282 $cm.^{-1}$.

$(3\text{-ClpyH})_2SnCl_6$ was prepared by two methods. Firstly 27.6 mmoles of 3-ClpyH^+Cl^- (prepared from dissolving the base in cHCl followed by removal of the solvent on the vacuum line) dissolved in 100 mls. of CH_2Cl_2 were added to 13.6 mmoles of $SnCl_4$ in 10 mls. CH_2Cl_2, thus producing a white solid. The mixture was then stirred for 36 hrs. before filtration and washing of the product with 30 - 40° petroleum ether were performed. This preparation was carried out under a dry nitrogen atmosphere.

Analysis:

$(3\text{-ClpyH})_2SnCl_6$ requires C 21.40% H 1.78% N 4.99% Sn 21.17% Cl 50.65%

found C 20.33% H 1.97% N 4.62% Sn 20.10% Cl 47.96%

i.r. spectrum: strong absorptions at 335, 325, 310 and 285 $cm.^{-1}$.

The second preparation was performed in a similar manner to that of $(2\text{-ClpyH})_2SnCl_6$, except that the base used was 3-Clpy not 2-Clpy. White crystals were obtained.

Analysis of crystalline product: C 20.86% H 2.31% N 4.68%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 315(sh) and 295 $cm.^{-1}$.

$(3,5\text{-ClpyH})_2SnCl_6$ was prepared by two methods. Firstly $3,5\text{-ClpyH}^+Cl^-$ was prepared by dissolving the base in excess cHCl followed by removal of the solvent under vacuum. The solid thus obtained was further purified by sublimation. 25.0 mmoles of the pure chloride were then dissolved in 200 mls. of CH_2Cl_2 and 11.5 mmoles of $SnCl_4$ were added to yield a white powdery precipitate, which was filtered off and washed with CH_2Cl_2 and 30 - 40° petroleum ether. This reaction was performed under a dry nitrogen atmosphere.

Analysis:

$(3,5\text{-ClpyH})_2SnCl_6$ requires C 19.06% H 1.27% N 4.45% Cl 56.38%

found C 20.62% H 0.90% N 4.78% Cl 50.76%

i.r. spectrum: absorptions at 338, 315 and 290 $cm.^{-1}$.

The second preparation was essentially the same as that used for $(2\text{-ClpyH})_2SnCl_6$ except that 3,5-Clpy was used instead of 2-Clpy. White crystals of product were obtained.

Analysis of crystals: C 18.49% H 1.38% N 4.06%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 303 and 292(sh) $cm.^{-1}$.

$(3,5\text{-lutH})_2SnCl_6$ was prepared using similar methods to the previous compound, except that 3,5-lut was used as the base, and in the preparation of $3,5\text{-lutH}^+Cl^-$ no sublimation was performed. The non-aqueous preparation yielded an off-white powder:

Analysis:

$(3,5\text{lutH})_2SnCl_6$ requires C 30.68% H 3.65% N 5.11% Sn 21.64% Cl 38.90%

found C 31.19% H 3.84% N 4.90% Sn 23.6% Cl 39.2%

i.r. spectrum: broad absorption centred at 305 $cm.^{-1}$.

The preparation using cHCl yielded white crystals:

Analysis: C 30.69% H 3.78% N 4.80%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 315(sh) and 290 $cm.^{-1}$.

$(pyH)_2SnCl_6$ was prepared using the two methods described for $(3,5\text{-ClpyH})_2SnCl_6$ except that py was used instead of 3,5-Clpy, and the hydrochloride pyH^+Cl^- was not sublimed. The non-aqueous preparation yielded a white powder:

Analysis:

$(pyH)_2SnCl_6$ requires C 24.42% H 2.44% N 5.70% Sn 24.16% Cl 43.32%

found C 27.40% H 2.74% N 5.93% Sn 20.0% Cl 40.2%

This method, when repeated but with stirring the reaction mixture for 36 hrs. before filtering off the solid, gave better analyses:

C 24.19% H 2.49% N 5.66%

i.r. spectrum: broadish absorption at 310 cm.$^{-1}$.

The preparation using a cHCl medium gave white crystals as the product.

Analysis: C 24.24% H 2.49% N 5.34%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 310 and 286 cm.$^{-1}$.

$(3\text{-IpyH})_2SnCl_6$ was prepared by two methods. Firstly, 3-IpyH^+Cl^- (obtained from dissolving the base in cHCl, followed by removal of the solvent under vacuum) and $SnCl_4$, in a 2:1 ratio, were stirred together in CH_2Cl_2 for 48 hrs. The white powder thus obtained was filtered off and washed with CH_2Cl_2 and 30 - 40° petroleum ether. The preparation was carried out under a dry nitrogen atmosphere.

Analysis:

$(3\text{-IpyH})_2SnCl_6$ requires C 16.14% H 1.34% N 3.76% Sn 15.96% Cl 28.64% I 34.15%

found C 17.15% H 1.48% N 3.73% Sn 12.15% Cl 24.2% I 34.5%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 310(sh) and 297 cm.$^{-1}$.

The second preparation was similar to that of $(2\text{-ClpyH})_2SnCl_6$ except that 3-Ipy was used instead of 2-Clpy. White crystals were obtained.

Analysis: C 16.68% H 1.48% N 2.78% Sn 15.74% Cl 28.2% I 33.97%

i.r. spectrum: strong absorptions at 330, 298 and 282(sh) cm.$^{-1}$.

$(Ph_2I)_2SnCl_6$ was prepared from reacting a suspension of 8.7 mmoles of $Ph_2I^+Cl^-$ in 150 mls. of CH_2Cl_2 with 4.3 mmoles of $SnCl_4$ by stirring together for 3 hrs. under a dry nitrogen atmosphere. A white powder was produced which was filtered off and washed with 30 - 40° petroleum ether. No recrystallisation of this compound was possible due to its insolubility in a large number of solvents.

Analysis:

$(Ph_2I)_2SnCl_6$ requires C 32.22% H 2.24% Sn 13.28% Cl 23.83% I 28.42%

found C 33.11% H 2.09% Sn 11.6% Cl 22.9% I 28.6%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 312, 296 and 287 $cm.^{-1}$ (lit.[113] 311, 294 and 284 $cm.^{-1}$).

$(SCl_3)_2SnCl_6$ was prepared according to a method in the literature.[128] Neat SCl_2 and $SnCl_4$ in a 4:1 ratio were mixed together and allowed to stand in a stoppered flask, under a dry nitrogen atmosphere. Orange, cubic crystals of the product appeared after several hours. These were filtered off and quickly washed with 30 - 40° petroleum ether before transfer to a sealed ampoule for n.q.r. experiments. The product was found to disappear if left to stand around in an open vessel, even under dry nitrogen, thus necessitating its storage in an ampoule. The disappearance probably involves decomposition into volatile components of the type SCl_2, Cl_2 and $SnCl_4$, although other species might be present.

Because of its instability, analysis of the product was difficult: Sn, S and Cl elemental analyses all produced low values, though the ratio of these three elements was 0.85:1.95:12.00 whereas the Sn:S:Cl ratio should be 1.00:2.00:12.00. The i.r. spectrum showed a band in the region expected for $SnCl_6^{2-}$ at 309 $cm.^{-1}$.

Analysis:

$(SCl_3)_2SnCl_6$ requires Sn 19.52% Cl 69.96% S 10.52%

found Sn 15.4% Cl 64.8% S 9.5%

$(2\text{-CNpyH})_2SnCl_6$, $(3\text{-CNpyH})_2SnCl_6$ and $(4\text{-CNpyH})_2SnCl_6$ were found not to be preparable from the cHCl medium which had been used successfully for many of the other hexachlorostannates. The procedure followed in attempts at making these compounds was that used for $(2\text{-ClpyH})_2SnCl_6$, except that

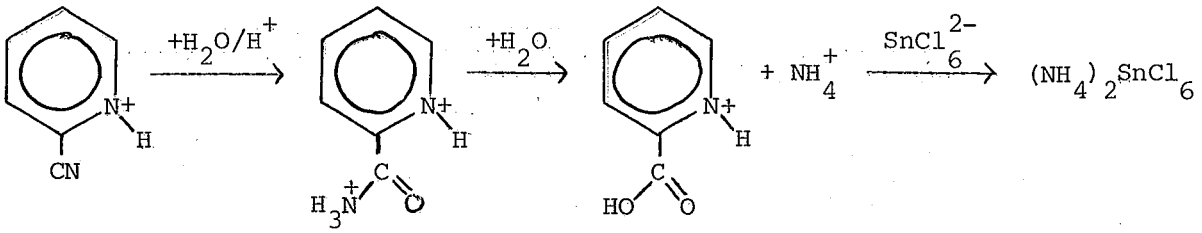
2-CNpy, 3-CNpy or 4-CNpy were used instead of 2-Clpy for the respective preparations. All three products of these preparations showed evidence of the $SnCl_6^{2-}$ ion through their i.r. spectra: from the $(2\text{-CNpyH})_2SnCl_6$ attempt, a band at 322 $cm.^{-1}$; from the $(3\text{-CNpyH})_2SnCl_6$ attempt, bands at 322, 315 and 285(sh) $cm.^{-1}$; and from the $(4\text{-CNpyH})_2SnCl_6$ attempt, bands at 320 and 310(sh) $cm.^{-1}$. The elemental analyses however, clearly show the desired products were not obtained.

Analyses:

$(2\text{-,3- or 4-CNpyH})_2SnCl_6$ requires	C 26.58%	H 1.85%	N 10.34%	Sn 21.91%	Cl 39.32%
$(2\text{-CNpyH})_2SnCl_6$ attempt:	C -	H 2.74%	N 7.96%	Sn 32.2%	Cl 55.1%
$(3\text{-CNpyH})_2SnCl_6$ attempt:	C 17.33%	H 2.69%	N 8.84%	Sn 26.4%	Cl 45.7%
$(4\text{-CNpyH})_2SnCl_6$ attempt:	C 17.08%	H 3.13%	N 8.05%	Sn 12.05%	Cl 47.5%

The analyses from the 2-CNpy reaction product are consistent with $(NH_4)_2SnCl_6$ which requires H 2.2% N 7.6% Sn 32.3% Cl 57.9%, while the figures for the 3-CNpy and 4-CNpy attempts suggest that a mixture of NH_4^+ and 3- or 4-$CNpyH^+$ cations may be present in each product. The low Sn value for $(4\text{-CNpyH})_2SnCl_6$ is attributable to the difficulties experienced by the analyst in determining tin content in the presence of chlorine. Further evidence of the presence of NH_4^+ ions in each of the products was afforded by the observation of broad i.r. absorptions around 3200 $cm.^{-1}$, which correspond to N-H stretches.[129] The product from the attempted $(2\text{-CNpyH})_2SnCl_6$ preparation also showed a single ^{35}Cl n.q.r. frequency at 15.435 MHz at 300K (c.f. 15.453 at 300K for $(NH_4)_2SnCl_6$ from the literature)[19] while that from the $(4\text{-CNpyH})_2SnCl_6$ preparation showed three frequencies at 15.442, 15.512 and 15.580 MHz at 300K.

The formation of ammonium ions from cyano-pyridine species most probably occurs via acid hydrolysis of the cyanide groups as illustrated below:



Although no attempt was made to confirm this suggested mechanism, acid hydrolysis of cyanides via amides to ammonium salts is well-established for organic compounds. Since the 2-CNpy underwent complete reaction to produce $(NH_4)_2SnCl_6$ only, whereas 3-CNpy and 4-CNpy yielded mixed products, it is clear that the hydrolysis occurs faster for 2-CNpy. This is possibly due to rate enhancement from the proximity of the ring nitrogen of the pyridine to the cyanide group for this compound.

Another form of reaction could have occurred between $SnCl_4$ and CNpy which would not have led to the formation of hexachlorostannates; this is the formation of cyanide adducts of the type $2(CNpy).SnCl_4$. Cyanide adducts of tin tetrachloride have indeed been studied by other workers.[17] To test for this reaction 4-CNpy was added to $SnCl_4$ in a 2:1 ratio, in CH_2Cl_2, under dry nitrogen conditions, and a white precipitate was instantly formed.

Analysis:

$SnCl_4.2$(4-CNpy) requires	C 30.24%	H 1.71%	N 11.95%	Sn 25.34%	Cl 30.27%
found	C 31.17%	H 2.28%	N 13.03%	Sn 21.9%	Cl 30.9%

The ^{35}Cl n.q.r. spectrum showed resonances at 17.755 and 18.310 MHz at 300K, and its i.r. spectrum contained bands in the Sn-Cl stretching region at 349 and 332 $cm.^{-1}$ (higher than typical $SnCl_6^{2-}$ bands). The product from the attempted $(4\text{-CNpyH})_2SnCl_6$ preparation showed no similarity in either its i.r. or ^{35}Cl n.q.r. spectra, so the formation of cyanide adducts is thought unlikely. The reason that adduct formation does not occur in

cHCl is most probably because of the inability of cyanide groups to compete with chloride ligands for co-ordination with the tin.

A preparation of $(4\text{-CNpyH})_2SnCl_6$ was attempted from CH_2Cl_2 as a solvent by reaction of a 2:1 ratio of 4-CNpyH^+Cl^- and $SnCl_4$, under a dry nitrogen atmosphere. This mixture was stirred overnight before the resulting white powder was filtered off and washed with 30 - 40° petroleum ether.

Analysis: C 26.84% H 3.04% N 9.51%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 315, 295(sh) and 283(sh) $cm.^{-1}$.

The 4-CNpyH^+Cl^- used above was prepared from 4-CNpy in cHCl followed by removal of the solvent on the vacuum line, but despite this the cation appears, from the analyses, to have remained fairly intact. The reason for this may be due to less heating of the compound than in the recrystallisation stage of the attempted preparation of $(4\text{-CNpyH})_2SnCl_6$ from cHCl solution.

The product obtained from the non-aqueous preparation of $(4\text{-CNpyH})_2SnCl_6$ gave no ^{35}Cl n.q.r. signals at 77, 196 or 300K. For this reason further attempts at preparation of $(CNpyH)_2SnCl_6$ compounds were not made.

$[(Me_2N)_2CH]_2SnCl_6$ has been prepared by Russian workers.[46] Their method was attempted but unfortunately the preparation proved unrepeatable despite several attempts.

The literature method[46] proceeeded as follows. Dimethylformamide (DMF), Ph_2SiCl_2 and $SnCl_2$, in the molar ratio of 8:2.5:1, were heated from 438 to 458K for a period of 8 hrs., until evolution of gas ceased. The yield of the hexachlorostannate was reported as quantitative. The crude product was recrystallised from CH_3CN. No mention, however, was made of the hygroscopic nature of $(Me_2N)_2CH^+$ as found for $(Me_2N)_2CH^+Cl^-$ in the

literature,[130-133] or any precautions taken to exclude water. Furthermore it was found impossible to heat the reaction mixture to the reported temperature,[46] since it reached boiling point at around 425K, at atmospheric pressure; no mention of high pressures was made in the preparation given.

The unsuccessful attempts at $[(Me_2N)_2CH]_2SnCl_6$ in this work were all carried out in a similar manner to the preparation detailed in the previous paragraph. The presence of water was excluded after the first attempt, which was not performed under rigorously anhydrous conditions and yielded NH_4Cl (analysis: found H 8.83% N 25.75%; NH_4Cl requires H 7.48% N 26.19%, i.r. spectrum very similar to that of a sample of commercial NH_4Cl), indicating that even if the cation $(Me_2N)_2CH^+$ had been produced, it had been further attacked to yield NH_4^+, possibly via hydrolysis. In a second attempt 3.78 g. $SnCl_2$, 12 mls. Ph_2SiCl_2 and 22 mls. DMF were refluxed for 20 hrs. The reaction mixture contained more than the quantity of DMF stated in the literature[46] in an attempt to raise the reaction temperature, but only 425K could be obtained. The reaction time was also extended since it proved impossible to judge at which point the evolution of gas stopped under reflux conditions. On cooling the reaction mixture with an ice bath, fine colourless needles of product were obtained. Analysis:

$[(Me_2N)_2CH]_2SnCl_6$ requires C 22.48% H 4.87% N 10.49%

found C 28.48% H 11.75% N 15.16%

During analysis the sample was noticed to be gaining weight, indicating its hygroscopic nature. The presence of high C and N values shows, however, that the product was not the desired one. Furthermore the reaction mixture from this attempted preparation (before precipitation of the product) when dissolved in CH_3CN, showed a single ^{119}Sn n.m.r. peak at

-88.5 ppm. $SnCl_6^{2-}$ ions, however, give ^{119}Sn n.m.r. peaks around -730 ppm [e.g. $(Pent_4N)_2SnCl_6$ in CH_2Cl_2: -734.6 ppm]. The peak at -88.5 ppm is more consistent with an inorganic tin (II) compound than a tin (IV) one, which tends to come at higher field.

Since no evidence of tin (IV) was obtained by using the Russian preparation[46] (no evidence of $SnCl_6^{2-}$ in the i.r. spectrum as well as the n.m.r. results), an adaptation of their method was tried. A 2:5:8 molar ratio of Ph_2SiCl_2 and DMF was refluxed for 16 hrs., and the precipitate obtained on cooling this mixture was filtered off and washed with 30 - 40° petroleum ether. This precipitate [assumed to be $(Me_2N)_2CH^+Cl^-$] was then dissolved in CH_2Cl_2 and the calculated quantity of $SnCl_4$ was added, such that a 2:1 ratio of precipitate to $SnCl_4$ was obtained; a new white powder now formed. The powder was removed and recrystallised from CH_3CN to give white needles. All operations were carried out under a dry nitrogen atmosphere.

Analysis: C 18.54% H 4.69% N 9.15%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 310, 295, 283 $cm.^{-1}$; strong band at 1700 $cm.^{-1}$.

The elemental analyses obtained from this preparation were the closest to those for the title compound, and the presence of an i.r. band at 1700 $cm.^{-1}$ is in accordance with a band at 1702 $cm.^{-1}$ in the literature.[46] The melting point of the product, however, was low at 478K (c.f. lit.[46] 540K). Its i.r. spectrum also showed a number of bands found in the spectrum of $(Me_2NH_2)_2SnCl_6$, in particular one at 3190 $cm.^{-1}$ corresponding to N-H stretches. The preparation was therefore not successful.

$(PhCH{=}NH_2)_2SnCl_6$. Attempts were made to prepare this compound according to methods in the literature.[48,133] $SnCl_2$ was finely ground, suspended in

anhydrous Et_2O in an ice bath and HCl gas was bubbled through the suspension until all the solid had dissolved, and 2 liquid layers were formed. PhCN (such that the ratio of PhCN:$SnCl_2$ was 2:3) was added and the solution stirred vigorously for 10 mins.: after standing for 2 hrs., a white precipitate formed. This was filtered off, washed with Et_2O and dried in a desiccator.

Analysis:

$(PhCH=NH_2)_2SnCl_6$ requires C 30.90% H 2.94% N 5.15% Sn 21.83% Cl 39.18%

found C 25.90% H 3.31% N 8.50% Sn 23.8% Cl 38.6%

i.r. spectrum: strong $SnCl_6^{2-}$ bands at 310 and 285 $cm.^{-1}$. Despite evidence of $SnCl_6^{2-}$ formation, the analysis shows a high proportion of N, and low proportion of C, possibly indicating the presence of NH_4^+ ions (conceivably originating from hydrolysis of the cation). The preparation was therefore repeated but this time under a dry nitrogen atmosphere, and with the HCl gas dried by passing it through concentrated sulphuric acid and $CaCl_2$. The analysis of the product from this preparation is shown below:

C 26.23% H 3.24% N 3.17% Sn 17.63% Cl 39.2%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 310 and 285 $cm.^{-1}$.

The low Sn value is possibly attributable to analytical problems, but the low C and N values indicate the failure of the preparation. A final preparation under anhydrous conditions was then attempted, except that no vigorous stirring of the reaction mixture was performed; instead it was allowed to stand for 48 hrs. when crystals of the product, rather than powder, were obtained.

Analysis: C 26.61% H 3.35% N 3.56%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 315(sh), 295 and 280(sh) $cm.^{-1}$.

Again the analyses indicate the failure of this preparation, despite evidence of $SnCl_6^{2-}$ anions from the i.r. spectrum.

$(PCl_4)_2SnCl_6$. An attempt was made to prepare this compound by adding 13.5 mmoles of $SnCl_4$ to 25.9 mmoles of PCl_5 dissolved in 200 mls. of CH_2Cl_2. The mixture was stirred for 48 hrs. and the resulting white powder was filtered off and washed with 30 - 40° petroleum ether. All operations were carried out under a dry nitrogen atmosphere due to the sensitivity of PCl_4^+ to moisture. The product was stored under nitrogen as it fumed in moist air.

Analysis:

$(PCl_4)_2SnCl_6$ requires Cl 73.76% P 9.15% Sn 17.52%

found Cl 54.2% P 8.4% Sn 19.1%

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 315 and 300 $cm.^{-1}$; possible $SnCl_5^-$ absorptions at 350 and 330 $cm.^{-1}$; PCl_4^+ absorptions at 650, 470 and 252 $cm.^{-1}$ (lit.[131] 658, 458 and 251 $cm.^{-1}$).

Solid state ^{31}P n.m.r.: single peak at 89 ppm (lit.[120] 85 ppm).

The elemental analysis of the product was considerably hindered by the problems of separating phosphorous and tin and is therefore somewhat in doubt (especially as the total percentage is well below 100). For characterisation of the compound, other techniques were relied on. The identification of the cation is fairly clear from the i.r. spectrum and is confirmed by the ^{31}P n.m.r., which also shows it to be the only phosphorus species (or at least by far the most abundant one) present in the compound. The i.r. spectrum in the Sn-Cl stretching region indicates the possible presence of a mixture of $SnCl_5^-$ and $SnCl_6^{2-}$ anions, though from the intensities of the bands, the latter are more prevalent. The product of this reaction was therefore not the desired compound.

$(Ph_4P)_2SnCl_6$ was obtained by stirring a 2:1 ratio of $Ph_4P^+Cl^-$ dissolved in

$EtNO_2$ and $SnCl_4.5H_2O$ in cHCl for 3 hrs. The solid formed on removing the solvents on a rotary evaporator was washed with acetone and 30 - 40° petroleum ether to leave white crystals of the product.

Analysis:

$(Ph_4P)_2SnCl_6$ requires C 57.05% H 3.96%

found C 56.18% H 4.19%

i.r. spectrum: strong $SnCl_6^{2-}$ bands at 307(sh), 300 and 285(sh) $cm.^{-1}$.

$(Ph_2PCl_2)_2SnCl_6$. Preparation of this compound was attempted by dissolving Ph_2PCl in CH_2Cl_2, cooling with an ice bath, and then passing excess chlorine gas through it to obtain Ph_2PCl_3 in solution. The stoichiometric amount of $SnCl_4$ to obtain a 1:2 ratio with Ph_2PCl_3, was then added, and the mixture stirred for 3 hrs. The resulting white solid was filtered off and washed with CH_2Cl_2 and 30 - 40° petroleum ether. All operations were carried out under a dry nitrogen atmosphere.

Analysis:

$(Ph_2PCl_2)_2SnCl_6$ requires C 34.14% H 2.37% P 7.35%

found C 29.45% H 2.68% P 7.7%

i.r. spectrum: $SnCl_6^{2-}$ absorptions at 307(sh), 295 and 285(sh) $cm.^{-1}$.

Solid state ^{31}P n.m.r.: two peaks at 90.4 and 46.7 ppm (lit.[132] 93.6, 92, 89.7 ppm for $Ph_2PCl_2^+$ in various compounds).

The intensities of the ^{31}P n.m.r. peaks suggest that $Ph_2PCl_2^+$ was the major phosphorous containing species. The second peak is probably due to Ph_2POCl which occurs at 42.7 ppm in solution; co-ordination with $SnCl_4$ probably moves its chemical shift downfield to the value observed in the solid. A downfield shift on addition of $SnCl_4$ has been observed for Ph_3PO in CH_2Cl_2 (see next section). The source of water causing hydrolysis was not identified. The anion, in contrast, showed evidence

of $SnCl_6^{2-}$ only from its i.r. spectrum.

$(Ph_3PCl)_2SnCl_6$. Ph_3P was dissolved in CH_2Cl_2 under the influence of a stream of chlorine gas, and sufficient $SnCl_4$ was added to make a 2:1 ratio of phosphine to stannic chloride. The resulting mixture was then stirred for 3 hrs., the product was filtered off, and washed with CH_2Cl_2 and 30 - 40° petroleum ether. All operations were performed in a dry nitrogen atmosphere.

i.r. spectrum: strong $SnCl_6^{2-}$ absorptions at 292 and 285 $cm.^{-1}$.

Solid state ^{31}P n.m.r.: two peaks of similar intensity 62.9 and 45.3 ppm (lit.[132] 62, 65, 64.3 ppm for Ph_3PCl^+ in various compounds).

Similar results to the previous compound were obtained from this reaction i.e. a single anion (judging from the i.r. spectrum) but two phosphorous species of equal populations (from the ^{31}P n.m.r. spectrum). The additional peak at 45.3 ppm is again probably a hydrolysis product. Ph_3PO in CH_2Cl_2 gave at ^{31}P shift at 27.4 ppm which shifted downfield to 40.4 ppm when $SnCl_4$ was added. It seems likely, therefore, that the contaminant is Ph_3PO co-ordinated to $SnCl_4$. The source of the water causing the hydrolysis of Ph_3PCl^+ to Ph_3PO was not identified.

(ii) Hexabromostannates

$(MeNH_3)_2SnBr_6$ was prepared by dissolving $MeNH_3^+Cl^-$ in an excess of concentrated aqueous HBr (cHBr) and then adding sufficient $SnBr_4$, also dissolved in cHBr, to make up a 2:1 ratio of reactants in favour of $MeNH_3^+Cl^-$. A precipitate formed which was filtered off and recrystallised from cHBr. The yellow crystals which resulted were then washed with CH_2Cl_2 and dried in vacuo.

Analysis:

$(MeNH_3)_2SnBr_6$ requires C 3.68% H 1.84% N 4.29%

found C 3.67% H 2.22% N 4.36%

Raman spectrum below 300 $cm.^{-1}$: 187(vs), 140(w), 122(w), 90(w), 32(vw) $cm.^{-1}$.

$(Me_2NH_2)_2SnBr_6$ was prepared in the same way as the previous compound except that $Me_2NH_2^+Cl^-$ was used instead of $MeNH_3^+Cl^-$.

Analysis:

$(Me_2NH_2)_2SnBr_6$ requires C 6.96% H 2.32% N 4.06%

found C 6.94% H 2.97% N 4.08%

Raman spectrum below 300 $cm.^{-1}$: 187(vs), 141(w), 92(w), 27(vw) $cm.^{-1}$.

$(Me_3NH)_2SnBr_6$ was prepared using the same method as for $(MeNH_3)_2SnBr_6$ except that Me_3N in ethanol (33% w/w) was used instead of $MeNH_3^+Cl^-$.

Analysis:

$(Me_3NH)_2SnBr_6$ requires C 10.03% H 2.79% N 3.90%

found C 10.06% H 3.07% N 3.98%

Raman spectrum below 300 $cm.^{-1}$: 181(vs), 139(m), 106(m), 62(w), 27(w) $cm.^{-1}$.

$(Me_4N)_2SnBr_6$ was prepared using the same method as for $(MeNH_3)_2SnBr_6$ except that $Me_4N^+Br^-$ was used instead of $MeNH_3^+Cl^-$.

Analysis:

$(Me_4N)_2SnBr_6$ requires C 12.87% H 3.22% N 3.75%

found C 12.76% H 3.41% N 3.80%

Raman spectrum below 300 $cm.^{-1}$: 182(vs), 133(w), 109(m), 88(w) $cm.^{-1}$

[lit.[134] 185(10), 138(3), 95(3) $cm.^{-1}$, values in brackets are the relative intensities; lit.[126] 187, 137, 108 $cm.^{-1}$].

$(Et_4N)_2SnBr_6$ was prepared from stirring a 2:1 ratio of $Et_4N^+Cl^-$ and $SnBr_4$ in cHBr for 1 hr. The precipitate formed was filtered off and recrystallised from a 1:1 mixture of cHBr and H_2O, to yield yellow crystals of the product

which were washed with CH_2Cl_2 and dried in vacuo.

Analysis:

$(Et_4N)_2SnBr_6$ requires C 22.53% H 4.69% N 3.29%

found C 22.75% H 5.09% N 3.16%

Raman spectrum below 300 $cm.^{-1}$: 183(vs), 140(w), 105(m) $cm.^{-1}$ (lit.[126] 185, 136 and 103 $cm.^{-1}$; lit.[50] 182, 135 and 101 $cm.^{-1}$).

$(Prop_4N)_2SnBr_6$ was prepared by reacting a 2:1 ratio of $prop_4N^+I^-$ and $SnBr_4$ in an excess of cHBr. The solution was heated to boiling and filtered while hot to remove traces of iodine; on cooling crystals of the product appeared which were removed and washed with CH_2Cl_2 and Et_2O.

Analysis:

$(Prop_4N)_2SnBr_6$ requires C 29.69% H 5.77% N 2.87%

found C 29.68% H 6.57% N 2.94%

Raman spectrum below 300 $cm.^{-1}$: 184(s), 171(mw), 141(w), 97(m) $cm.^{-1}$.

$(Me_3S)_2SnBr_6$ was obtained from adding a 2:1 molar ratio of $Me_3S^+I^-$ to $SnBr_4$ in excess cHBr, producing an instant white precipitate. This was removed, washed with acetone, recrystallised from cHBr, washed with acetone and 30 - 40° petroleum ether, and finally dried in a desiccator.

Analysis:

$(Me_3S)_2SnBr_6$ requires C 9.57% H 2.39% S 8.51% Sn 15.78%

found C 9.44% H 2.59% S 8.5% Sn 15.85%

Raman spectrum below 300 $cm.^{-1}$: 285(vw), 183(s), 139(w), 106(mw), 62(w), 34(vw) $cm.^{-1}$.

$(Ph_2I)_2SnBr_6$ was obtained by stirring a 2:1 ratio of $Ph_2I^+Br^-$ and $SnBr_4$ in CH_2Cl_2 for 48 hrs. The yellow powder was then filtered off and washed with CH_2Cl_2 and 30 - 40° petroleum ether.

Analysis:

$(Ph_2I)_2SnBr_6$ requires C 24.83% H 1.72% Sn 10.23% Br 41.33% I 21.68%

found C 24.91% H 1.41% Sn 10.1% Br 41.6% I 22.44%

Raman spectrum below 300 $cm.^{-1}$: 264(m), 219(w), 213(w), 184(vs), 155(mw), 102(m), 47(m), 29(m), 16(m) $cm.^{-1}$.

$(pyH)_2SnBr_6$ was prepared by adding together a 2:1 ratio of py and $SnBr_4$ in cHBr, filtering off the precipitate, and recrystallising this from a 1:1 mixture of cHBr and H_2O. The yellow crystals formed were washed with CH_2Cl_2 and Et_2O.

Analysis:

$(pyH)_2SnBr_6$ requires C 15.85% H 1.58% N 3.70%

found C 15.53% H 1.78% N 3.51%

Raman spectrum below 300 $cm.^{-1}$: 188(vs), 158(w), 137(vw), 108(w) $cm.^{-1}$.

(iii) Halogeno-complexes of Tin (II)

NH_4SnCl_3. An attempt was made to prepare this compound by the reaction of a 1:1 ratio of NH_4Cl and $SnCl_2$, in H_2O, in oxygen-free conditions (degassed solvent and nitrogen atmosphere). The solution was heated to dissolve all the solids and slowly cooled to give white crystals. These were filtered off and dried in vacuo.

Analysis:

NH_4SnCl_3 requires N 5.76% H 1.64% Sn 48.81% Cl 43.79%

found N 7.73% H 2.93% Sn 24.4% Cl 39.7%

$NH_4Cl.NH_4SnCl_3$ requires N 9.48% H 2.70% Sn 40.07% Cl 47.86%

The tin analysis of the product is most probably low due to the problems associated with its determination; the chlorine value might also be low for similar reasons. Despite this, the nitrogen figures suggest a mixed product intermediate between NH_4SnCl_3 and $NH_4Cl.NH_4SnCl_3$. The i.r. spectrum

shows few features: an absorption at 3250 - 3100 cm.$^{-1}$, corresponding to the NH_4^+ ion, and a broad absorption from 300 - 200 cm.$^{-1}$ (200 cm.$^{-1}$ is the lower limit of the i.r. range for the spectrometers used) corresponding possibly to Sn-Cl stretches or lattice modes of the product. The i.r. spectrum also showed that the product did not contain any water of crystallisation, through the absence of peaks in the region expected for O-H species (3500 - 3300 and 1650 - 1550 cm.$^{-1}$).

Attempts at preparing NH_4SnCl_3 without the exclusion of oxygen yielded products containing $(NH_4)_2SnCl_6$ due to oxidation of the tin (II) compound by the atmosphere.

$MeNH_3^+SnCl_3^-$ was prepared from the reaction of $MeNH_3^+Cl^-$ and $SnCl_2$ in a 1:1 ratio in H_2O, in oxygen-free conditions. (A few drops of cHCl were added to the solution to help dissolve all the $SnCl_2$ before the chloride was added.) The solution was heated to dissolve all the solids, and then cooled to yield white crystals. These were washed with Et_2O and dried in a desiccator.

Analysis:

$MeNH_3^+SnCl_3^-$ requires C 4.67% H 2.23% N 5.44% Sn 46.15% Cl 41.41%

found C 4.95% H 2.10% N 5.42% Sn 45.64% Cl 40.7%

$Me_2NH_2^+SnCl_3^-$ was prepared in the same way as the previous compound except that $Me_2NH_2^+Cl^-$ was used instead of $MeNH_3^+Cl^-$.

Analysis:

$Me_2NH_2^+SnCl_3^-$ requires C 8.85% H 2.95% N 5.16% Sn 43.77% Cl 39.27%

found C 9.11% H 3.27% N 5.01% (Sn 35.0%) Cl 38.9%

$Me_3NH^+SnCl_3^-$ was prepared in the same way as $MeNH_3^+SnCl_3^-$ except that $Me_3NH^+Cl^-$ was used instead of $MeNH_3^+Cl^-$.

Analysis:

$Me_3NH^+SnCl_3^-$ requires C 12.62% H 3.51% N 4.91% Sn 41.62% Cl 37.34%

found C 12.72% H 3.63% N 5.27% Sn 39.71% Cl 37.1%

$Me_4N^+SnCl_3^-$ was prepared by the same method as $MeNH_3^+SnCl_3^-$ except that $Me_4N^+Cl^-$ was used instead of $MeNH_3^+Cl^-$.

Analysis:

$Me_4N^+SnCl_3^-$ requires C 16.04% H 4.01% N 4.68% Sn 39.67% Cl 35.59%

found C 15.62% H 4.98% N 3.68% Sn 39.9% Cl 40.8%

The Cl result appears to be anomalous in view of the proximity of the other values to the theoretical figures.

$Et_4N^+SnCl_3^-$ was prepared by the same method as $MeNH_3^+SnCl_3^-$ except that $Et_4N^+Cl^-$ was used instead of $MeNH_3^+Cl^-$.

Analysis:

$Et_4N^+SnCl_3^-$ requires C 27.03% H 5.63% N 3.94% Sn 33.42% Cl 29.98%

found C 26.96% H 5.71% N 3.77% (Sn 18.5%) Cl 29.5%

$pyH^+SnCl_3^-$. Preparation of this compound was attempted, according to a method in the literature,[59] by adding a 1:1 ratio of py and $SnCl_2$ in excess cHCl, heating the solution to dissolve the solids, and slowly cooling to yield white crystals of product. These were washed with EtOH and dried in a desiccator.

Analysis:

$pyH^+SnCl_3^-$ requires C 19.66% H 1.77% N 4.59% Sn 38.89% Cl 34.90%

found C 21.39% H 2.17% N 4.63%

i.r. spectrum: absorptions at 310 and 285 $cm.^{-1}$.

The observation of an i.r. band at 310 $cm.^{-1}$ is consistent with the presence of $(pyH)_2SnCl_6$ in this sample (see the earlier section on hexachlorostannate preparation). This is also supported by the high carbon percentage in the analysis of this compound:

$(pyH)_2SnCl_6$ requires: C 24.42% H 2.44% N 5.70% Sn 24.16% Cl 43.32%

A mixture of $(pyH)_2SnCl_6$ and $pyH^+SnCl_3^-$ therefore seems to be the product

from this reaction, with the Sn (IV) species produced by atmospheric oxidation.

A recrystallisation performed from EtOH gave the following analysis: C 21.92% H 2.64% N 4.93% Sn 37.7% Cl 35.2%. The increase of the carbon value, on further exposure to the atmosphere, confirms the occurrence of oxidation, though the figures for tin and chlorine indicate the major product to contain the $SnCl_3^-$ ion rather than $SnCl_6^{2-}$.

This preparation would be better carried out with the exclusion of oxygen.

$RbSnCl_3$. Preparation was attempted by the same method as $MeNH_3^+SnCl_3^-$ except that RbCl was used instead of $MeNH_3^+Cl^-$.

Analysis:

$RbSnCl_3$ requires	Rb 27.52%	Sn 38.20%	Cl 34.28%
found	Rb 15.42%	Sn 53.6%	Cl 28.1%
$RbSn_2Cl_5$ requires	Rb 17.09%	Sn 47.44%	Cl 35.47%

The i.r. spectrum of the product showed no evidence of H_2O in the 3500 - 3300 $cm.^{-1}$ region, although there was a fairly sharp band at 1585 $cm.^{-1}$ which could indicate the presence of H_2O.

The elemental analysis of the product suggests that a mixture of products, predominantly $RbSn_2Cl_5$ was formed.

$KSnCl_3$. A 1:1 ratio of KCl and $SnCl_2$ was reacted in H_2O under oxygen-free conditions. The mixture was heated to dissolve the solids and then slowly cooled to give white crystals. These were filtered off, washed with a little water and dried in vacuo.

Analysis:

$KSnCl_3$ requires	K 14.79%	Sn 44.91%	Cl 40.30%
found	K 14.5%	Sn 49.5%	Cl 31.8%
KSn_2Cl_5 requires	K 8.61%	Sn 52.29%	Cl 39.09%

This product showed evidence of H_2O by bands in its i.r. spectrum at 3600, 3520 and 1608 $cm.^{-1}$ before drying under vacuum; these bands were fairly sharp, however, and therefore probably due to water in definite positions in the crystal lattice of the product, rather than just dampness. These bands disappeared from the i.r. spectrum after pumping the product on the vacuum line.

The elemental analysis is confusing. The high tin value argues for the presence of KSn_2Cl_5, but the chlorine value does not support this. Indeed the low chlorine value cannot be accounted for via any reasonable combination of structures (e.g. $KCl.KSnCl_3$) and is most probably erroneous.

$KCl.KSnCl_3.H_2O$. An attempt was made to prepare this compound according to a method in the literature.[75] Equimolar proportions of KCl and $SnCl_2$ in saturated aqueous solution were cooled to yield white crystals. These were filtered off, washed with EtOH and dried briefly in a desiccator.

Analysis:

$KCl.KSnCl_3.H_2O$ requires K 21.89% Sn 33.30% Cl 39.78%

found K 21.6% Sn - Cl 38.0%

$Me_4N^+SnBr_3^-$ was prepared by stirring an equimolar mixture of $SnBr_2$ and Me_4NBr in H_2O for 3 hrs. under oxygen-free conditions. The yellow powder formed was filtered off, washed with a small amount of H_2O and dried in vacuo.

Analysis:

$Me_4N^+SnBr_3^-$ requires C 11.10% H 2.78% N 3.24% Sn 27.45% Br 55.43%

found C 10.94% H 2.55% N 3.28% Sn 28.0% Br 54.7%

The i.r. spectrum of the product showed it to be free of H_2O.

$Me_3NH^+SnBr_3^-$ was prepared by stirring a 1:1 ratio of $Me_3NH^+Br^-$ and $SnBr_2$ in EtOH for 16 hrs. in oxygen-free conditions. The EtOH was then heated

to boiling and the solution filtered while still hot. Cooling the filtrate then yielded yellow crystals of the product. [The $Me_3NH^+Br^-$ used in this preparation was obtained by mixing Me_3N (33% w/w in EtOH) with excess cHBr and then removing the solvent on the vacuum line. The crude product was then washed with CH_2Cl_2 and further dried in vacuo before use.]

Analysis:

$Me_3NH^+SnBr^-$ requires C 8.60% H 2.39% N 3.35%

found C 8.62% H 2.75% N 2.92%

The i.r. spectrum showed the final product to be anhydrous.

$pyH^+SnBr_3^-$ was prepared in a similar manner to the previous compound except that py was used instead of Me_3N to prepare the cation pyH^+Br^-.

Analysis:

$pyH^+SnBr_3^-$ requires C 13.69% H 1.37% N 3.19%

found C 13.67% H 1.64% N 3.45%

The i.r. spectrum showed the product to be dry.

CHAPTER 4

Temperature Variation Studies of Halostannates by n.q.r.

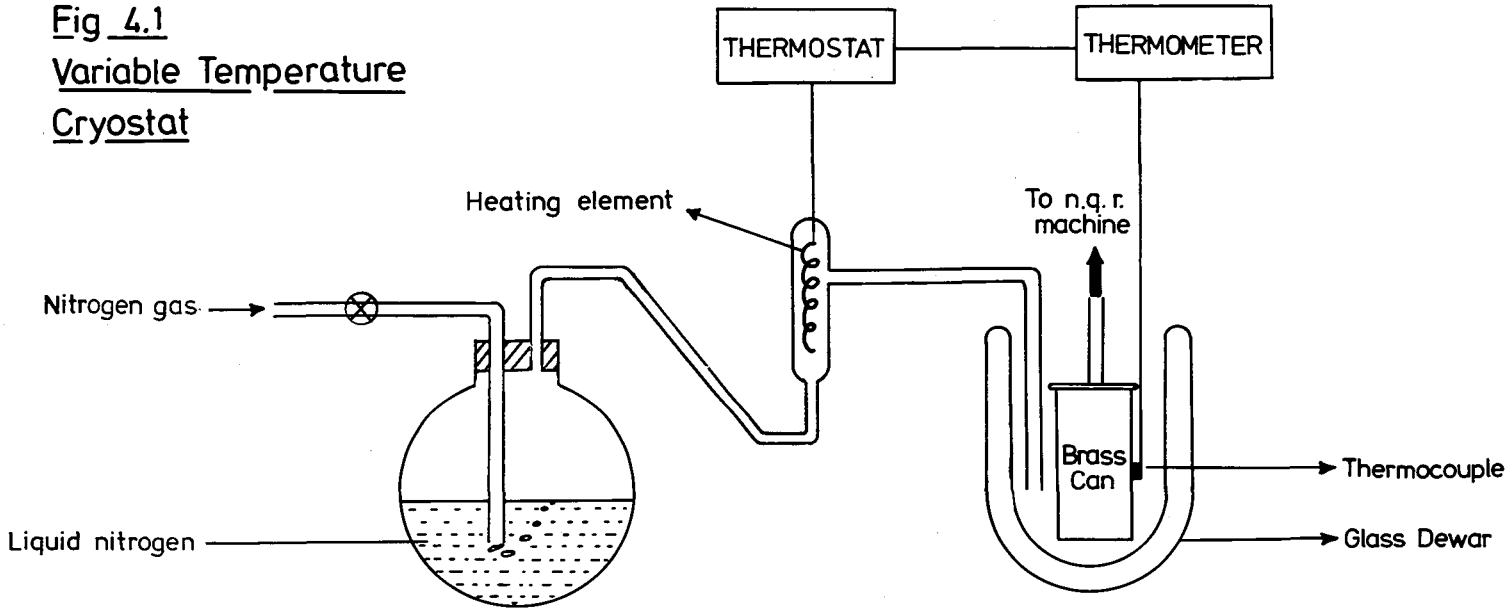
(a) Introduction

Several temperature dependence studies of the halostannates have been carried out using n.q.r. spectroscopy. Ammonium hexachlorostannate has been studied by several workers.[25,29,135] It shows a single resonance for all temperatures and has an anomalous increase in temperature coefficient (n.q.r. frequency versus temperature) with increasing temperature. It has no structural phase changes above 4.2K. The corresponding hexabromostannate,[27] however, shows two phase changes at 144K and 157K, going from three to two to a single resonance above the latter temperature. Both potassium hexachloro- and hexabromostannate show similar behaviour,[27] with transitions at 256K and 263K, and 375K and 396K, respectively. The last transition of K_2SnBr_6 has also been detected by DSC[37] at 399.8K. $(MeNH_3)_2SnCl_6$ and $(MeNH_3)_2SnBr_6$ both show one resonance frequency in the range 77 - 300K; the former exhibits a phase change at 156K and the latter at 149K.[31] $CaSnCl_6.6H_2O$ has also been studied[30] and shows a single n.q.r. resonance for the range 77 - 390K but is reported to go through four different crystal phases in this region (as evidenced by DTA and other measurements).[30] $CsSnCl_3$ shows three lines in the region 273 - 388K whereas $CsSnBr_3$ shows a phase change at 292K with one line splitting into two for lower temperatures.[77]

(b) Variable Temperature Measurements

In order to measure the resonance frequencies of samples at temperatures intermediate between liquid nitrogen (77K), solid CO_2 (196K) and room temperature (300K) a variable temperature cryostat was used. This is

Fig 4.1
Variable Temperature
Cryostat



shown in Figure 4.1. Nitrogen gas was passed through liquid nitrogen and was led via a heating element to the n.q.r. spectrometer. The temperature of the sample was monitored by a Comark copper-constantan thermometer attached to the outside of the brass can which contains the sample. (The actual temperature of the sample inside the can was not directly measurable but since brass has good thermal conductivity the error here should be small.) A home-built thermostat controlled the heating current in response to the temperature of the sample. The temperature was controlled by presetting the thermostat and by adjusting the flow rate of the nitrogen gas (faster for lower temperatures). The whole system was well lagged with cotton wool.

By using the system described above, temperatures stable to $\pm$ 0.1K could be obtained after 20 - 30 mins. had been allowed for thermal equilibrium to be reached. It was found that in practice temperatures down to 135K could be satisfactorily reached for the spectrometer used in ^{35}Cl n.q.r. frequency measurements, whereas only about 165K could be attained for the higher frequency machine used for Br measurements, due to the spectrometer design. Temperatures between these minima and 77K were obtained crudely by allowing the samples to warm up from 77K and quickly scanning through the resonance, or by stabilisation at the desired temperature through patient dropwise addition of liquid nitrogen. The latter method, with practice, could achieve an accuracy of $\pm$ 0.5K. A few spectra above room temperature were measured by removing the liquid nitrogen, thus enabling warm gas to be circulated around the sample. For these measurements a Comark thermometer operating over a higher temperature range was used.

Changes in the relaxation behaviour of nuclei over a temperature range cause variation in the lineshape of the observed spectrum. This made it

difficult to assign unambiguously the centre of some resonance lines. In these cases the same branch of the signal was followed throughout the study. Furthermore, near a phase change, where signals were splitting, it was often difficult to judge when a line had actually divided due to the overlap of the signals and sidebands. The deciding factor here was in noting when the lineshape of the resonance had become unsymmetrical, and then assigning the centres of the new resonances by comparison with the signals at different temperatures where the lines were well separated.

(c) Temperature Dependence Studies of Hexachlorostannates

(i) Symmetry Considerations in Hexahalometallates

The interpretation of structural phase changes in these compounds has been described in symmetry terms by McElroy et al.[23] and is used later in this work. These workers made an extensive study of a large number of reasonable distortions of the cubic antifluorite lattice and the accompanying qualitative changes of the halogen n.q.r. spectra. Distortions from octahedral to lower symmetry of the hexahalometallate ion in its immediate surroundings (a cubic cage of eight cations) were predicted from observation of four readily observable properties of the temperature dependence plots. This is summarised in Table 4.1. The number of lines refers to the number of lines produced on cooling a sample showing a single line to below its phase transition temperature. The centre of mass is said to be conserved if the weighted average of the frequencies of the split lines is the same as the frequency of the single line at the phase change.

Recently this work has been comprehensively extended[137] to include consideration of space group symmetries. The results obtained previously[23] were verified, and it is the first paper[23] which is used in the

Table 4.1.

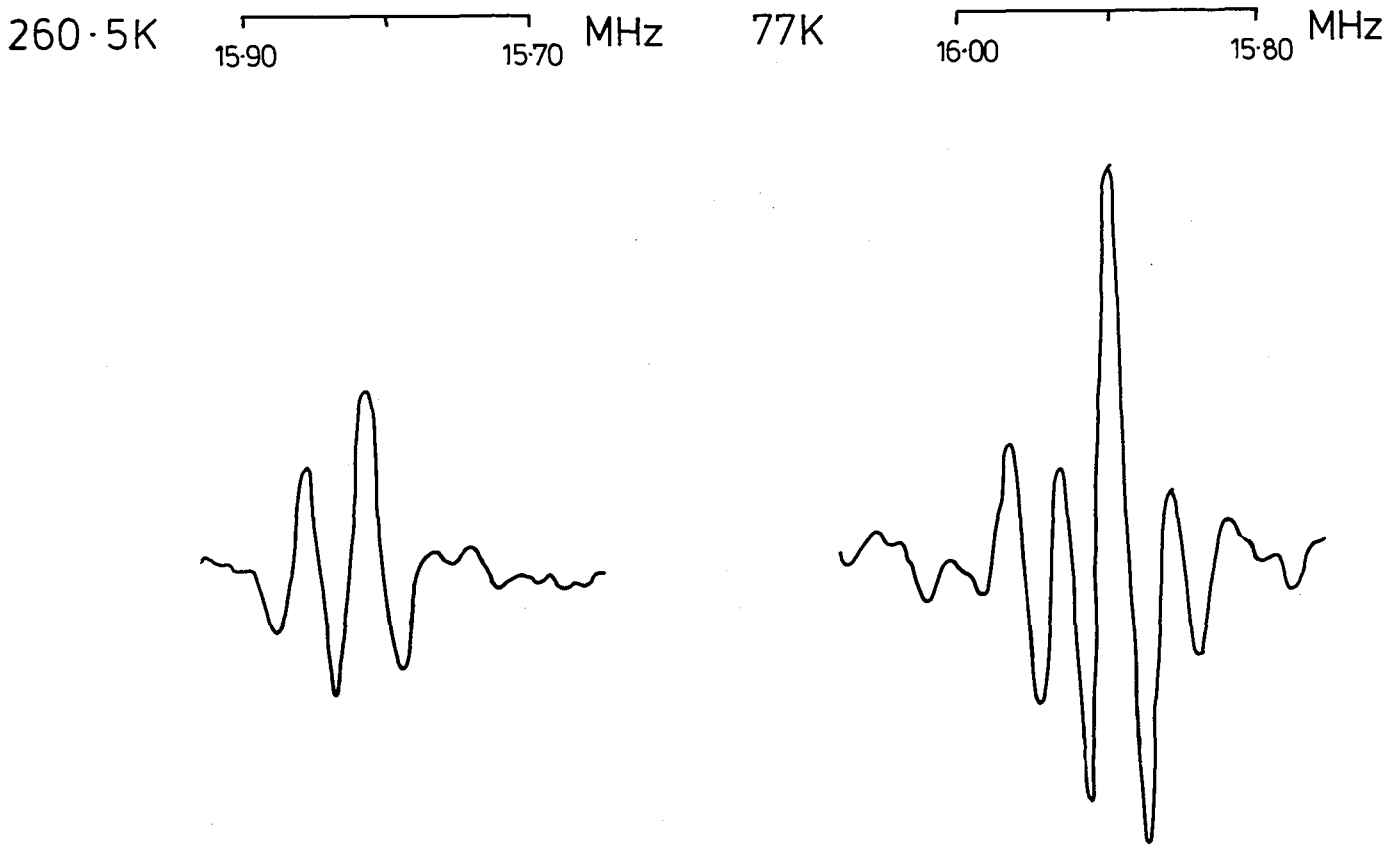
Symmetry Considerations on Phase Changes in Hexahalometallates

Property	Observation
Number of lines?	1 / 2 / 3
Intensity ratio?	1:1 / 2:1 / 1:4:1 / 1:1:1
Centre of mass conserved?	Yes / No
Discontinuity at transition?	Yes / No
Unit cell point group symmetry	D_{3d}, S_6, D_3, C_{3v}, D_{4h}, C_{2h}^1, D_{2h}^1, D_{2d}, C_{2v}^1, C_{4v}, D_{2h}, C_{2v}^1

NB. The distinction between D_{2h} and D_{2h}^1 is that for the former, all the C_2 axes correspond with M-X bonds, whereas in the latter they bisect the angles between these bonds. C_{2v}^1 is a sub-graph of D_{2h}^1.

Figure 4.2

^{35}Cl n.q.r. Spectra of $(MeNH_3)_2\ SnCl_6$



interpretation of results in the present work.

(ii) $(MeNH_3)_2SnCl_6$

A study of this compound by ^{35}Cl n.q.r. has been carried out already,[31] and is reported to show a phase change at 156K. This manifests itself by a cusp in the plot of temperature versus frequency, with a single line only for the whole temperature range under study. The position of the change was also confirmed by relaxation studies and is not disputed.

In this work however, the spectrum of the sample at 77K appears to show two resonances, not one as reported. The spectra of this sample at 260.5K and 77K are shown in Figure 4.2. A full temperature dependence study from 77 to 300K was not fruitful as it was difficult to see at which point the two signals came into being, due to their overlapping. (It was observed however, that the lineshape changed on traversing 156K.) For this reason the nature of the phase change at 156K and the structure of the distorted low temperature structure cannot be discussed in terms of Table 4.1. The compound does warrant study, however, on an instrument capable of better resolution of the signals.

(iii) $(Me_2NH_2)_2SnCl_6$

This compound was chosen for study as it shows two ^{35}Cl n.q.r. lines at 77K and 196K with their respective intensities reversed at each temperature, the lines therefore appearing to cross at an intermediate temperature. The results obtained are shown in Table 4.2., and plotted in Figure 4.3.

The plot clearly shows that the two lines do not cross, but instead they begin to diverge below about 115K. At the time this occurs, the higher frequency line begins to decrease in intensity and shows saturation

Table 4.2.

Temperature Variation of the ^{35}Cl n.q.r. of $(Me_2NH_2)_2SnCl_6$

Temperature/K[a]	^{35}Cl n.q.r. frequencies/± 0.003 MHz	
279.2	15.950 (1.1)[d]	16.448 (1.7)
261.5	16.018 (3.5)	16.482 (10.6)
251.0	16.032 (5.0)	16.510 (13.2)
230.8	16.048 (8.1)	16.505 (16.6)
209.9	16.075 (8.6)	16.530 (17.3)
198.8	16.075 (9.9)	16.530 (17.7)
189.5	16.085 (9.5)	16.552 (17.4)
179.6	16.093 (10.1)	16.550 (17.5)
169.3	16.105 (10.0)	16.575 (18.7)
159.3	16.110 (9.7)	16.580 (17.8)
149.4	16.110 (10.6)	16.587 (18.0)
128[b]	16.112 (12.7)	16.622 (18.8)
118[b]	16.120 (13.5)	16.637 (19.2)
90[b]	16.090 (14.0)	16.728 (12.4)
77[c]	16.052 (14.3)	16.710 (8.7)

(a) errors ± 0.1K unless otherwise stated;

(b) ± 0.5K; (c) sample immersed in liquid nitrogen;

(d) values in brackets show approximate signal heights in centimetres; the noise level was about 0.8 cm. on average.

Figure 4.3a)
Temperature dependence of $(Me_2NH_2)_2SnCl_6$

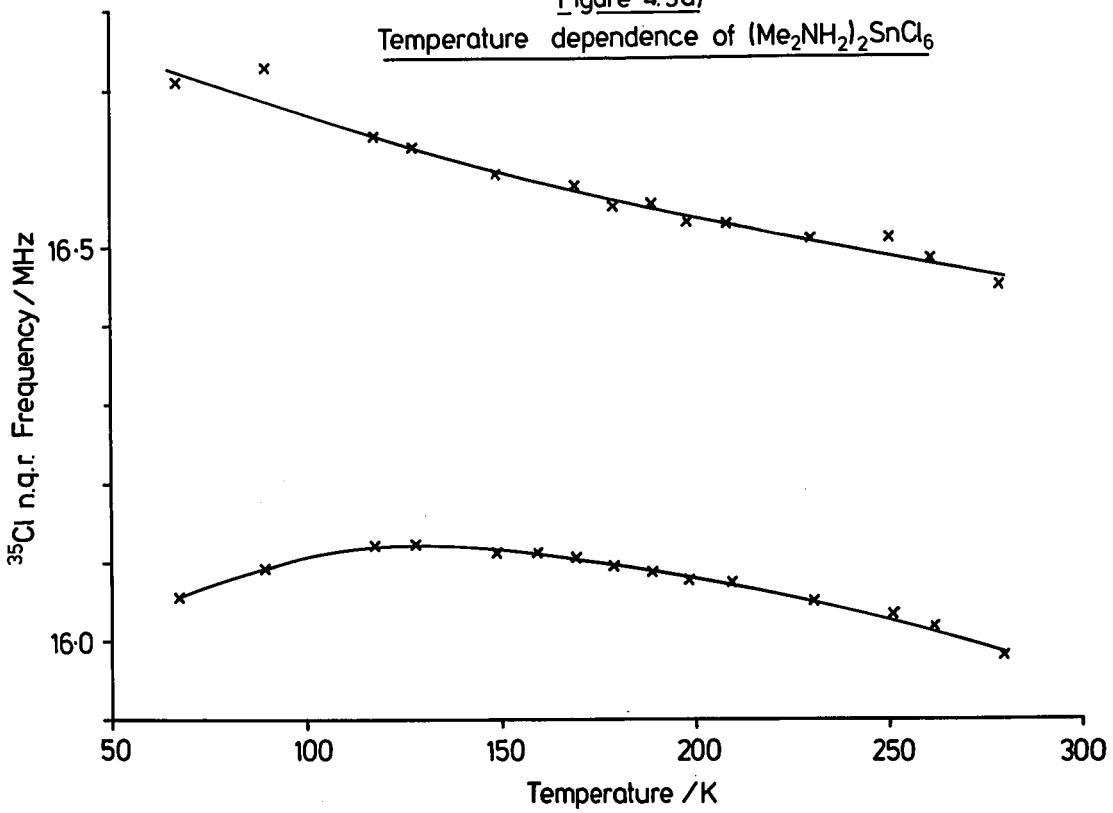
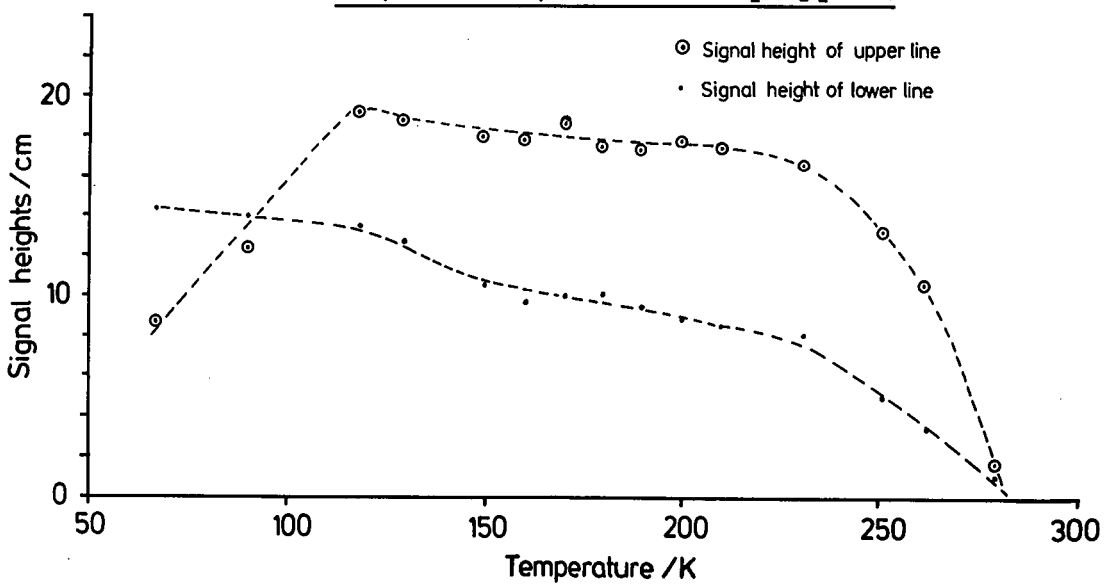


Figure 4.3b)
Temperature dependence of $(Me_2NH_2)_2SnCl_6$



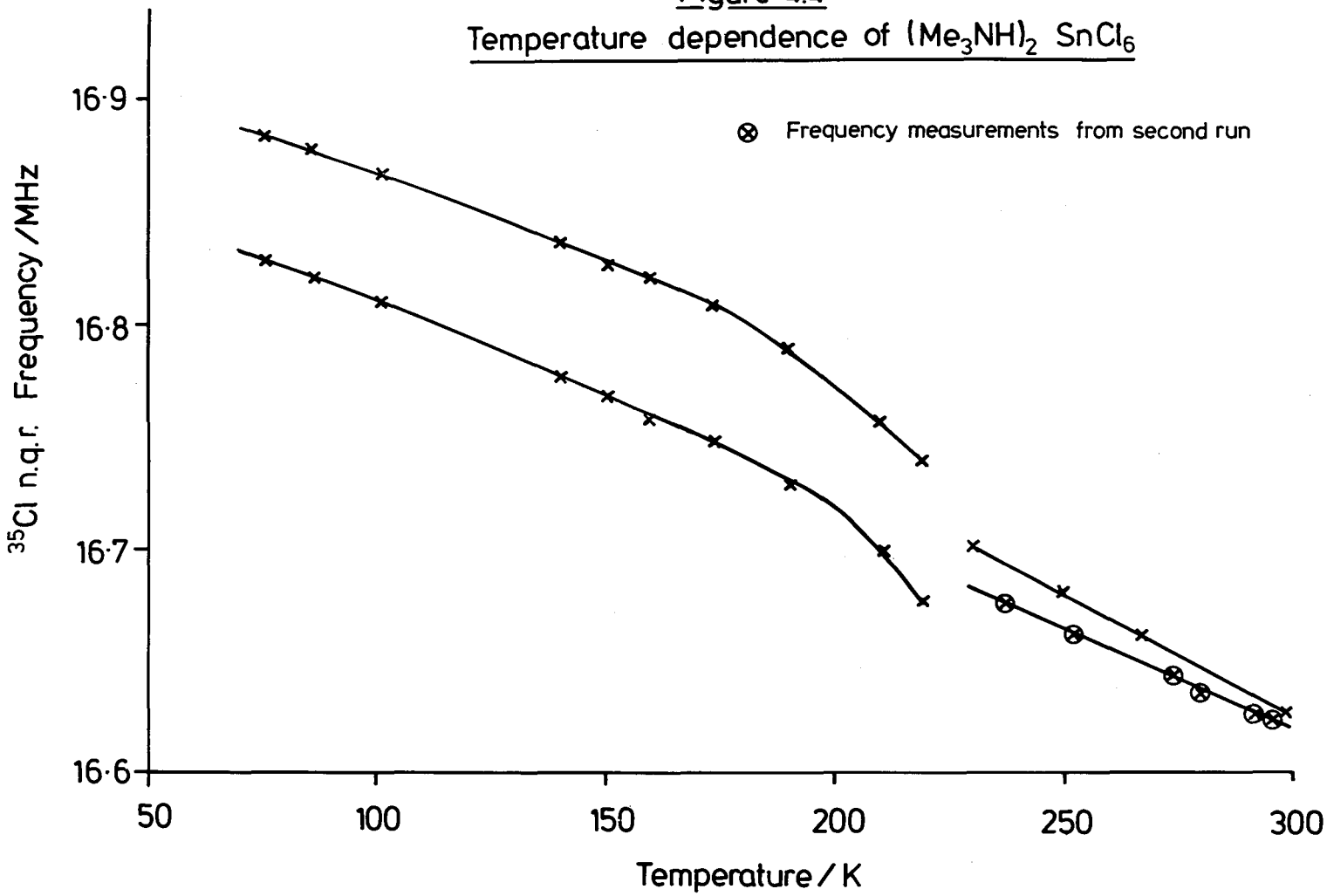
behaviour. (This was shown by decreasing the applied r.f. intensity and noticing an increase in the height of the signal. At the same time the size of the lower signal diminished.) A more quantitative measure of the divergence is given by the temperature coefficients of the lines above and below 115K. The upper line goes from $\sim$ -1.0 to $\sim$ -1.6 $kHzK^{-1}$ and the lower one from $\sim$ -0.8 to $\sim$ +1.6 $kHzK^{-1}$ at 200K and 80K respectively. This change in behaviour could well be indicative of a phase change occurring.

The positive temperature coefficient is unusual. The existing theories[6,7] describing n.q.r. temperature dependence predict normal behaviour as the exhibition of a negative temperature gradient. These are based on the assumption that the M-X bond behaves primarily as a torsional oscillator and so averages the e.f.g. at the quadrupolar nuclei to a value between that of a bent and a straight bond. Thus as oscillations increase with increasing temperature, a greater contribution to the e.f.g. is gained from the bent bond type which reduces the overall e.f.g. and hence the n.q.r. frequency. Now if the atom was hydrogen bonded,[141,142] or more generally secondarily bonded,[138] it would have bonding electrons on both sides of the nucleus, and hence a lower e.f.g. (and n.q.r. frequency). So for this case as the temperature is raised, the hydrogen bond is weakened by thermal vibrations, and the n.q.r. frequency increases since the contribution to the e.f.g. from the covalent bond becomes more important. This is one possible explanation for the observed positive coefficient of the lower line. Positive temperature coefficients have recently been reviewed by Lücken[26] and alternative causes discussed.

From the preceding discussion the phase change probably involves the formation of hydrogen bonds, between 110K and 150K, to the chlorines responsible for the lower line. As the upper line is twice as intense

Figure 4.4

Temperature dependence of $(Me_3NH)_2\ SnCl_6$



as the lower one (until saturation) this means that two chlorines per hexachlorostannate anion would be involved. These could conveniently interact with the four available N-H hydrogens from the two dimethylammonium cations per anion, possibly via bifurcated hydrogen bonds. The chlorines responsible for the upper line remain largely unaltered to judge by their temperature coefficient, but the slight decrease in this parameter may indicate a marginally changed environment for these atoms.

(iv) $\underline{(Me_3NH)_2SnCl_6}$

This compound shows two frequencies in the ratio 2:1 at 77K but only one at room temperature. A detailed temperature dependence study was therefore carried out and a phase change at 225 $\pm$ 5K was detected (Figure 4.4.). The experimental results obtained are shown in Table 4.3.

The phase change can be interpreted by invoking Table 4.1. We see that there is a discontinuity at the transition, on inspection of the lower line, and that the centre of gravity is approximately conserved. A unit cell point group of D_{4h}, i.e. orthorhombic, is therefore presumed for the distorted structure. This corresponds to an elongation or compression of the unit cell in one of the high symmetry directions, or an equal change in bond length for two opposite chlorines in each anion. (A note of caution should be added here when deciding on whether the centre of mass is conserved. It is not clear from the literature[23] whether approximate conservation is good enough. If it is not then Table 4.1. predicts C_{2h}^1 or D_{2h}^1 for the distorted phase.)

The temperature coefficients are $\sim$ -1.0 and $\sim$ -0.8 $kHzK^{-1}$ for the lines above and below the phase change respectively. This difference is negligible and suggests that hydrogen bonding is not the driving force behind the transition.

Table 4.3.*

Temperature Variation of the ^{35}Cl n.q.r. of $(Me_3NH)_2SnCl_6$

	Temperature/K[a]	^{35}Cl n.q.r. frequencies/± 0.003 MHz			
1st run	298.0	16.625	(5.8)[d]		
	266.8	16.660	(6.8)		
	250.0	16.680	(6.1)		
	230.7	16.698	(5.9)		
	219.1	16.676	(6.9)	16.740	(1.3)
	210.4	16.698	(6.6)	16.755	(2.1)
	190.0	16.728	(7.6)	16.788	(2.2)
	173.2	16.747	(8.4)	16.808	(2.7)
	160.0	16.757	(8.8)	16.820	(3.5)
	150.2	16.767	(9.4)	16.825	(4.2)
	141.0	16.775	(10.4)	16.835	(4.2)
	101.5[b]	16.810	(9.6)	16.865	(4.9)
	86.7[b]	16.820	(9.0)	16.877	(4.5)
	77[c]	16.828	(8.9)	16.882	(4.6)
2nd run	296.0	16.622	(6.6)		
	291.5	16.625	(6.9)		
	279.6	16.635	(6.6)		
	273.3	16.643	(6.6)		
	252.1	16.660	(6.3)		
	237.7	16.675	(7.3)		

* See Table 4.2. for definition of superscripts.

Figure 4.5a)

Temperature dependence of $(Me_4N)_2SnCl_6$

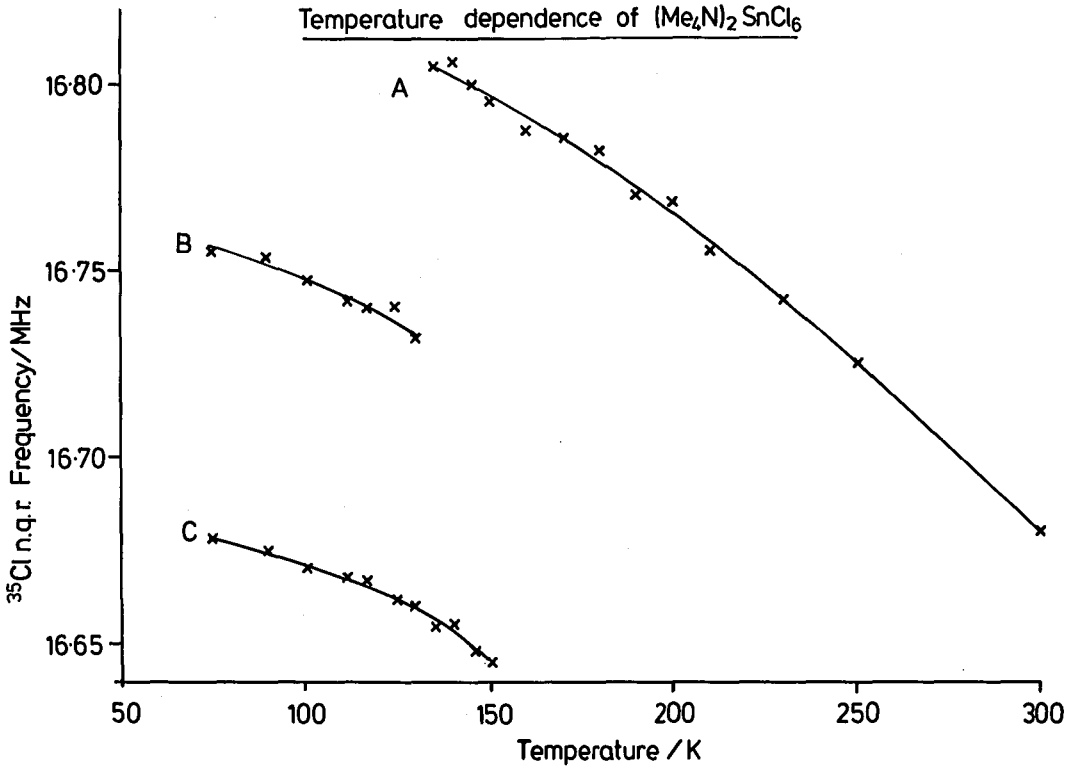
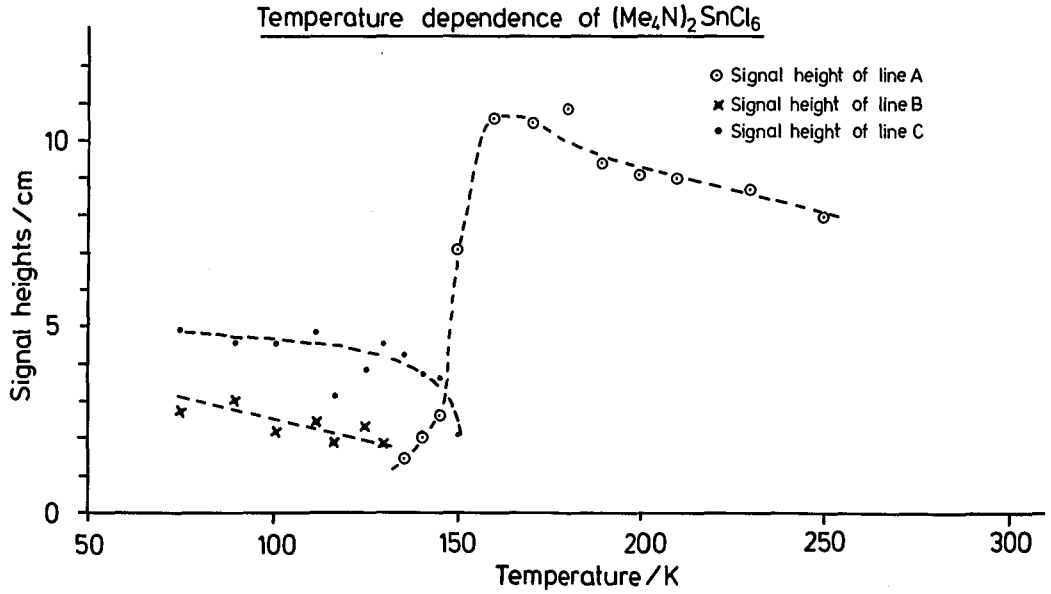


Figure 4.5b)

Temperature dependence of $(Me_4N)_2SnCl_6$



An interesting anomaly was noticed in the study of this compound. The frequencies measured for the single line above the phase transition temperature altered on repeating the measurements; below the phase change the values remained congruent. This small change is thought to be due to minor effects on the crystal lattice caused by repeated heating and cooling of the compound, possibly creating or removing strains within the crystal and thus altering its dynamic behaviour.

(v) $\underline{(Me_4N)_2SnCl_6}$

This hexachlorostannate shows two n.q.r. resonances at 77K in an approximate 2:1 intensity ratio but only a single line at room temperature. The detailed temperature dependence behaviour is shown in Table 4.4. and plotted in Figure 4.5. It can be seen from these results that the single line begins to fade out at $\sim$ 150K with the emergence of the two new lower lines (the weaker line is presumed present but undetected until 130K). This process becomes complete at about 130K and is clear evidence of the phase change which has already been studied by other workers[32,136] using vibrational spectroscopy. They reported the transition to occur at 145 $\pm$ 10K[32] or 149 $\pm$ 7K,[136] and postulated the formation of weak hydrogen bonds between the chlorines and methyl protons to precipitate the phase change. The gradual fade-out of the n.q.r. lines clearly shows that the process occurs over a temperature range and is not sudden, thus accounting for the large error limits quoted in the literature.[32,136] This illustrates the advantage that n.q.r. has as a technique in that it looks directly at the atoms (via their electronic environments). The phase change was found to halt when the temperature was held constant i.e. when the temperature was set at a constant value for a number of hours, no changes in n.q.r. frequency or signal intensity were seen. There is therefore, no evidence

Table 4.4.*

Temperature Variation of the ^{35}Cl n.q.r. of $(Me_4N)_2SnCl_6$

Temperature/K[a]	^{35}Cl n.q.r. frequencies/± 0.003 MHz			
300.0	16.680			
250.1	16.725 (7.9)[d]			
230.4	16.742 (8.6)			
210.5	16.755 (8.9)			
200.0	16.768 (9.0)			
190.4	16.770 (9.3)			
180.4	16.782 (10.8)			
170.5	16.785 (10.4)			
160.2	16.787 (10.5)			
150.6	16.795 (7.0)			16.645 (2.1)
145.6	16.800 (2.6)			16.648 (3.6)
140.3	16.805 (2.0)			16.665 (3.7)
135.7	16.805 (1.4)			16.665 (4.2)
130.0[b]			16.732 (1.8)	16.660 (4.5)
125.0[b]			16.740 (2.3)	16.662 (3.8)
117.0[b]			16.740 (1.9)	16.667 (3.1)
112.0[b]			16.742 (2.4)	16.668 (4.8)
101.0[b]			16.747 (2.1)	16.670 (4.5)
90.0[b]			16.753 (3.0)	16.675 (4.9)
77[c]			16.755 (2.7)	16.678 (4.8)

* See Table 4.2. for definition of superscripts.

for hysteresis: the change was also found to be reversible

The temperature gradient of the upper line is ~ -0.7 kHzK^{-1} whereas the middle and lower lines have coefficients of -0.3 and -0.35 kHzK^{-1} respectively. These latter values are relatively positive for the hexachlorostannates [cf. $(Me_3NH)_2SnCl_6$] and give complementary evidence for the formation of weak hydrogen bonds in the low temperature structure for reasons outlined earlier (section 4(i)(c)). The drop in average frequency in going from the high to the low temperature forms is also consistent with H-bond formation. The presence of extra bonding electrons on the opposite side of the Cl nucleus to the Sn nucleus increases the electron density on that side, and thus reduces the overall e.f.g. The net result is a drop in observed n.q.r. frequency. Since both lines show the same effects, it can be concluded that all the chlorines are involved in some sort of secondary bonding.

$(Me_4N)_2SnCl_6$ has also been investigated by variable temperature ^{35}Cl n.q.r. in a very recent Japanese study.[164] These workers observed two, widely separated, broad resonances below the phase transition temperature, which were measured at 16.70 $\pm$ 0.05 and 17.51 $\pm$ 0.05 MHz at 77K. The former is in accord with the results in this thesis, while the latter was not observed, due to the insensitivity of the equipment used. The Japanese paper, however, did not report the splitting of the lower line below the phase change temperature and it is conceivable that the upper line observed by them might also prove to be split under careful scrutiny. There is therefore some ambiguity as to the actual number of signals and their intensities (the Japanese paper only stated the upper line to be weaker than the lower without giving any quantitative measure), and hence Table 4.1. cannot be invoked to interpret the results.

Table 4.5.*

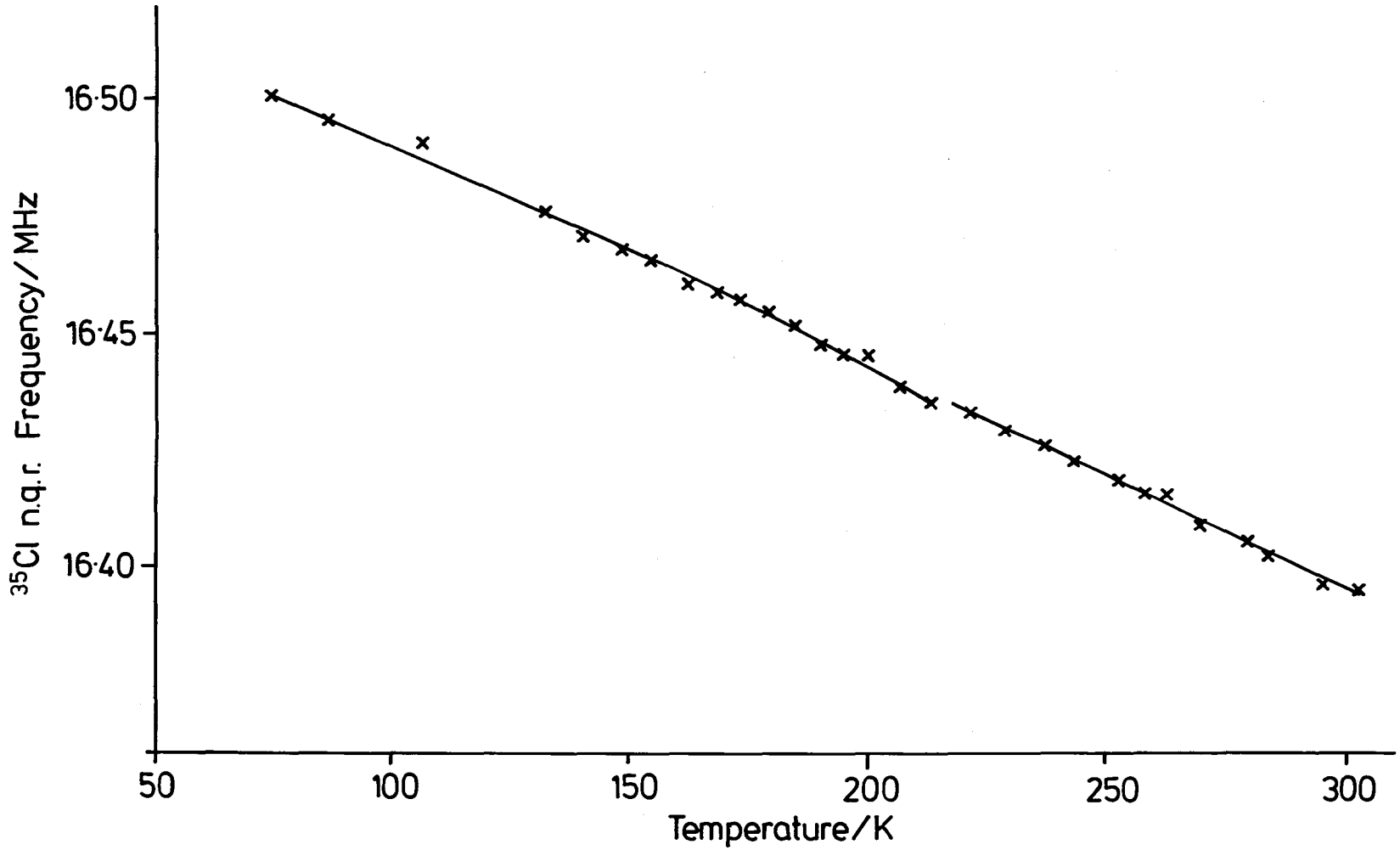
Temperature Dependence of the ^{35}Cl n.q.r. of $(Me_3S)_2SnCl_6$

Temperature/K[a]	^{35}Cl n.q.r. frequency/± 0.003 MHz	Temperature	Frequency
302.4	16.395	195.6	16.445
294.3	16.396	190.1	16.447
283.8	16.402	185.3	16.451
279.2	16.405	179.2	16.454
270.4	16.408	173.5	16.457
263.4	16.415	168.3	16.458
258.2	16.415	162.4	16.460
252.1	16.418	154.4	16.465
243.6	16.422	148.1	16.467
237.3	16.425	140.2	16.470
229.4	16.429	132.0[b]	16.475
222.0	16.433	106.0[b]	16.490
213.6[†]	16.435	87.0[b]	16.495
207.3	16.438	77.0[c]	16.500
200.2	16.445		

* Superscripts a, b, and c are those used in Table 4.2.

† For this temperature and below two unresolved n.q.r. signals are seen.

Figure 4.6.
Temperature dependence of $(Me_3S)_2SnCl_6$



(vi) $\underline{(Me_3S)_2SnCl_6}$

This compound shows a change from a single signal at room temperature to two signals of an intensity ratio 2:1 below 196K. The two signals are very close together and were only satisfactorily resolved by running the spectra at very slow scan speeds. For this reason the temperature dependen study was performed by observing the main signal, but by noticing at which point the lineshape became unsymmetrical the position of the phase change could be unambiguously located. The results are plotted in Figure 4.6. and recorded in Table 4.5.

As can be seen from Figure 4.6., the temperature plot for this hexachlorostannate is reasonably linear and has a temperature coefficient of $\sim$ -0.8 $kHzK^{-1}$. This is similar to that of $(Me_3NH)_2SnCl_6$ and shows no evidence of hydrogen bonding. At the phase transition at 216 $\pm$ 2K the centre of mass appears to be approximately conserved and a discontinuity occurs. The symmetry of the unit cell of the distorted phase is thus predicted from Table 4.1. to be D_{4h}. The behaviour of this compound mimics that of $(Me_3NH)_2SnCl_6$ which perhaps is not surprising in view of the similarity of the two cations.

(vii) $\underline{(pyH)_2SnCl_6}$

Pyridinium hexachlorostannate shows a remarkable change on cooling from room temperature to 77K; it exhibits only one resonance at the former temperature whilst eight are apparent at the latter. The fuller investigation performed here suggests that three lines should have been seen at room temperature, but that two of them fade out around 290K. This is presumably due to their different relaxation behaviour as there is no evidence to support a phase change at this temperature. There does however appear to be a phase change at 140 $\pm$ 5K. The three lines of

Table 4.6.*

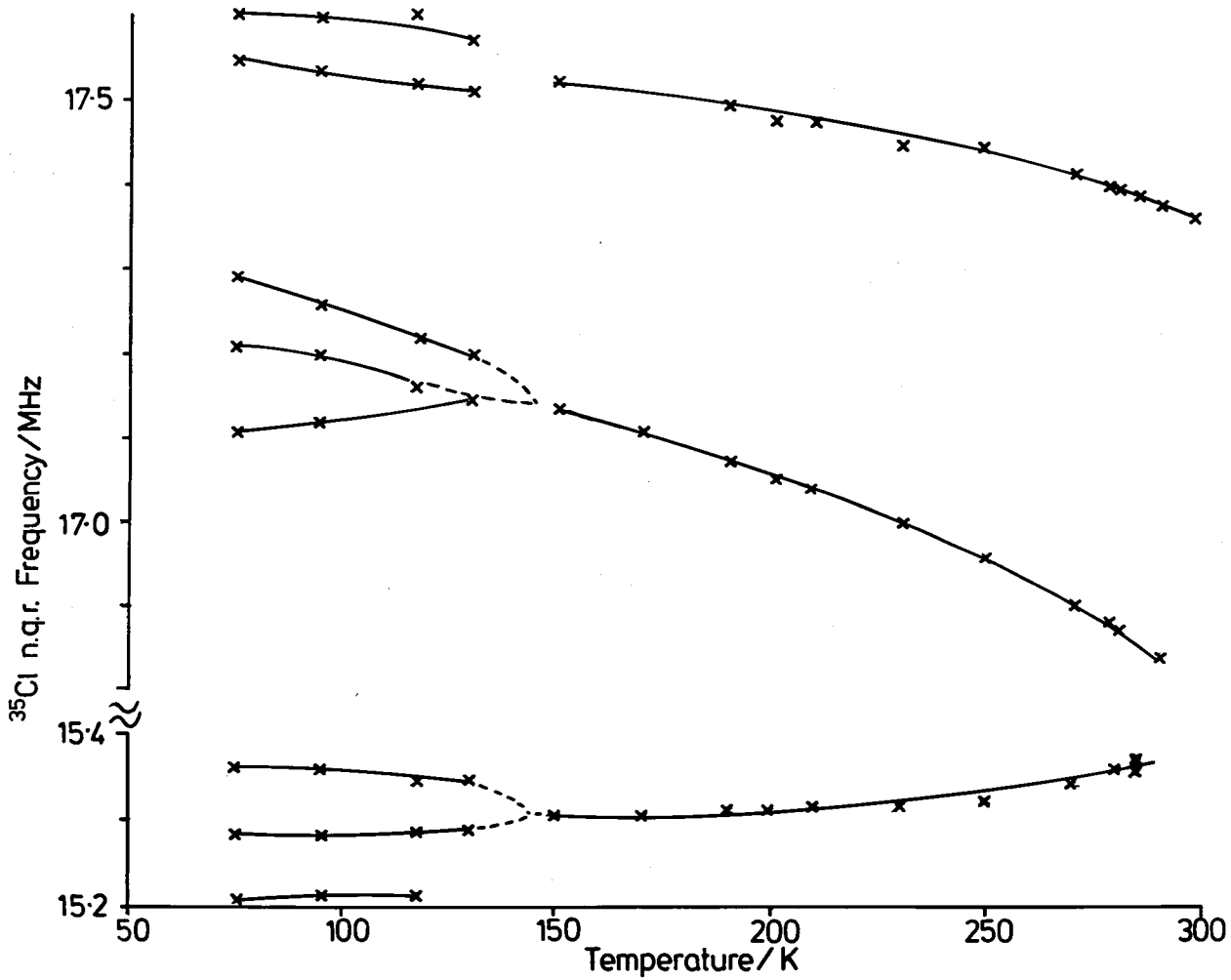
Temperature Dependence of the ^{35}Cl n.q.r. of $(pyH)_2SnCl_6$

Temperature/K[a]	^{35}Cl n.q.r. frequencies/± 0.003 MHz		
298.2	17.360 (3.9)[d]	-	-
290.4	17.375 (3.7)	16.840 (1.1)	15.350 (1.3)
285.4	17.385 (3.4)	16.855 (2.4)	15.362 (1.9)
280.4	17.392 (3.8)	16.875 (3.0)	15.357 (2.5)
278.5	17.397 (3.8)	16.885 (3.4)	15.355 (3.0)
270.5	17.412 (4.1)	16.902 (4.6)	15.343 (4.0)
249.2	17.445 (3.7)	16.960 (4.8)	15.328 (4.1)
230.3	17.445 (3.8)	17.000 (4.8)	15.322 (4.0)
209.4	17.475 (4.0)	17.042 (5.3)	15.315 (5.1)
201.0	17.475 (3.8)	17.052 (5.0)	15.312 (4.1)
190.5	17.493 (4.5)	17.075 (5.4)	15.312 (5.0)
170.5	17.500 (4.6)	17.110 (6.0)	15.312 (5.8)
150.2	17.520 (4.3)	17.135 (5.9)	15.310 (5.7)
117.0[b]	17.600 (2.1)	17.217 (3.1)	15.345 (2.1)
	17.517 (4.1)	17.160 (6.5)	15.287 (6.5)
			15.513 (1.3)
130.0[b]	17.565 (2.5)	17.200 (2.9)	15.348 (2.6)
	17.510 (4.8)	17.147 (6.2)	15.290 (5.9)
95.0[b]	17.595 (2.0)	17.255 (2.7)	15.362 (2.2)
	17.535 (3.1)	17.200 (4.8)	15.285 (4.5)
		17.118 (1.3)	15.212 (1.3)
77[c]	17.600 (1.8)	17.290 (1.9)	15.365 (2.0)
	17.545 (2.9)	17.210 (4.1)	15.288 (3.8)
		17.107 (1.2)	15.207 (1.9)

* See Table 4.2. for definition of superscripts.

Figure 4.7

Temperature dependence of $(pyH)_2SnCl_6$



roughly equal intensity seen between 140 and 290K split to eight others below this temperature. The split lines occur in three groups with two of them having the appearance of approximate 1:2:1 intensity triplets; the third group might also be a triplet, although only two lines are seen. The missing line could well be masked by the spectral noise which had an average height of 0.8 cm. (cf. signal heights in Table 4.6.). The results for this compound are plotted in Figure 4.7. and recorded in Table 4.6.

(viii) $(SCl_3)_2SnCl_6$

This compound shows only one single resonance between room temperature and 145K, at which point the signal fades out. The fade out was not found to be due to saturation effects since reducing the power of the applied radiofrequency radiation did not produce an increase in the signal size near this temperature. The results for this compound are shown in Table 4.7. and Figure 4.8.

Table 4.7.

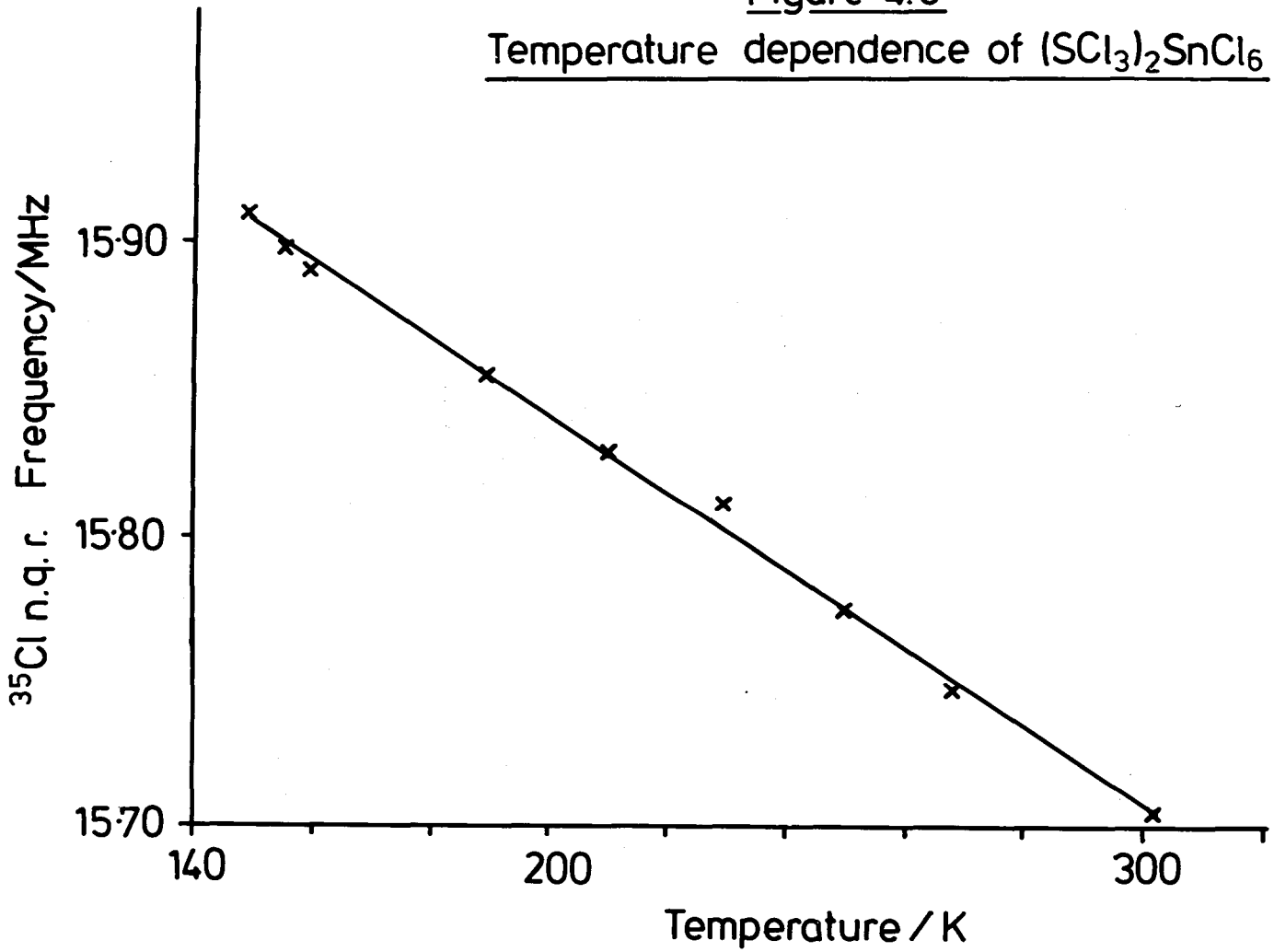
Temperature Dependence of the ^{35}Cl n.q.r. of $(SCl_3)_2SnCl_6$

Temperature/K[a]	^{35}Cl n.q.r. frequency/±0.003 MHz
301.4	15.703 (6.5)[b]
268.0	15.747 (7.7)
249.4	15.773 (7.7)
229.5	15.805 (7.7)
209.8	15.827 (7.6)
189.6	15.855 (7.6)
160.0	15.890 (4.4)
155.0	15.898 (3.2)
149.8	15.910 (2.4)

(a) Errors ±0.1K; (b) Signal heights in cm. shown in brackets.

Figure 4.8

Temperature dependence of $(SCl_3)_2SnCl_6$

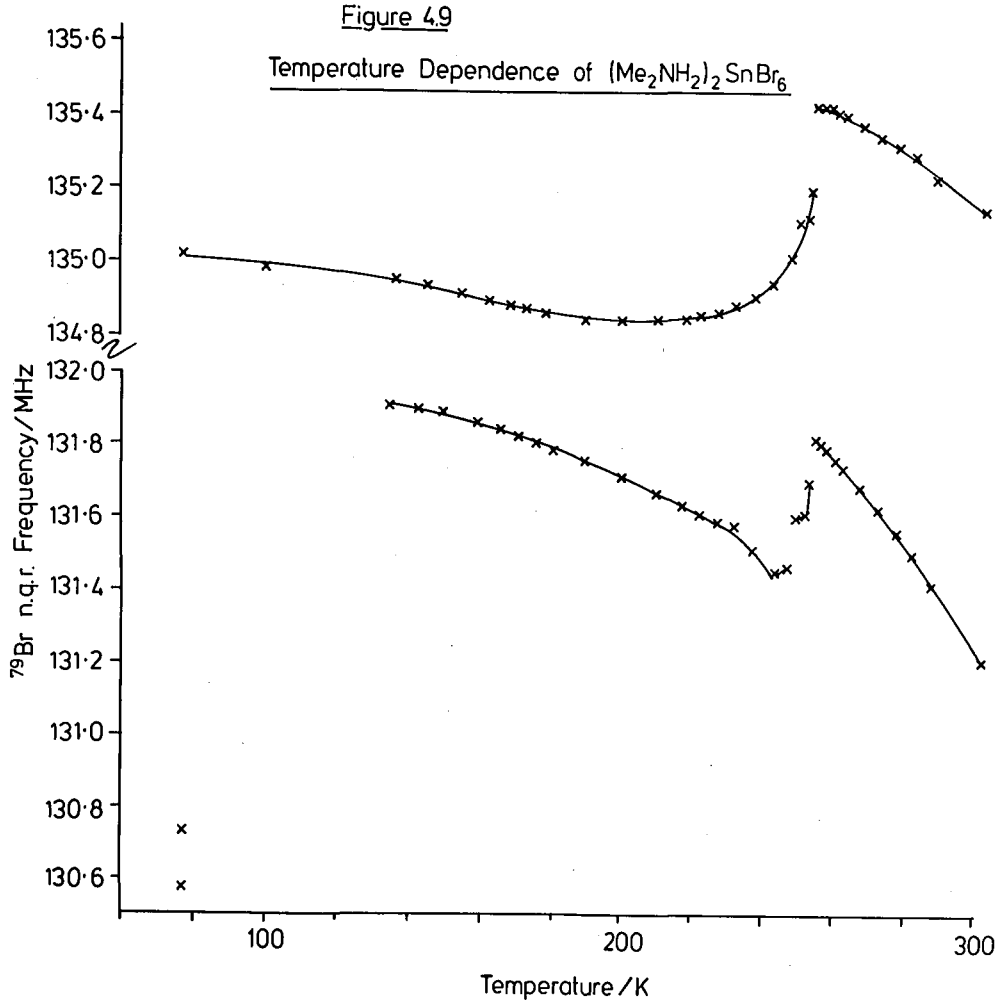


The temperature coefficient of ~ -1.4 kHzK^{-1} is quite normal and gives no indication of secondary bonding interactions.[138] This is also implied by the existence of a single line only. If interaction occurred, a distorted ion should be produced, and more than one resonance seen. On the basis of cation size (Figure 3.2.), one might expect $(SCl_3)_2SnCl_6$ to produce a higher average n.q.r. frequency at 300K than 15.703 MHz, when compared to the frequency of $(Me_3S)_2SnCl_6$, than it actually does. The latter compound is chosen for comparison as it should have a similar sized cation to the former compound (the Van der Waals radius of a methyl group is 2.0Å, while that of a chlorine atom 1.8Å[109]) and so their M_2SnCl_6 volumes should be reasonably congruent. This argument could fail however, if sufficient secondary bonding occurs to compact the structure though this is unlikely as a very large contraction from 427.8Å^3 for $(Me_3S)_2SnCl_6$ (Table 3.6.) would have to occur to place the average n.q.r. frequency at 15.7 MHz which approximately corresponds to an M_2SnCl_6 volume of 300Å^3 (from Figure 3.2.). It is therefore concluded that the presence of undetected ^{35}Cl n.q.r. resonances from the $SnCl_6^{2-}$ ions in this compound, above 15.7 MHz, is a possibility, and if correct, then the anion is distorted and not regularly octahedral or rhombohedral, as implied by the observation of a single line. The undetected lines would presumably in that case be undergoing relaxation broadening thus making them undetectable.

The fade-out of the signal below 145K is anomalous since normal behaviour dictates an increase in signal intensity with decreasing temperature. A change in relaxation of the chlorine nuclei studied could account for this. Alternatively a phase change might be occurring which could possibly involve the formation of the type of Cl_3S^+----Cl secondary interaction seen in other compounds e.g. $SCl_3^+ICl_4^-$,[139] or $SCl_3^+AuCl_4^-$.[140] If

Figure 4.9

Temperature Dependence of $(Me_2NH_2)_2SnBr_6$



this was the case resonances near those for $SnCl_4$ (lit.[116] 24.294, 24.226, 24.140, 23.719 MHz at 77K), might be expected, as the compound approached the form of $SnCl_4.2SCl_4$, on the assumption of a strong interaction. On carrying out a careful search from 26 MHz down to 12 MHz at 77K, however, no signals could be detected.

(d) Temperature Dependence Studies of Hexabromostannates

(i) $(Me_2NH_2)_2SnBr_6$

This compound showed two ^{79}Br n.q.r. frequencies in the 77K to 300K temperature range. The higher frequency signal is approximately twice as intense as the lower at all temperatures, thus reflecting the room temperature structure (see Chapter 3) with each hexabromostannate ion possessing two longer and four shorter Sn-Br bonds.

The results for the temperature range of 77K to 302K are plotted in Figure 4.9., and are recorded in Table 4.8. The plot reveals a dramatic phase change at 253 $\pm$ 1K, at which point a definite break occurs. On further cooling several discontinuities are apparent before the compound settles into a low temperature phase at 242 $\pm$ 1K. This transition is not interpretable in terms of the theories of McElroy, Sutton and Armstrong[23,137] as these require the splitting of a single resonance whereas in this case there are two frequencies at all temperatures and no splitting.

The observation of more positive temperature coefficients, at temperatures below the phase change than above it, argues in favour of stronger hydrogen bonding at low temperature. The respective temperature coefficients for the upper and lower lines are $\sim$ -2.0 $kHzK^{-1}$ and $\sim$ -4.5 $kHzK^{-1}$, between 140K and 190K, and $\sim$ -5.0 $kHzK^{-1}$ and -12.0 $kHzK^{-1}$, between 260K and 300K (the regions in which the coefficients were estimated were chosen to be at points apparently free from the effects of the phase change).

Table 4.8.

Temperature Variation of ^{79}Br N.q.r. of $(Me_2NH_2)_2SnBr_6$

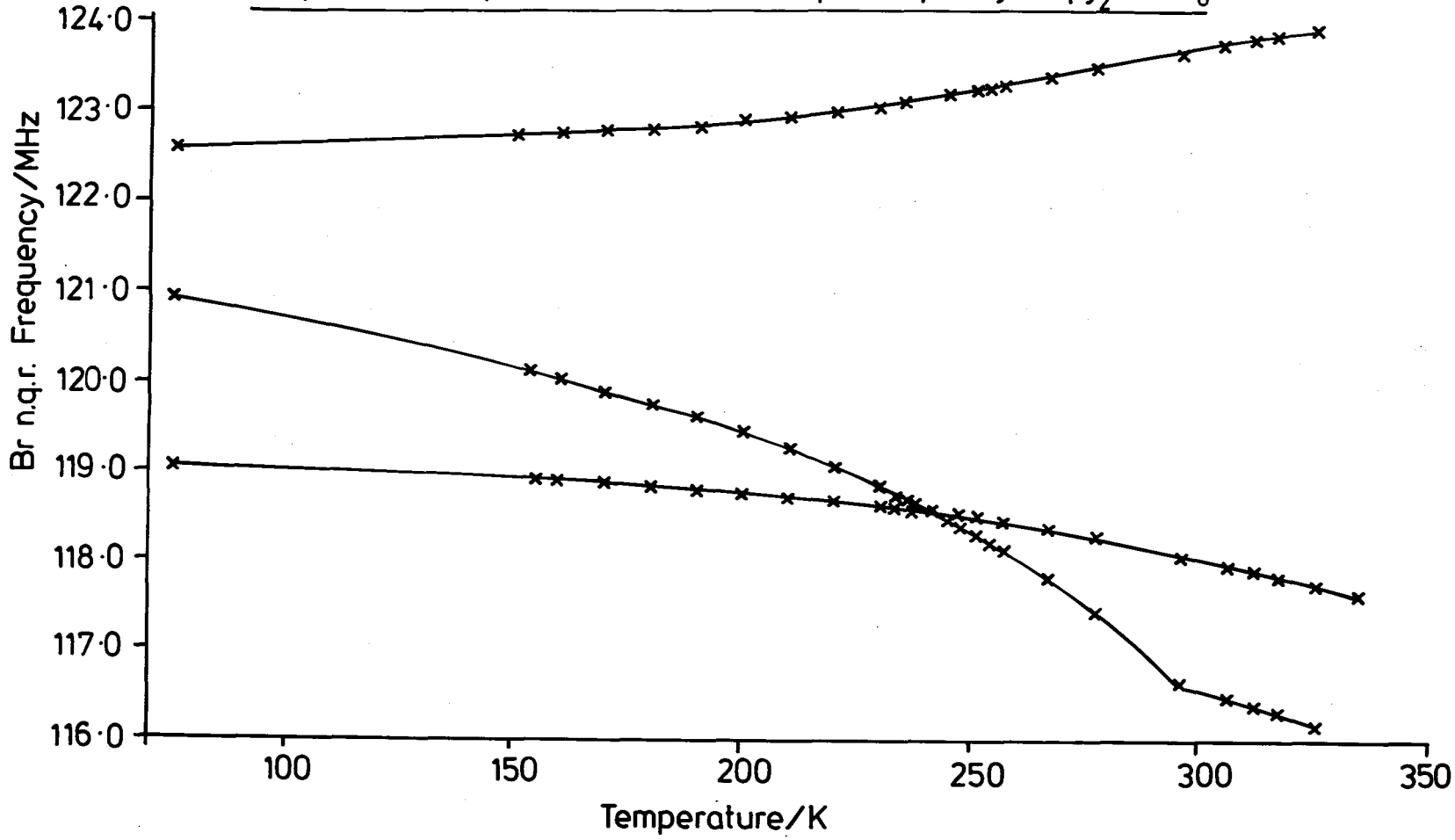
Temperature/±0.1K	^{79}Br n.q.r. frequencies/±0.005 MHz	
301.4	135.150	131.205
287.6	135.240	131.415
281.5	135.300	131.500
276.9	135.322	131.560
271.9	135.348	131.628
266.7	135.382	131.682
261.5	135.408	131.742
259.6	135.414	131.766
257.0	135.430	131.798
255.8	135.428	131.802
254.9	135.432	131.810
253.7	135.434	131.816
252.7	135.200	131.620
251.6	135.126	131.608
249.6	135.014	131.600
246.9	135.020	131.460
242.1	134.944	131.450
236.9	134.910	131.508
231.6	134.886	131.575
226.8	134.864	131.588
221.5	134.856	131.608
217.6	134.848	
216.5		131.632
209.5	134.844	131.666
199.5	134.842	131.708
189.5	134.846	131.756
179.7[a]		131.784
177.1	134.866	
175.0		131.804
172.0	134.874	
170.0		131.822
167.3	134.882	
165.1		131.842
161.9	134.892	
158.5		131.860
154.0	134.914	
149.0		131.886
145.2	134.932	
142.2		131.898
135.9	134.950	
134.7		131.906
99.5	134.986	
77.0[b]	135.020	130.730
		130.575

(a) for this temperature and below, signals were measured by rapidly scanning resonances as the sample was allowed to warm up from 77K; only one frequency was measured for each temperature;

(b) sample immersed in liquid nitrogen.

Figure 4.10

Temperature dependence of Br n.q.r. frequency of py_2SnBr_6



It may therefore be concluded that the transition occurs in order to accommodate the formation of stronger hydrogen bonds in the low temperature phase. The evidence for hydrogen bonding at room temperature has been presented in Chapter 3.

A further phase change is indicated by the discontinuity between the slope of the points to 134.7K and the points at 77K for the lower line. Unfortunately it was not possible to obtain measurements at intermediate temperatures due to experimental difficulties.

(ii) $\underline{(pyH)_2SnBr_6}$

The temperature dependence of this compound was followed by observing its three n.q.r. lines in the 116 MHz to 124 MHz region of the spectrum between 77K and 340K. The lower and middle lines correspond to ^{81}Br n.q.r. frequencies, while the upper line is due to a ^{79}Br n.q.r. frequency (see Section 3(c)(i)). Since the ratio of ^{79}Br to ^{81}Br n.q.r. frequencies is a constant (lit.[108] 1.19207:1) no ambiguity is entailed in comparison of the lines. A consistent set of measurements on one nucleus was not possible due to difficulties in operating the high frequency Decca spectrometer in parts of the region required. The results obtained are plotted in Figure 4.10. and detailed in Table 4.9.

The only evidence of a phase change in this compound comes from a cusp at 296 $\pm$ 1K in the lower ^{81}Br line. A similar feature is perhaps present in the upper ^{81}Br line but is less marked. Little can be deduced from this observation alone. There was no sign of the low temperature splitting seen at 140 $\pm$ 5K for the corresponding hexachlorostannate, although evidence of similar relaxation behaviour at higher temperatures is afforded by the fade-out of two of the three lines at about 325K.

The temperature coefficients for the three lines from 100K to 200K are $\sim$ +3.0 $kHzK^{-1}$, $\sim$ -12.0 kHK^{-1} and $\sim$ -2.5 $kHzK^{-1}$ for the upper, middle and lower lines of Figure 4.10. The positive temperature coefficient of

Table 4.9.

Temperature Variation of the Br N.q.r. of $(pyH)_2SnBr_6$

Temperature/±0.1K	Br n.q.r. frequency/±0.003 MHz		
	^{81}Br		^{79}Br
334.5	-	117.608	-
325.5	116.17[a]	117.713	123.86[a]
317.0	116.320	117.818	123.800
312.0	116.380	117.861	123.765
306.5	116.475	117.925	123.715
296.0	116.642	118.021	123.612
277.7	117.415	118.239	123.462
267.7	117.800	118.345	123.354
257.7	118.118	118.425	123.261
254.6	118.200	118.447	123.236
251.5	118.289	118.468	123.209
249.4	118.333	118.480	
247.5	118.389	118.497	
245.?	118.432	118.505	123.160
243.8	118.500	lines coalesce,	
242.0	118.530	signals	
239.6	118.550	indistinguishable	
237.7	118.635	118.554	
235.9	118.672	118.562	123.087
233.9	118.713	118.572	
230.6	118.822	118.595	123.031
220.4	119.040	118.649	122.973
210.4	119.237	118.694	122.919
200.4	119.418	118.728	122.868
190.6	119.583	118.764	122.822
180.4	119.737	118.798	122.788
170.6	119.870	118.827	122.758
160.5	120.026	118.863	122.737
155.9		118.874	
153.6	120.118		
150.8			122.708
77[b]	120.910	119.034	122.595

(a) These peaks were very weak and broad, hence error ±0.01 MHz;

(b) liquid nitrogen temperature; (c) blanks in the table indicate that the resonances were not sought at those particular temperatures.

the ^{79}Br line suggests that these bromines may be hydrogen bonded. A similar structure to the pyridinium hexachlorostannates is envisaged, with the N-H protons of the cations responsible for this interaction (see section 4(c)(vii)). Furthermore if the ^{79}Br frequency is converted to the corresponding ^{81}Br value (i.e. between 102 MHz and 104 MHz for the range studied) then it is apparent that there are two lines of significantly higher frequency than the third. This can be rationalised if the third line is due to hydrogen bonded bromine atoms. The presence of additional bonding electrons, on the opposite side of the atom to its main Sn-Br bond causes an overall decrease in the electric field gradient experienced by the bromine nucleus. Since the n.q.r. frequency is proportional to the e.f.g., this decrease causes a fall in frequency.

The x-ray diffraction determination of the structure of this compound (section 3(c)(ii)) gave inconclusive evidence for specific hydrogen bonds owing to indications of statistical disorder in the positions of the ions. The structure found therefore gives an average picture of the actual one. No direct confirmation of the hydrogen bonding indicated by the n.q.r. results was therefore provided. The proposed hydrogen-bonded bromine n.q.r. line does correspond to the longest Sn-Br bond length found (from relative intensity considerations of the three lines). It is probable that hydrogen bonding would increase the Sn-Br distances so this observation is consistent with the n.q.r. spectrum.

(e) Temperature Dependence Study of $Me_3NHSnCl_3$

Table 4.10.

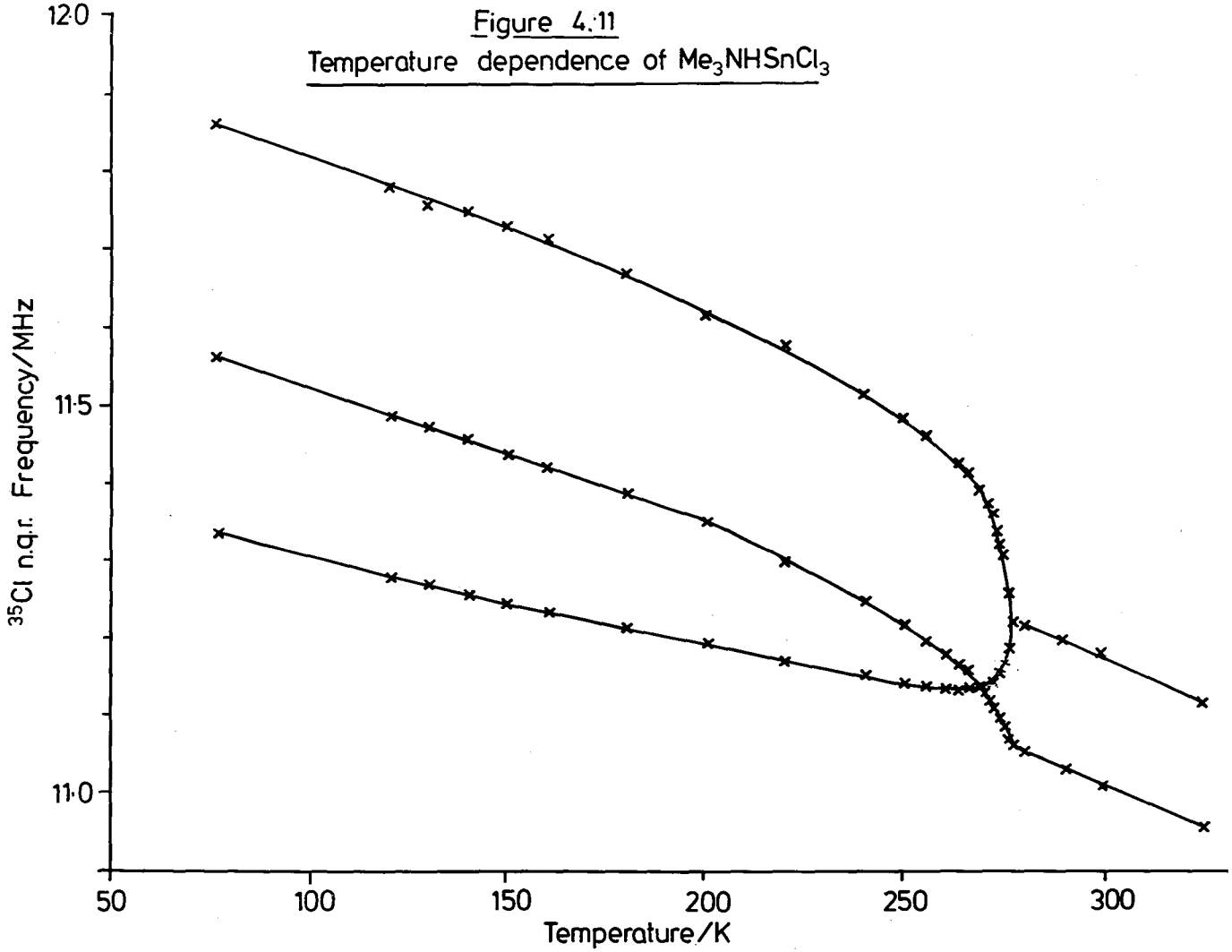
Temperature Variation of the ^{35}Cl N.q.r. of $Me_3NHSnCl_3$

Temperature/0.1K	^{35}Cl n.q.r. frequencies/± 0.003 MHz		
77[a]	11.332	11.560	11.859
120.9	11.276	11.482	11.775
130.6	11.265	11.471	11.753
140.4	11.254	11.454	11.742
150.5	11.241	11.436	11.727
160.7	11.232	11.419	11.709
180.6	11.211	11.384	11.677
200.6	11.191	11.345	11.611
220.6	11.167	11.293	11.571
240.7	11.147	11.245	11.510
250.2	11.138	11.211	11.479
255.7	11.135	11.193	11.455
260.8	11.132	11.174	unmeasured
264.1	11.130	11.162	11.422
266.6	11.132	11.151	11.411
269.1	11.133		11.388
270.3	11.136	11.123	unmeasured
271.4	11.136	11.117	11.370
273.0	11.140	11.107	11.358
273.9	11.145	11.099	11.334
274.5	11.152	11.090	11.317
275.9	11.158	11.080	11.305
276.5	11.186	11.064	11.255
277.9	11.219	11.057	
280.5	11.211	11.050	
290.3	11.193	11.028	
300.0	11.177	11.002	
325.0	11.111	10.958	

(a) Liquid nitrogen temperature.

Figure 4.11

Temperature dependence of $Me_3NHSnCl_3$



This compound was the only trihalostannate studied in this work which produced n.q.r. signals with sufficient strength and separation to make it amenable to a temperature dependence study. The results are plotted in Figure 4.11. and listed in Table 4.10.

From the plot a phase change at 278 ± 1K is clearly apparent, with two lines of 2:1 intensity going to three of equal intensity for temperatures below the transition point. This indicates that the low temperature phase contains three chlorines per trichlorostannate ion in distinctly different crystallographic environments. At higher temperatures however, (at least from 278K to 325K) there exist only two discrete environments for the chlorines of each anion, with one position twice as numerous as the other.

The temperature coefficients of the lines are ~ -1.9 kHzK^{-1}, ~ -1.7 kHzK^{-1} and ~ -1.2 kHzK^{-1} for the upper, middle and lower lines of the plot, below the phase change, and ~ -2.3 kHzK^{-1} and ~ -2.1 kHzK^{-1} for the upper and lower lines above the phase change. This behaviour is totally normal and offers no evidence of any hydrogen bonding interactions with the trichlorostannate ion which might have provided a driving force for the phase change. The transition is therefore probably due to the freezing in of one of the vibrational modes of the compound, creating the inequivalence of environments which has already been mentioned.

(f) Differential Scanning Calorimetry

D.S.C. measurements were performed on $(Me_2NH_2)_2SnBr_6$ from 230K to 400K in order to check the position of the phase change observed. The trace obtained, however, did not show the phase change. This implies that the transition for this compound involves only very slight thermodynamic changes which the D.S.C. instrument could not detect. Unfortunately instrumental difficulties also precluded the detection of phase changes below about 230K so it was not possible to study any of the phase changes observed via ^{35}Cl n.q.r. for the hexachlorostannates.

CHAPTER 5

^{119}Sn N.m.r. Studies of Some Inorganic Tin (II) Compounds

(a) Introduction

^{119}Sn n.m.r. data on inorganic tin (II) compounds in the literature[81,83,85,86] is confined to the study of stannous halides, apart from one measurement on $SnSO_4$[83] in a saturated aqueous solution which gave a chemical shift (δ) of -909 ppm. $SnCl_2$ has been shown[83] to have a chemical shift variation of 180 ppm in the single resonances seen for hydrochloric acid solutions of different concentration (δ = -341.2 ppm for a 4.8M solution of $SnCl_2.2H_2O$ in H_2O, and δ = -521.3 ppm for $SnCl_2.2H_2O$ in 12.17M HCl) while other workers[85] have found a value of δ = -388.1 ppm for a single measurement on $SnCl_2$ saturated in 12M HCl. Other measurements of saturated solutions are δ = -236 ppm for $SnCl_2$ in tetrahydrofuran[83] and δ = -385.0 ppm for $SnBr_2$ in 9M HBr.[85] No signals could be detected for SnF_2 saturated in H_2O.[83] Yeh and Geanangel[86] have made a comprehensive study of SnF_2, $SnCl_2$, $SnBr_2$ and SnI_2 in solution in four solvents: hexamethylphosphoramide, dimethyl ether, dimethylsulphoxide and dimethylformamide. They reported a general increase in δ values in the order $SnF_2 < SnCl_2 < SnBr_2 < SnI_2$ as well as noting a marked concentration and temperature-dependence for these figures. Similar solvent effects have been noticed in the ^{119}Sn n.m.r. of several organotin (IV) compounds dissolved in co-ordinating liquids such as acetone, pyridine or dimethylsulphoxide.[81]

(b) Stannous Halides in Solution and Their Concentration Behaviour

(i) Chemical Shifts of Stannous Halides in Saturated Solution

The existence of acute temperature and solvent variations for solutions of stannous halides makes it necessary to quote both these

variables when measurements of ^{119}Sn chemical shift values are quoted. The magnet of the spectrometer used in this study was thermostatically controlled to a fixed temperature of 307.2K and was not variable. To enable convenient comparison with other work, therefore, measurements were made on a number of saturated solutions. These solutions have the advantage of placing the maximum number of ^{119}Sn nuclei possible in the n.m.r. probe, thus enhancing the signal to noise ratios of the spectra. Table 5.1. shows the data obtained from the stannous halides in a variety of solvents.

Table 5.1. reveals that no signals could be detected for SnI_2 in any of the solvents used. Furthermore, samples of SnI_2 in saturated solution with CS_2, $CHCl_3$ and 2-iodopropane also gave no signals. This lack of resonances is probably attributable for the most part to the very low solubility of SnI_2, while for H_2O as a solvent, reaction is indicated by the almost immediate formation of a white precipitate, presumably hydrolysis

Table 5.1.

^{119}Sn N.m.r. of Stannous Halides in Saturated Solutions

Solvent	$-\delta/\pm0.5$ ppm				
	SnF_2	SnClF	$SnCl_2$	$SnBr_2$	SnI_2
MeOH	716.1	340.4	457.7	279.3	NS[a]
EtOH	NS	283.7	458.3	209.6	NS
H_2O	796.0	707.7	554.6	457.3	NS
MeCN	NS	NS	277.3	NS	NS
Acetone[b]	NS	683.9	246.5	129.2	NS
CH_2Cl_2	NS	NS	NS	NS	NS

(a) NS = no signal observed after at least 2000 scans;

(b) see text for discussion of systems in this solvent.

products. The hydrolysis of tin (II) has been studied in detail elsewhere.[155] SnI_2 also yielded large amounts of white precipitate with .880 ammonia solution and gave no ^{119}Sn n.m.r. signals, which was surprising in view of its reported high solubility in NH_4OH.[109]

Where the stannous halides were soluble, solutions generally gave strong resonances with narrow linewidths (< 2 ppm) after only a few scans. For this reason, therefore, unless reaction with the solvent was indicated, the insolubility of samples was inferred from their failure to produce resonance signals. It is thus concluded that all the stannous halides studied are insoluble in CH_2Cl_2, $SnBr_2$, SnClF and SnF_2 are also insoluble in MeCN, as is SnF_2 in EtOH.

The figures quoted in Table 5.1. for acetone as a solvent are those obtained initially, immediately after preparing the solutions. It was found that for $SnBr_2$ the observed chemical shift of -129.2 ppm increased progressively with time and the solution turned from an initial yellow colour to blood red. After several weeks this system gave a shift of 6.7 ppm. SnF_2 also showed signs of reacting with acetone since, despite no signals being detected initially, a signal at -166.7 ppm was observed after several weeks. $SnCl_2$ also showed signs of reaction. A saturated solution in acetone, which was initially colourless, turned orange-red after several days while its chemical shift showed a slight but steady decrease from -249.6 ppm initially to -262.3 ppm after 6 days. These systems were not studied further to try to discover the cause of the changes occurring in them, but it is apparent that acetone is an unsuitable solvent for the stannous halides in view of their reactivity with it.

A difference in δ was noticed for a saturated solution of $SnBr_2$ in H_2O prepared in the presence of air. The shift obtained for this solution

was -433.3 ppm as opposed to -457.3 ppm for a similar solution prepared with the exclusion of oxygen. This difference is presumably due to the effects of oxidation by atmospheric O_2 and reflects the sensitivity of tin (II) compounds to oxidation.[78] Similarly the value of δ for a saturated solution of $SnBr_2$ in EtOH was found to occur at -203.7 ppm for a solution prepared in the presence of O_2 as compared with -209.6 ppm for one made up under N_2. The solutions of SnF_2, SnClF and $SnCl_2$, on the other hand, exhibited little change in δ whether prepared with or without the exclusion of O_2. Nevertheless, the solutions of tin (II) were generally prepared and handled in such a way as to eliminate the possibility of atmospheric oxidation. The data shown in Table 5.1. are for such systems.

The existence of changing shifts for varying temperatures of all the tin (II) halides in solution points towards an equilibrium between several different species for each one. Each system studied showed a steady decrease in δ before an equilibrium value was reached, corresponding to the solution heating up from room temperature to the spectrometer operating temperature (307.2K). Similar behaviour in dibutyltin dialkoxides as pure liquids has been explained previously in terms of an equilibrium between monomeric and dimeric species caused by autoassociation.[81] The equilibria present for the tin (II) halides in solution, however, are likely to be of the type:[86]

$$SnX_2 \text{ (solv.)} + S \rightleftharpoons SnX_2.S \text{ (solv.)} \qquad \text{eq. 5.1.(a)}$$

$$SnX_2.S \text{ (solv.)} + S \rightleftharpoons SnX_2.2S \text{ (solv.)} \qquad \text{(b)}$$

$$2SnX_2 \text{ (solv.)} \rightleftharpoons SnX^+ \text{ (solv.)} + SnX_3^- \text{ (solv.)} \qquad \text{eq. 5.2.}$$

In the above equations solv. represents solvation by a general co-ordination

sphere of solvent molecules (S) as opposed to more tightly bound complexes of the type $SnX_2.S$. The effect of changing temperature on these equilibria would be to change the concentrations of the species present according to their thermodynamic properties and thus change the average value of δ actually observed. The observation of a single n.m.r. peak only from each solution means that there must be rapid exchange between the tin-containing species present, so that the spectrometer only detects an average value of the chemical shifts of each. The fact that no coupling between the ^{19}F and ^{119}Sn nuclei is observed for SnF_2 or SnClF, confirms that rapid exchange is occurring which averages the effect out. These equilibria are discussed further in section 5(b)(ii).

The general trend for δ values to increase in the order SnF_2 < (SnClF <) < $SnCl_2$ < $SnBr_2$, as observed by Yeh and Geanangel,[86] was noticed for H_2O and acetone. For MeOH and EtOH however, SnF_2, $SnCl_2$ and $SnBr_2$ gave shifts in the expected order while SnClF produced values intermediate between those of $SnCl_2$ and $SnBr_2$. The explanation for this behaviour is not apparent, though it might be misleading to some extent to compare these figures for saturated solutions, since SnF_2 and SnClF were only sparingly soluble in MeOH and EtOH whereas $SnCl_2$ and $SnBr_2$ could be readily dissolved.

(ii) The Effect of Concentration on δ for $SnCl_2$ and $SnBr_2$

The appreciable solubility of both $SnCl_2$ and $SnBr_2$ in H_2O, MeOH and EtOH enabled a study of their chemical shifts to be made over a large range of concentrations. The effect of concentration was also investigated for solutions of $SnCl_2$ in acetone. The measurements obtained are shown in Tables 5.2. to 5.8. and are plotted in Figures 5.1. to 5.7.

For each system studied, a steady increase in δ was observed as the concentration was reduced, except where solvolysis was indicated.

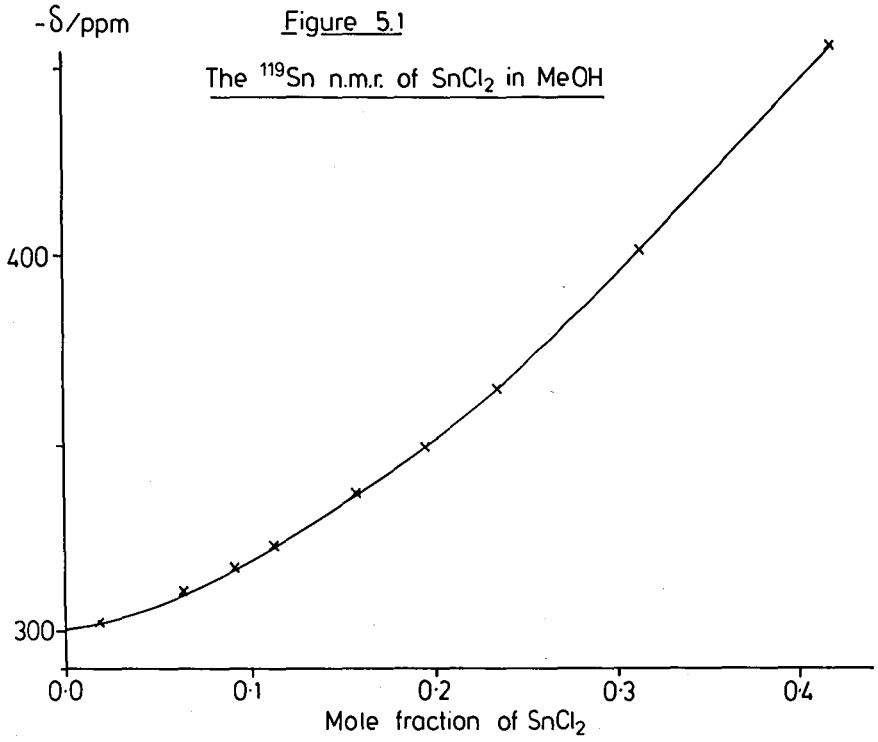


Figure 5.1

The ^{119}Sn n.m.r. of $SnCl_2$ in MeOH

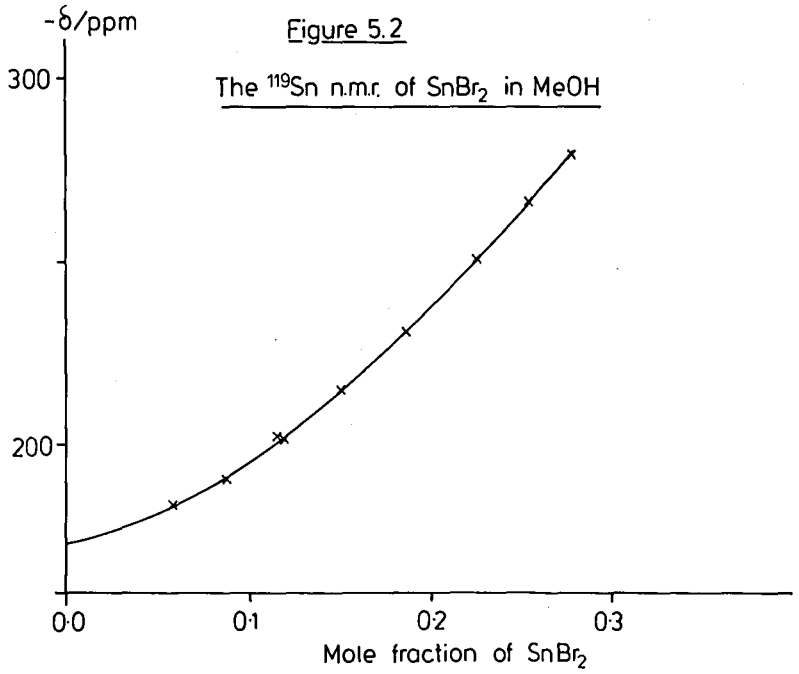


Figure 5.2

The ^{119}Sn n.m.r. of $SnBr_2$ in MeOH

Table 5.2.

The ^{119}Sn N.m.r. of $SnCl_2$ in MeOH

Mole fraction of $SnCl_2$	$-\delta/\pm 0.5$ ppm	Mole fraction	$-\delta$
0.018	302.4	0.194	349.1
0.065	310.1	0.234	364.4
0.092	317.1	0.312	402.0
0.113	322.7	0.415[a]	457.7
0.157	336.3		

(a) Saturated solution containing some undissolved $SnCl_2$.

Table 5.3.

The ^{119}Sn N.m.r. of $SnBr_2$ in MeOH

Mole fraction of $SnBr_2$	$-\delta/\pm 0.5$ ppm	Mole fraction	$-\delta$
0.057	183.4	0.185	231.2
0.088	190.9	0.224	251.2
0.115	202.6	0.251	267.5
0.119	201.9	0.274[a]	279.3
0.150	214.6		

(a) Saturated solution containing some undissolved $SnBr_2$.

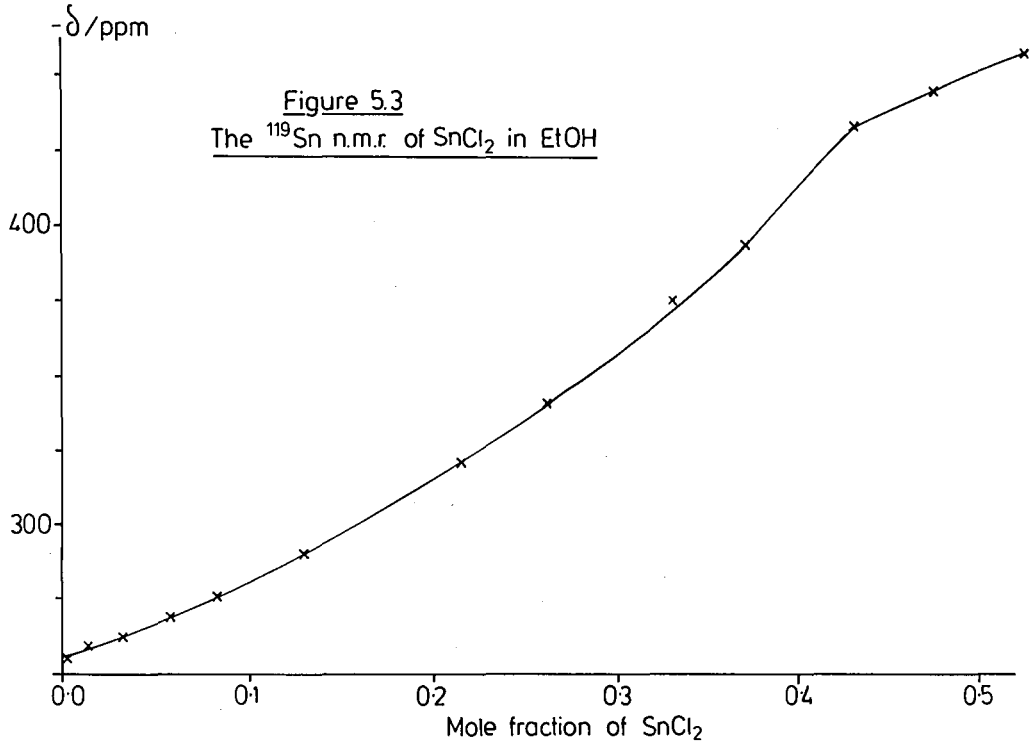


Figure 5.3
The ^{119}Sn n.m.r. of $SnCl_2$ in EtOH

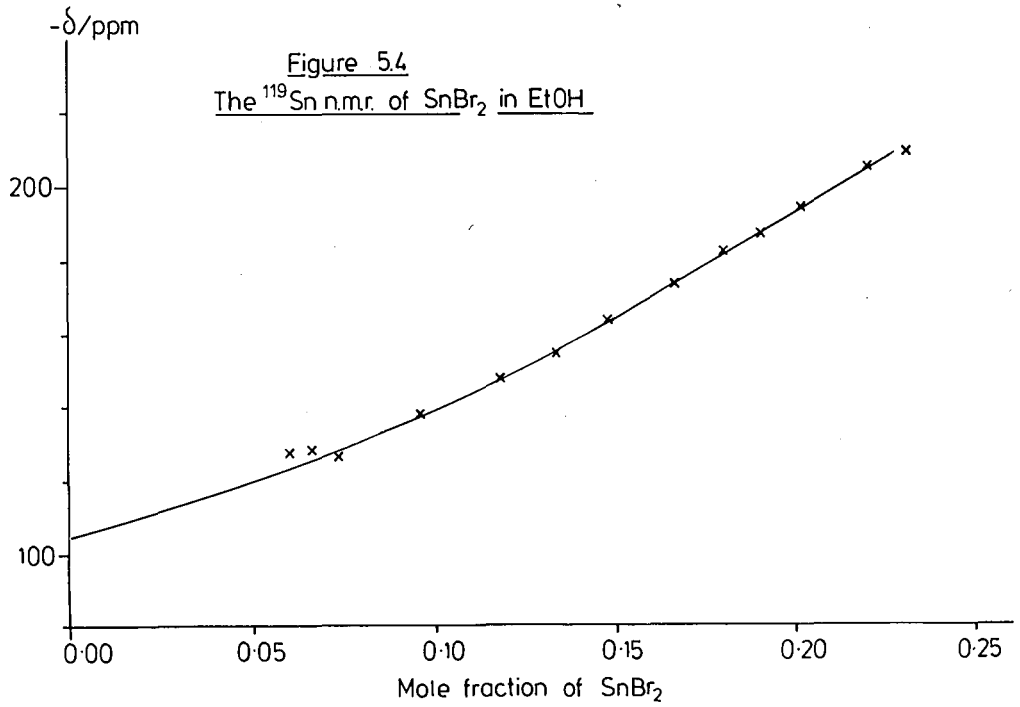


Figure 5.4
The ^{119}Sn n.m.r. of $SnBr_2$ in EtOH

Table 5.4.

The ^{119}Sn N.m.r. of $SnCl_2$ in EtOH

Mole fraction of $SnCl_2$	$-\delta/\pm0.5$ ppm	Mole fraction	$-\delta$
0.002	255.9	0.261	340.4
0.012	258.5	0.330	375.4
0.031	262.0	0.370	392.8
0.057	267.2	0.427	435.1
0.083	276.0	0.472[a]	445.1
0.130	289.8	0.521[a]	458.3
0.215	320.4		

(a) Solution contains some undissolved $SnCl_2$.

Table 5.5.

The ^{119}Sn N.m.r. of $SnBr_2$ in EtOH

Mole fraction of $SnBr_2$	$-\delta/\pm0.5$ ppm	Mole fraction	$-\delta$
0.060	127.2	0.166	172.7
0.066	128.1	0.179	182.6
0.073	126.7	0.190	186.7
0.095	138.4	0.201	194.1
0.117	147.7	0.219	205.2
0.133	154.8	0.230[a]	209.6
0.148	163.1		

(a) Saturated solution containing some undissolved $SnBr_2$.

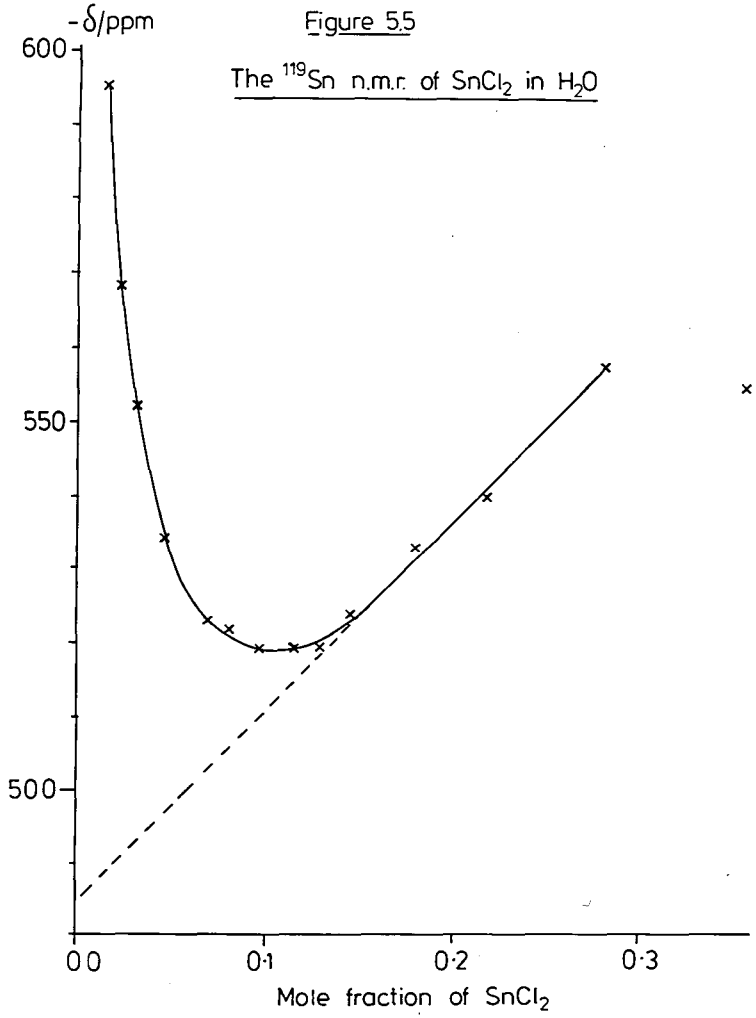


Figure 5.5

The ^{119}Sn n.m.r. of $SnCl_2$ in H_2O

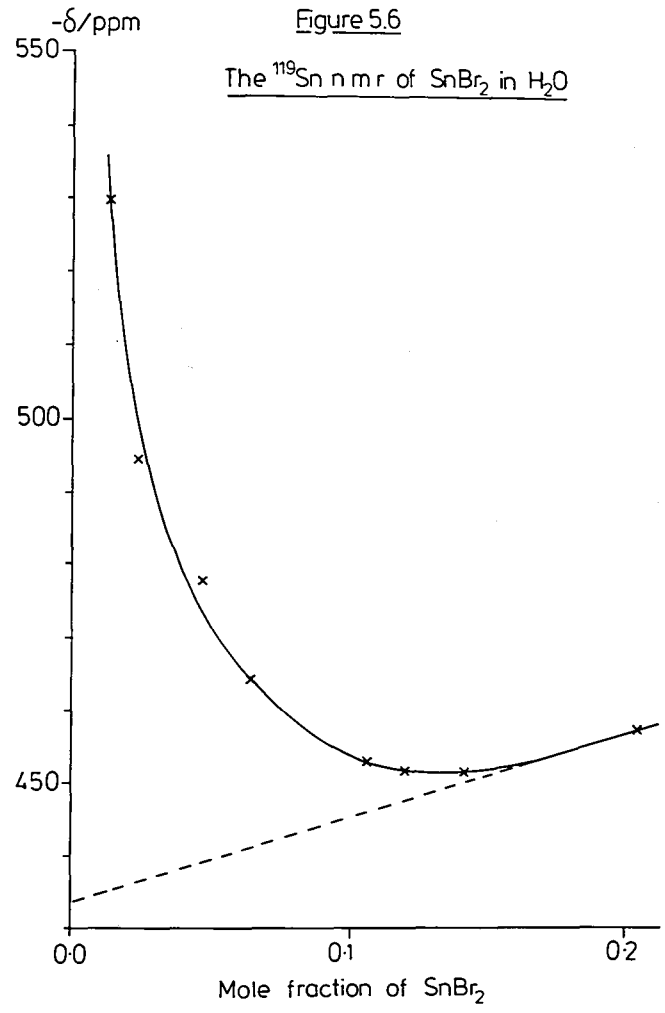


Figure 5.6

The ^{119}Sn n.m.r. of $SnBr_2$ in H_2O

Table 5.6.

The ^{119}Sn N.m.r. of $SnCl_2$ in H_2O

Mole fraction of $SnCl_2$	$-\delta/\pm0.5$ ppm	Mole fraction	$-\delta$
0.014[a]	595.6	0.115	519.1
0.023[a]	568.2	0.130	519.4
0.031[b]	552.3	0.146	523.7
0.047[b]	534.2	0.181	533.0
0.071[b]	522.6	0.219	539.8
0.081[b]	521.5	0.282	557.6
0.097	519.1	0.359[c]	554.6

(a) Slightly cloudy solution; (b) white precipitate in n.m.r. tube; (c) saturated solution containing some undissolved $SnCl_2$.

Table 5.7.

The ^{119}Sn N.m.r. of $SnBr_2$ in H_2O

Mole fraction of $SnBr_2$	$-\delta/\pm0.5$ ppm	Mole fraction	$-\delta$
0.023[a]	529.6	0.120	451.4
0.034[a]	494.4	0.142	451.2
0.047[b]	477.4	0.166	452.9
0.065[b]	463.9	0.204[c]	457.3
0.069[b]	452.6		

(a) Slightly cloudy solution; (b) white precipitate in n.m.r. tube; (c) saturated solution containing some undissolved $SnBr_2$.

Figure 5.7

The ^{119}Sn n.m.r. of $SnCl_2$ in Acetone

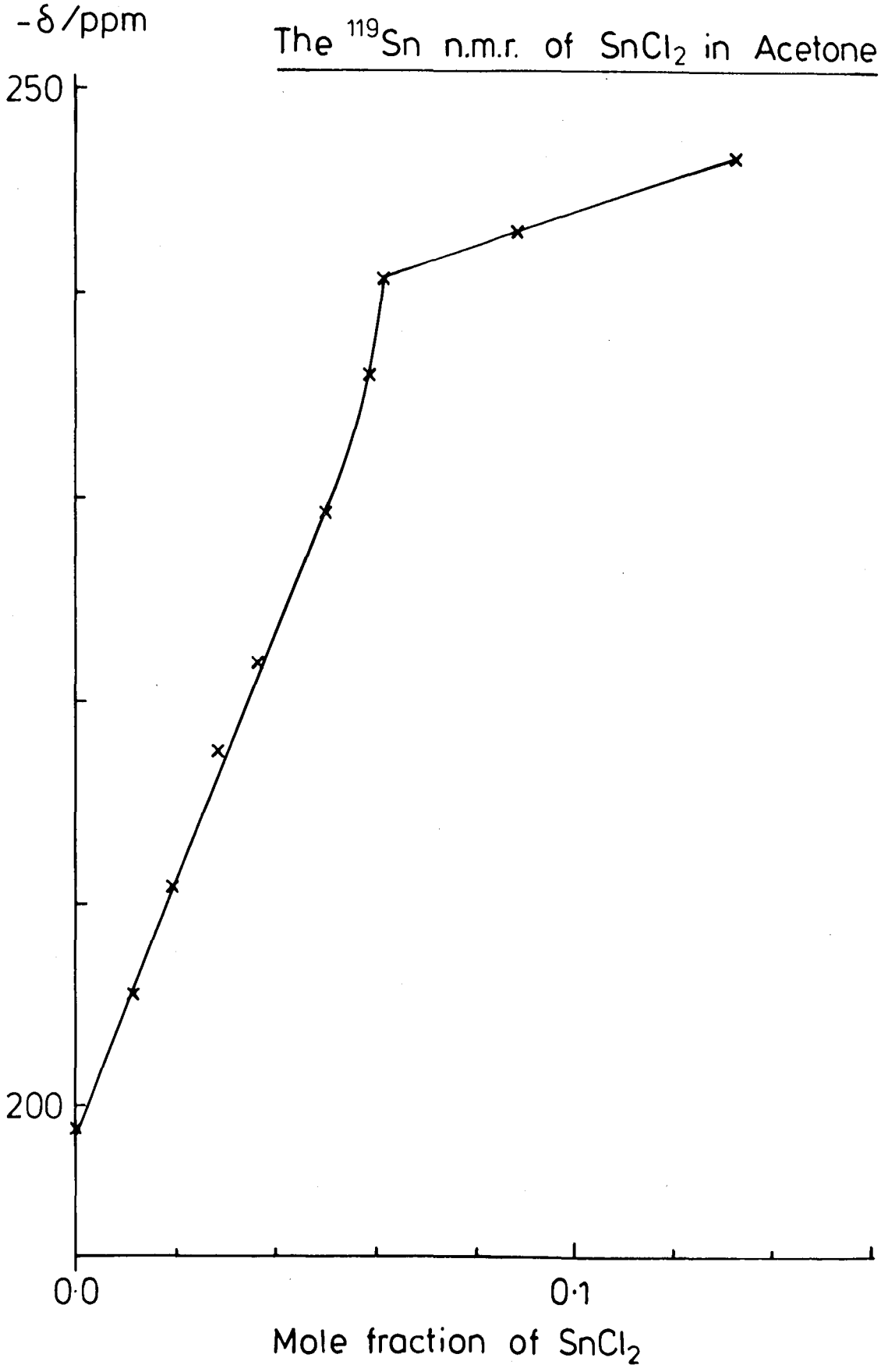


Table 5.8.

The ^{119}Sn N.m.r. of $SnCl_2$ in Acetone

Mole fraction of $SnCl_2$	$-\delta/\pm 0.5$ ppm	Mole fraction	$-\delta$
0.0122	205.4	0.0581	236.0
0.0195	210.7	0.0605[a]	240.6
0.0284	217.5	0.0872[a]	243.0
0.0363	221.8	0.1305[a]	246.5
0.0498	229.1		

(a) Saturated solutions containing some undissolved $SnCl_2$

This is most probably due to each dilution causing an imbalance in the equilibria present initially (equations 5.1. and 5.2.) which produces a different chemical shift when the new equilibria are reached. Co-ordinating solvents have been found to exhibit variable concentration behaviour in other tin compounds (e.g. $SnCl_2$, $SnBr_2$, SnF_2, SnI_2 in DMF or DMSO[86]), whilst water and alcohols are also expected to produce some ionisation of the solute[81] which would cause additional effects as shown in eq. 5.2. Evidence for the ionisation of $SnCl_2$ in H_2O is afforded by the crystal structure of $SnCl_2.1.5H_2O$ which was found to have a structure consisting of $SnCl_3^-$ and $[SnCl(OH_2)_2]^+$ ions.[76] Several x-ray diffraction studies have also been performed on $SnBr_2$ hydrates ($2SnBr_2.H_2O$, $6SnBr_2.5H_2O$ and $3SnBr_2.H_2O$)[143] and these show evidence of the co-ordination of water to tin by Sn-O distances ranging from 2.18 - 2.35Å cf. Sn-O distances of 2.316 and 2.342Å in $[SnCl(OH_2)_2]^+$.[76] A mixed hydrate $Sn_2Br_{0.65}Cl_{3.35}.3H_2O$ has also had its structure determined and this, too shows evidence of co-ordination by water to tin from the presence of the ions $[SnBr_{0.15}Cl_{0.85}(H_2O)_3]^+$ and

$(SnBr_{0.5}Cl_{2.5})^-$. The ^{119}Sn n.m.r. of mixtures of $SnCl_2$ and $SnBr_2$ in each of H_2O, MeOH, EtOH and acetone give single resonances for each system which indicates exchange between all the species present. The halides of $SnCl_2$ and $SnBr_2$, therefore, must freely exchange with each other in solution.

The fact that δ increases as the concentration of stannous halide is reduced shows that in the weaker solutions the average tin nucleus is less shielded by its electrons than in the more concentrated ones i.e. the equilibria of all the tin species present show a preponderance of compounds giving chemical shifts at lower field. Equations 5.1. would favour a shift to solvated species of the type $SnX_2.S$ and $SnX_2.2S$ as the concentration of S increases, so that in the limit, all the tin would be fully co-ordinated. It is not yet clear from the structural data available, however, whether fully co-ordinated complexes would involve the binding of one or two solvent molecules. Bonding considerations favour the mono-solvated molecules since this would involve sp^3 hybridisation of the tin bonding orbitals whereas for $SnX_2.2S$ to be formed, sp^3d hybrids would have to be used and these are expected to be of higher energy than the former.

One way in which the increase in chemical shift with dilution can be explained is through the interaction of the tin species in solution with each other. There are several examples in the literature[81] where the association of molecules in solution has been used to rationalise this effect for organotin compounds [e.g. $But_2Sn(OMe)_2$, Me_3SnCO_2H]. Interaction between the stannous halides studied in MeOH, EtOH and H_2O in this work is particularly likely for the concentrated solutions in view of the fact that they contain such high proportions of SnX_2 to the solvent (e.g. for $SnCl_2$ in EtOH in the most concentrated solutions there is almost one

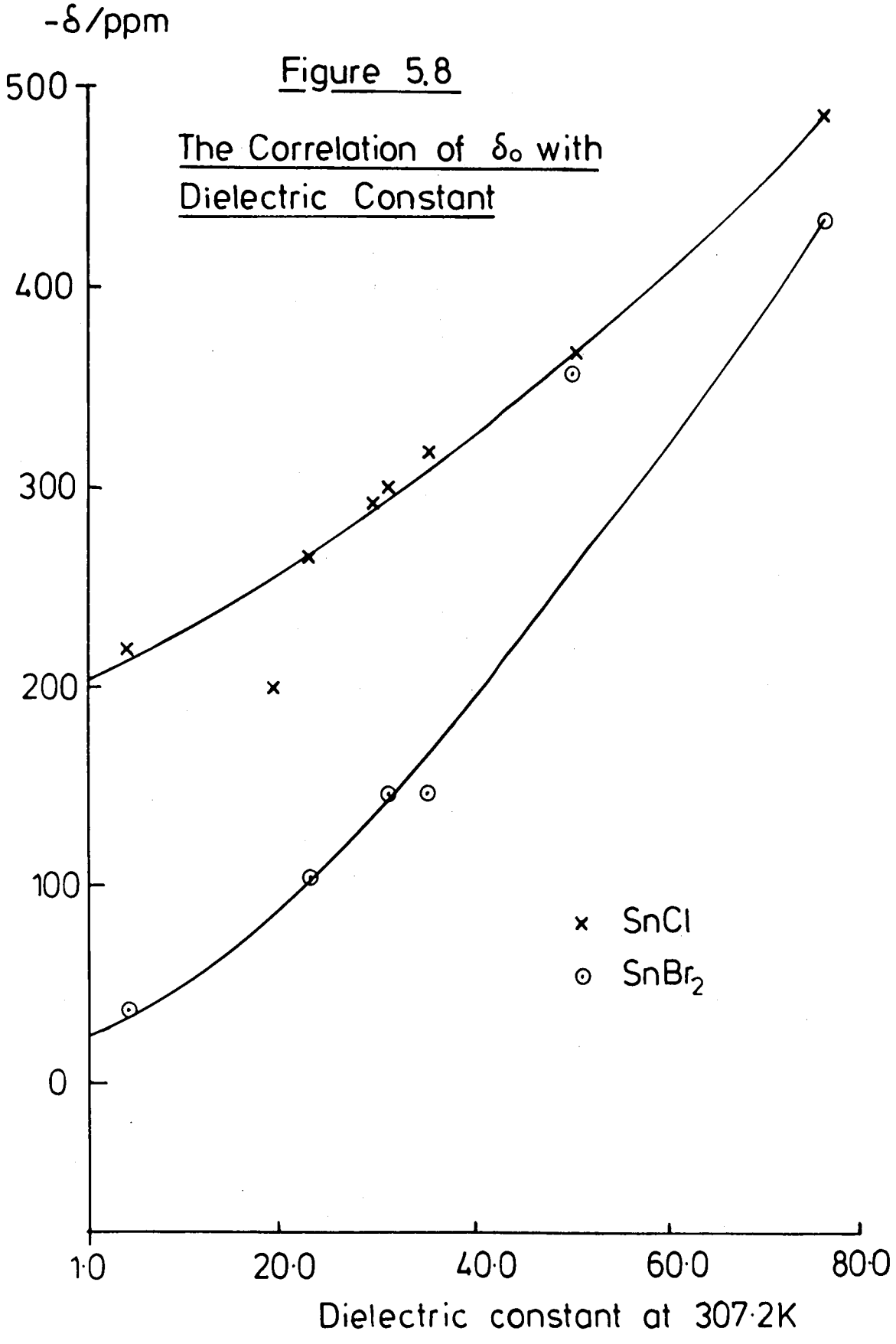


Figure 5.8

The Correlation of δ_o with Dielectric Constant

$SnCl_2$ molecule per molecule of EtOH). These interactions would diminish as the solutions become more dilute, up to a point where they have no effect on the chemical shift of the stannous halide at infinite dilution. The chemical shifts at infinite dilution (δ_o) have been estimated, by extrapolation to zero mole fraction of SnX_2, from the plots of δ versus mole fraction, are shown in Table 5.9. When using H_2O as a solvent, this extrapolation was performed for mole fractions above 0.1 since below this value the solutions of both $SnCl_2$ and $SnBr_2$ contained white precipitates. The quantity of these precipitates increased with each successive addition of H_2O and they probably arise because of hydrolysis of the tin to form insoluble oxides. The concomitant decrease in δ is not due to the production of excess H^+ and Cl^- (or Br^-) ions in solution which would accompany such hydrolysis since the addition of HCl to $SnCl_2$ increases the ^{119}Sn chemical shift.[83] A possible explanation would be if some tin (IV) was produced by disproportionation [also giving some tin (0)] since the shifts of $SnBr_4$ and $SnCl_4$ in water are rather lower than those of their tin (II) counterparts (see Chapter 6).

Figure 5.8. illustrates the correlation of δ_o with the dielectric constants of the solvents used and includes some data from the literature.[86] This plot clearly shows a dependence of δ_o on dielectric constant for both $SnCl_2$ and $SnBr_2$, although this relationship would not appear to be linear as stated by Yeh and Geanangel.[86] There are two points which appear some way off the estimated solid lines of best fit in Figure 5.8. $SnCl_2$ in acetone gives a δ_o figure of -200 ppm which seems to be quite low when compared to the other values for this compound. This figure was found to be reproducible and may indicate either that complexes of particular stability are formed by $SnCl_2$ and acetone, or alternatively could

Table 5.9.

Correlation of δ_o Values with Dielectric Constants

Solvent	$-\delta_o$/ppm		Dielectric constant of solvent at 307.2K[a]
	$SnCl_2$	$SnBr_2$	
H_2O	484	434	75.4
DMSO[b]	368[e]	357[e]	44.7[f]
DMF[c]	318[e]	172[e]	35.0[f]
MeOH	300	172	31.0
HMPA[d]	293[e]	-	29.5[f]
EtOH	264	104	23.0
Acetone	200	-	19.3
Me_2O	218[e]	38[e]	4.8

(a) Calculated from values at 298K using correction factors,[109] except where otherwise stated; (b) dimethylsulphoxide; (c) dimethylformamide; (d) hexamethylphosphoramide; (e) ref. 86; (f) estimated from figures quoted in ref. 86.

be due to the reaction of the stannous halides with acetone which was mentioned earlier. The latter reason, however, is perhaps unlikely because the chemical shifts for $SnCl_2$ in acetone were measured as soon as the solutions were prepared. The value of δ_o for $SnBr_2$ in DMSO was obtained[86] by extrapolation of three points along (at -319.5, -322.2 and -319.9 ppm at concentrations of 1.3, 0.98 and 0.87M respectively) and may be somewhat high: more figures would be desirable to perform an accurate extrapolation to zero concentration. The values of δ_o corresponding to a dielectric

constant of 1.0 represent figures for isolated $SnCl_2$ and $SnBr_2$ molecules in a vacuum. These values are roughly -200 ppm and -20 ppm for $SnCl_2$ and $SnBr_2$ respectively and may be of use to the theoretical chemist. A convergence of the two lines for high dielectric constants suggests that a region might be reached where δ_o becomes independent of stannous halide. This implies that the ionisation of the stannous halides is increasing as the dielectric constants are increasing, such that in the limit, totally dissociated Sn^{2+} and X^- ions would be present in the most ionising media.

(c) The Addition of Halides to $SnCl_2$ and $SnBr_2$

$SnCl_2$ was studied in H_2O with the addition of KCl and HCl, while $SnBr_2$ was studied with the addition of Pe_4NBr in EtOH. The results of these experiments are shown in Tables 5.10 to 5.12 and plotted in Figures 5.9. to 5.11. It was noticed that for each of these systems single, narrow (< 2 ppm) lines were produced in their n.m.r. spectra, and that the positions of these resonances were not as sensitive to temperature as those for the stannous halides alone. Each stannous halide showed a general increase in δ with added halide which suggests that complexation of SnX_2 species by halides decreases the shielding of the tin nuclei. This may happen by rehybridisation of the tin bonding orbitals, diminishing the s-character of the Sn-X bonds

Table 5.10.

The Variation of δ with the Addition of KCl to $SnCl_2$ in H_2O

Moles KCl/mole $SnCl_2$	$-\delta/\pm 0.5$ ppm	$KCl/SnCl_2$	$-\delta/\pm$ 0.5 ppm
0.000	534.0	0.962	422.2
0.314	492.0	1.170	412.4
0.572	457.1	1.333	390.7
0.616	440.5	1.755	390.7
0.818	432.7	2.025	390.7

Table 5.11.

The Variation of δ with the Addition of Hydrochloric Acid to $SnCl_2$ in H_2O

Moles HCl/mole $SnCl_2$	$-\delta/\pm 0.9$ ppm	$HCl/SnCl_2$	$-\delta/\pm 0.5$ ppm
0.000	533.4	1.593	341.3
0.071	522.8	1.824	332.5
0.128	510.6	1.981	327.3
0.249	491.5	2.188	323.8
0.385	467.0	2.398	320.3
0.517	446.0	2.523	320.3
0.677	422.0	2.772	316.8
0.830	400.6	3.068	316.8
0.983	380.6	3.403	315.0
1.147	369.2	3.795	315.0
1.290	357.0	4.625	316.8
1.443	348.2	6.225	318.5

Table 5.12.

The Variation of δ with the Addition of Pe_4NBr to $SnBr_2$ in EtOH

Moles Br^-/mole $SnBr_2$	$\delta/\pm 0.9$ ppm	$Br^-/SnBr_2$	δ
0.000	-161.0	0.504	31.0
0.093	-125.1	0.583	52.9
0.182	-85.9	0.676	83.1
0.254	-59.8	0.785	114.5
0.319	-35.4	0.870	135.5
0.382	-12.7	0.960	141.6
0.433	5.7	1.039	142.5

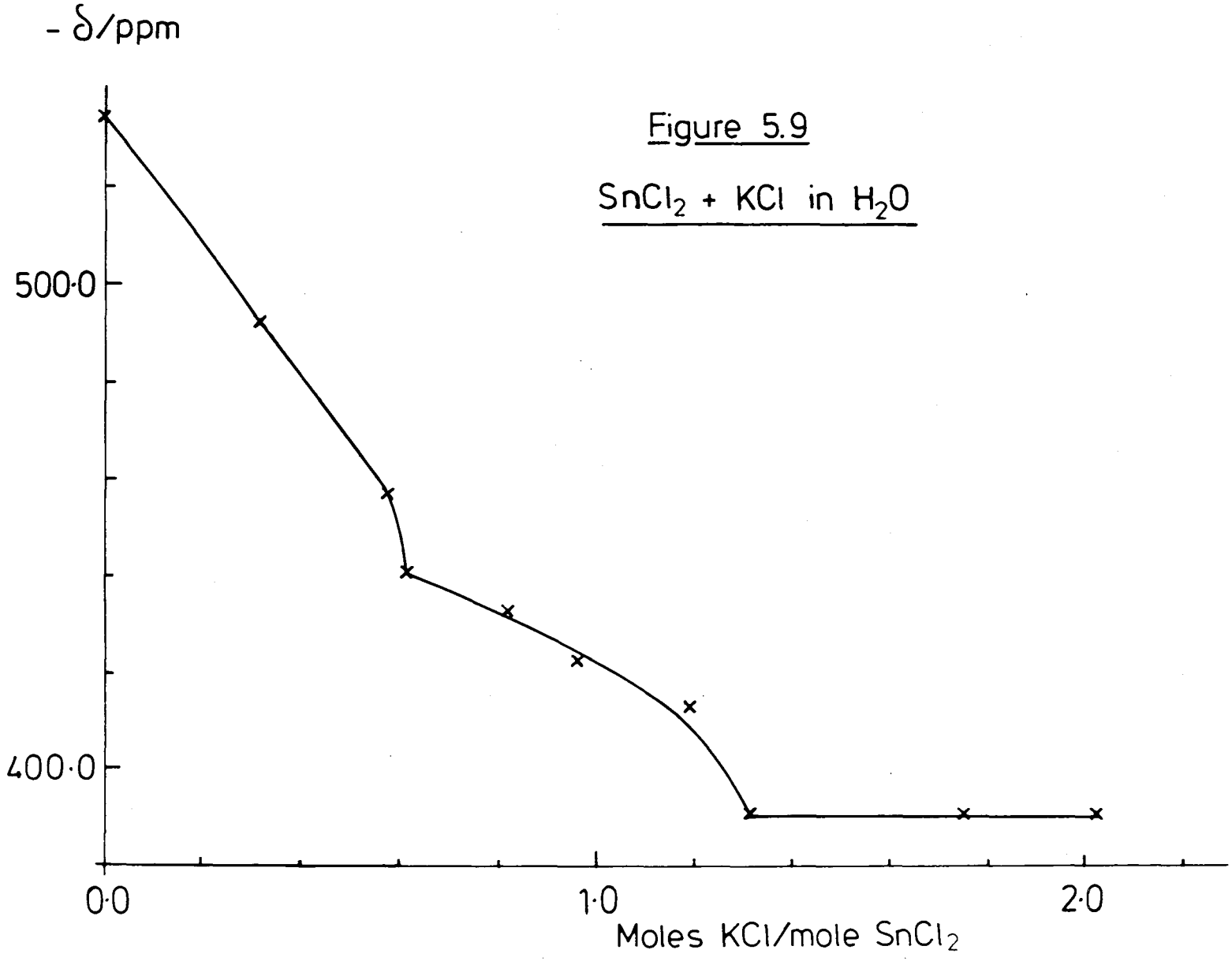


Figure 5.9

$SnCl_2$ + KCl in H_2O

and thus decreasing the shielding as mentioned in section 5(b)(ii). Alternatively the presence of an additional halide ion in the complex may draw electronic charge away from the tin nucleus, and so deshield it, since tin has a lower electronegativity than either chlorine or bromine (Pauling electronegativities:[145] Sn 1.7, Cl 3.0, Br 2.8).

The plot of δ for the $KCl/SnCl_2$ system shows three distinct regions. Up to the addition of 0.6 moles KCl/mole $SnCl_2$ δ increases linearly; from 0.6 to 1.3 moles KCl/mole $SnCl_2$ δ still increases but at a more gradual rate; and for higher proportions of KCl than 1.3, there is no change in δ regardless of the $KCl:SnCl_2$ ratio. Furthermore, as soon as a 1:1 ratio of $KCl:SnCl_2$ was reached large amounts of white precipitate began to be seen in the n.m.r. tubes. This white solid was presumed to be $KCl.KSnCl_3.H_2O$ since this compound has been isolated by precipitation from 1:1 mixtures of KCl and $SnCl_2$ in H_2O.[75]

The compounds $KSnCl_3$ and KSn_2Cl_5 have been isolated in the solid state[58] so it is probable that the anions $SnCl_3^-$ and $Sn_2Cl_5^-$ exist in solution. These anions may be formed by the following equilibria:

$$2SnCl_2 + Cl^- \rightleftharpoons Sn_2Cl_5^- \qquad \text{eq. 5.3.(a)}$$

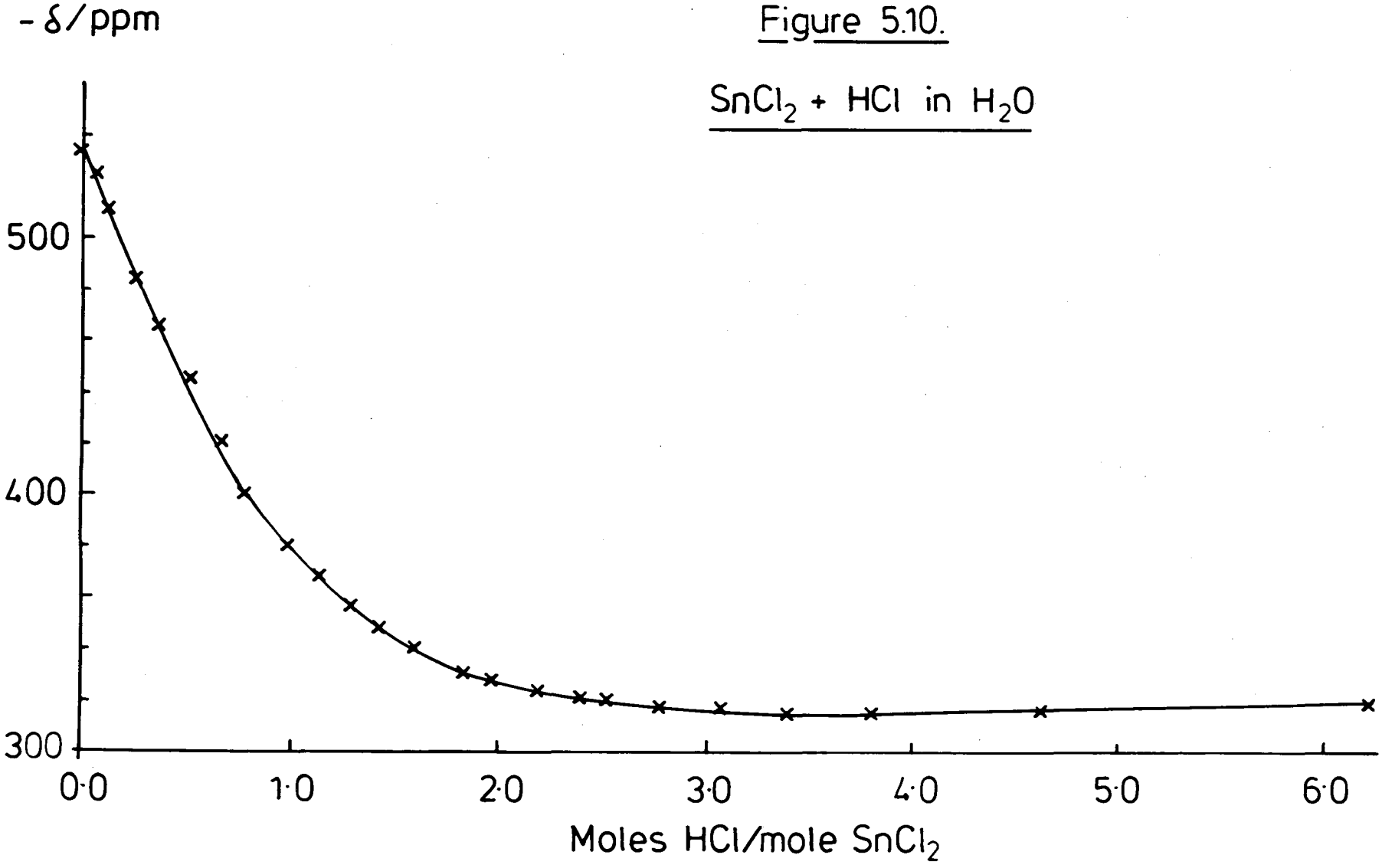
$$Sn_2Cl_5^- + Cl^- \rightleftharpoons 2SnCl_3^- \qquad \text{(b)}$$

$$SnCl_2 + Cl^- \rightleftharpoons SnCl_3^- \qquad \text{(c)}$$

The change in δ up to an added quantity of 0.6 moles KCl/mole $SnCl_2$ is probably due to a shift to the right of eq. 5.3.(a), which ought to be the dominant equilibrium occurring while an excess of $SnCl_2$ is present. As more KCl is added, eqs. 5.3.(b) and (c) become more important, and the quantity of $Sn_2Cl_5^-$ probably decreases. Eventually a point should be

Figure 5.10.

$SnCl_2$ + HCl in H_2O



reached where only $SnCl_3^-$ is present in solution, due to an excess of Cl^- ions pushing the equilibria to the right. This point is at a ratio of $KCl:SnCl_2$ of 1.3:1.0 and the shift of -390.7 ppm therefore corresponds to solvated $SnCl_3^-$. The precipitation of $KCl.KSnCl_3$ removes some of the KCl from solution so that more than a 1:1 ratio of $KCl:SnCl_2$ is needed before only $SnCl_3^-$ ions are present in solution and δ becomes independent of the quantity of added KCl.

The study of the addition of hydrochloric acid to $SnCl_2$ in water produced good agreement with Burke and Lauterbur,[83] who obtained a value of -341.2±5 ppm for $SnCl_2.2H_2O$ in 12N hydrochloric acid. This concentration corresponds to 1.624 moles HCl/mole $SnCl_2$ and represents a shift of -339 ppm from Figure 5.10. The plot for this system shows an almost smooth curve with δ increasing until there are 2 moles HCl/mole $SnCl_2$. After this point further addition of hydrochloric acid produces little change in δ. The shift of $SnCl_2$ in a fully complexed state in HCl solution is therefore about -320 ppm. This value is somewhat higher than that obtained from the $KCl/SnCl_2$ system and corresponds to a 2:1 ratio of $HCl:SnCl_2$ rather than the 1:1 ratio of $KCl:SnCl_2$. This difference is possibly due to formation of complexes akin to $KCl.KSnCl_3$ in HCl solution which are soluble, while $KCl.KSnCl_3$ is not. The formation of $SnCl_4^{2-}$ ions is another possibility, although previous reports of this ion have been shown to be erroneous.[65] The kinks in the plot between 0.0 and 1.0 moles HCl/mole $SnCl_2$ may be due to the type of equilibria shown in equations 5.3., but they are not very marked.

The addition of Pe_4NBr to $SnBr_2$ produced a steady increase in δ until about 0.9 moles Br^-/mole $SnBr_2$ had been added. After this point δ remained

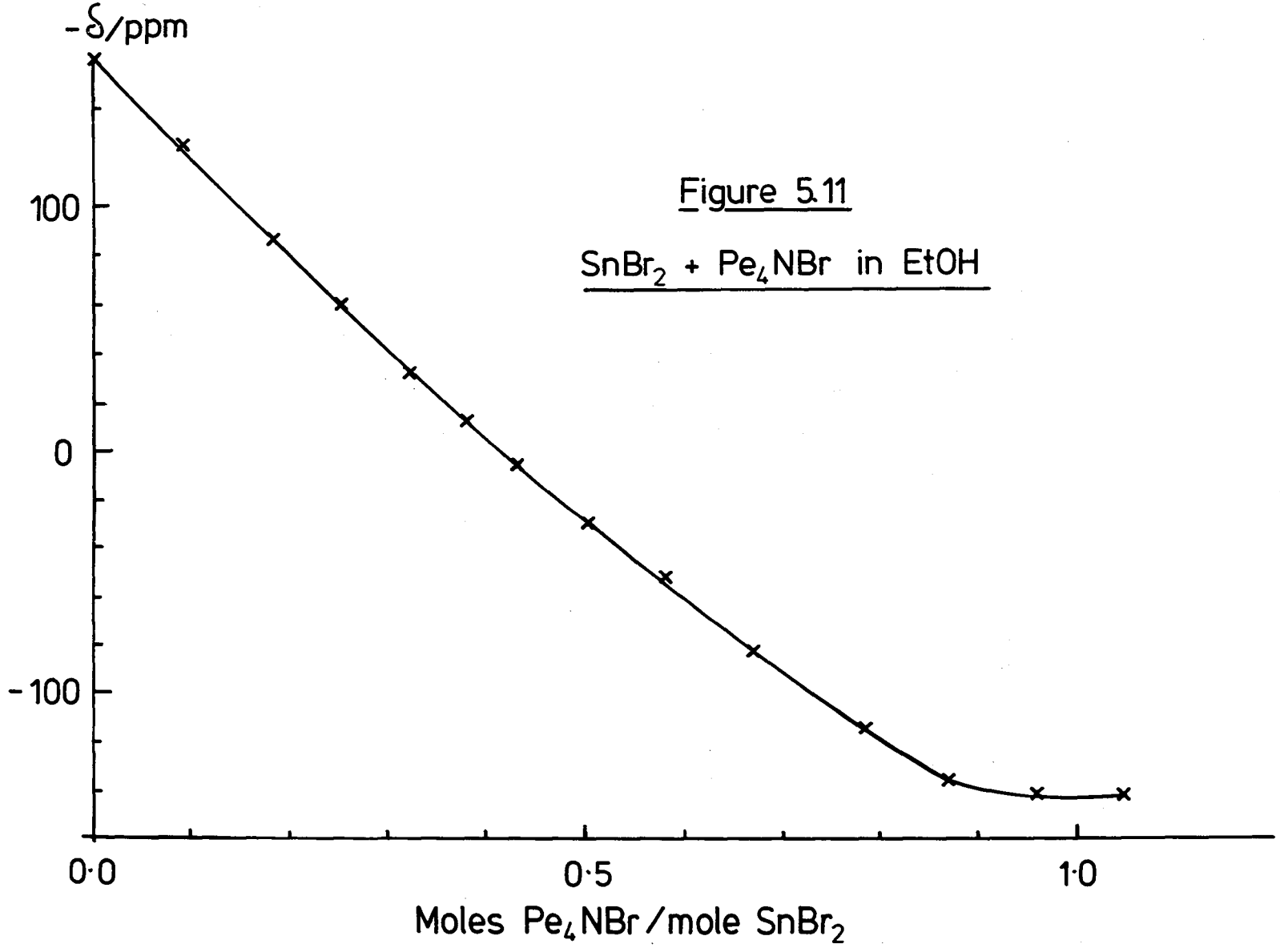


Figure 5.11

$SnBr_2$ + Pe_4NBr in EtOH

fairly constant at about 142 ppm. This shift is taken to represent that of fully complexed $SnBr_2$ by Br^- ions, which for this system corresponds to $SnBr_3^-$. No evidence of $Sn_2Br_5^-$ ions is afforded by the plot in Figure 5.11. despite the fact that compounds containing the $Sn_2Br_5^-$ ion have been isolated previously in the solid state (as KSn_2Br_5, $RbSn_2Br_5$ and $CsSn_2Br_5$).[58]

The shifts of $SnCl_2$ and $SnBr_2$ in CH_2Cl_2 with varying amounts of Pe_4NCl and Pe_4NBr, and in different concentrations, are shown in Tables 5.13. and 5.14. The tables reveal that both $SnCl_2$ and $SnBr_2$ dissolve in

Table 5.13.

The Variation of δ with the Addition of Pe_4NCl to $SnCl_2$ in CH_2Cl_2

Constituents	Relative ratios of constituents					
Pe_4NCl	1.31	0.75	1.04	1.04	1.04	1.04
$SnCl_2$	1.00	1.00	1.00	1.00	1.00	1.00
CH_2Cl_2	7.77	4.46	4.46	8.34	15.01	120.5
$-\delta/\pm 0.5$ ppm	23.6	36.3*	23.2	26.2	28.4	31.0

* Contains some undissolved $SnCl_2$.

Table 5.14.

The Variation of δ with the Addition of Pe_4NBr to $SnBr_2$ in CH_2Cl_2

Constituents	Relative ratios of constituents		
Pe_4NBr	0.62	1.13	2.30
$SnBr_2$	1.00	1.00	1.00
CH_2Cl_2	6.00	22.42	22.42
$\delta/\pm 0.5$ ppm	130.9*	139.5	135.4

* Contains some undissolved $SnBr_2$.

CH_2Cl_2 in the presence of halide ions to give observable ^{119}Sn n.m.r. signals, whereas SnX_2 compounds in CH_2Cl_2 give no signals by themselves (Table 5.1.). The ratios of $Cl^-:SnCl_2$ and $Br^-:SnBr_2$ required to dissolve all the stannous halide are 1:1; for lower halide ion ratios, undissolved $SnCl_2$ and $SnBr_2$ were seen in the n.m.r. tubes. The shifts of both $SnCl_2$ and $SnBr_2$ with the respective tetrapentylammonium halides are almost independent of concentration and virtually invariant under the influence of different quantities of halide ions. This concentration behaviour is expected since CH_2Cl_2 is a poorly co-ordinating solvent and should have little chemical influence on the species dissolved in it. The constant value of δ for different quantities of halide ions suggests that the tin is present as one complex only (i.e. SnX_3^- since a 1:1 ratio of $SnX_2:X^-$ was needed to dissolve all the SnX_2 present). CH_2Cl_2 does not seem to support the formation of $Sn_2X_5^-$ ions since if it did, all the stannous halide should be dissolved by the addition of 0.5 equivalents of tetrapentylammonium halide.

SnI_2 in excess concentrated hydroiodic acid gave a shift of -114.3 ppm, while SnF_2 with excess KF as a saturated solution in H_2O produced a shift of -701.4 ppm and $SnBr_2$ in excess concentrated hydrobromic acid produced value of -218.4 ppm. These figures together with a value of -320 ppm for $SnCl_2$ in concentrated hydrochloric acid place the shifts of SnX_2 fully co-ordinated by halide ions (X^-) in the order $SnI_n^{(n-2)-} > SnBr_n^{(n-2)-} > SnCl_n^{(n-2)-} > SnF_n^{(n-2)-}$; the most probable values of n are 3 or 4 (though values up to n = 8 have been reported for Me_4NI with SnI_2 [66]). These shifts are in the same order as those normally found for the free stannous halides in solution (see section 5(b)(i) and ref. 86).

SnF_2 gave a shift of -565.4 ppm with a one mole equivalent of

$But_4NF.27H_2O$ in CH_2Cl_2. This shift showed little change (-578.0 ppm) on doubling the fluoride concentration indicating that a 1:1 complex of SnF_2 and F^- forms in CH_2Cl_2 regardless of F^- concentration, (NB. for ratios of $F^-:SnF_2$ above 1:1 only). For SnF_2 with F^- both in water and in CH_2Cl_2 single peaks were seen. This suggests that rapid exchange occurs between the fluoride ions, which averages out any $^{119}Sn-^{19}F$ coupling so that no splitting of the ^{119}Sn n.m.r. signal is observed.

SnClF in water with excess KF gave a single resonance at -699.6 ppm while the same compound in an excess of concentrated hydrochloric acid yielded one signal only at -338.4 ppm. Both signals were fairly narrow (< 5 ppm). These results show that if mixed halogen species of the type $SnF_nCl^-_{3-n}$ (n = 1, 2) are formed in the solutions, then the exchange between them happens so fast on the n.m.r. time scale that the signals of each are averaged into one peak only. Further evidence of exchange is given by the absence of $^{119}Sn-^{19}F$ coupling. The signal at -699.6 ppm is virtually identical to the one obtained for SnF_2 with KF in water and indicates that the chloride ligands are completely displaced from the tin centres by the excess of fluoride ions. In an excess of chloride ions however, the shift obtained at -338.4 ppm is still somewhat lower than that for $SnCl_2$ in excess hydrochloric acid ($\sim$ -316 ppm) indicating that the fluoride present still contributes to this shift. Thus overall the Sn(II)-F bonds appear to be more stable than the Sn(II)-Cl ones. SnF_2 with one equivalent of Pe_4NBr in CH_2Cl_2 showed a very broad resonance ($\simeq$ 80 ppm wide) centred at -280 ppm with possible smaller peaks at -220 and -360 ppm. The small peaks were hard to discern due to a noisy spectrum (even after 34,000 scans). It would seem from these results therefore that exchange is occurring between the ions present in this system (probably of the type

$SnBr_{3-n}F_n^-$; n = 0 - 3) but that it is sufficiently slow to cause appreciable broadening of the peaks (cf. most resonances seen for the tin (II) species were no more than 5 ppm wide), and even to separate some of the resonances. One possible explanation for the slower exchange is the increased viscosity of the solution caused by the tetrapentylammonium cations: the solution needed to be made very concentrated to observe these weak resonances. Another possible explanation is that halide exchange may be discouraged in a solvent such as CH_2Cl_2 which has a low dielectric constant and should show little ionising ability.

Several fluoride containing samples were subjected to study by ^{19}F n.m.r., though little information of use to the present study was obtained. The spectra of SnF_2 + Pe_4NBr in CH_2Cl_2, SnF_2 in H_2O and SnF_2 + $But_4NF.32.8H_2O$ in CH_2Cl_2 each showed broad exchange peaks as their main features. Some evidence of a small amount of oxidation to form SnF_6^{2-} was also present in the form of smaller peaks with a splitting pattern characteristic of Sn-^{19}F spin coupling (there are numerous isotopes of tin: ^{117}Sn and ^{119}Sn have half-integral nuclear spins, while the majority of the others are non-active). Since these results offer complementary information to the ^{119}Sn n.m.r. data, no discussion of them is necessary.

(d) Reactions of Stannous Halides with Cyanides

This section describes some preliminary investigations of reactions of cyanides with stannous halides.

$SnCl_2$ in 4.47 equivalents of EtOH with 1.02 equivalents of $Zn(CN)_2$ gave a single resonance at -324.7 ppm which indicated that no reaction had occurred. Similarly, $SnBr_2$ in 9.89 equivalents of EtOH with 0.94 equivalents of $Zn(CN)_2$ gave one signal at -129.2 ppm which also suggested that no reaction had taken place. These figures did not change after several weeks. (These

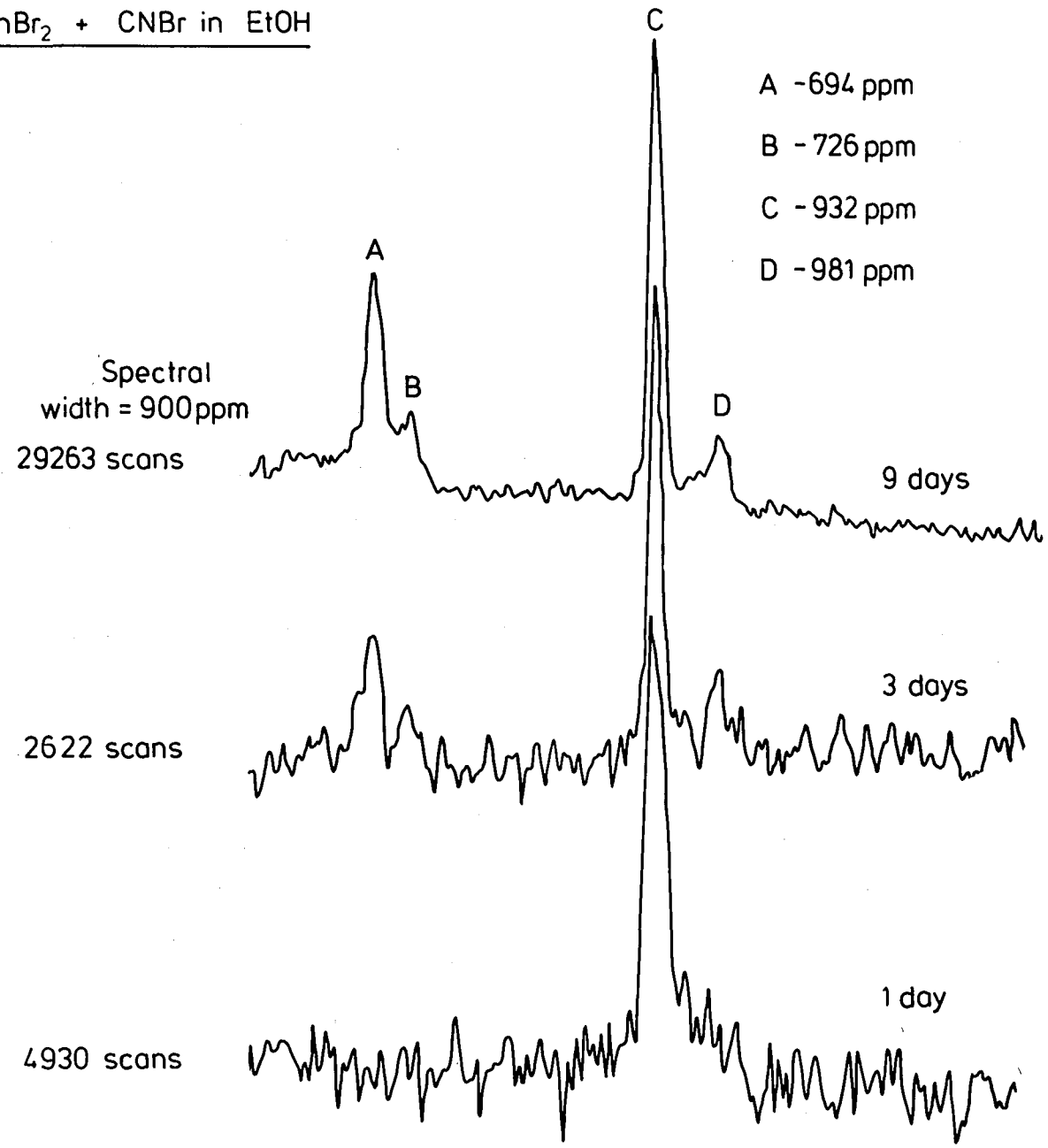
shifts were compared with those of the respective stannous halides in EtOH in Figures 5.3. and 5.4.). SnI_2 in 12.93 equivalents of EtOH with 0.84 equivalents of $Zn(CN)_2$ gave no signal initially, but after one week a single resonance at 317.1 ppm was seen. This shift is much higher than any for SnI_2 given by Yeh and Geanangel[86] and is thought therefore to represent a cyanide complex of tin (II) - possibly $Sn(CN)_2$ solvated by EtOH. $SnBr_2$ in 12.37 equivalents of EtOH with 1.88 moles of AgCN showed a steady increase in δ with time, changing from -123.1 ppm to 7.0 ppm after two months; a single resonance only was observed in each spectrum. Reaction to form cyanide complexes is again indicated, though a different product is present in this case. The increase in shift implies that the cyanides deshield the tin nuclei to a greater extent than the halogens, though the reason for this is not apparent.

$SnCl_2$ with one equivalent of But_4NCN in CH_2Cl_2 gave a broad resonance at -62.8 ppm while $SnBr_2$ with one equivalent of But_4NCN in CH_2Cl_2 yielded a broad resonance at 90.2 ppm. Both of these shifts are lower than those for the same stannous halides with their corresponding tetrapentylammonium halides (Tables 5.13. and 5.14.). This represents an increase in shielding by the CN ligands relative to Cl or Br for the anionic complexes most likely present in these solutions. A similar trend has been observed for the isoelectronic $PX_n(CN)_{3-n}$ (n = 0 - 3; X = I/Br/Cl) where decreasing n increases the shielding of the phosphorous.[154]

The oxidation of $SnCl_2$ using cyanogen chloride was attempted in the solvents, EtOH, CH_2Cl_2, and in ClCN *alone*. In each case, however, no reaction was indicated, and indeed only $SnCl_2$ with ClCN in EtOH gave any ^{119}Sn n.m.r. signals; one at -288 ppm for the unreacted $SnCl_2$. No change in these observations occurred after several weeks when the spectra were

Figure 5.12

$SnBr_2$ + CNBr in EtOH

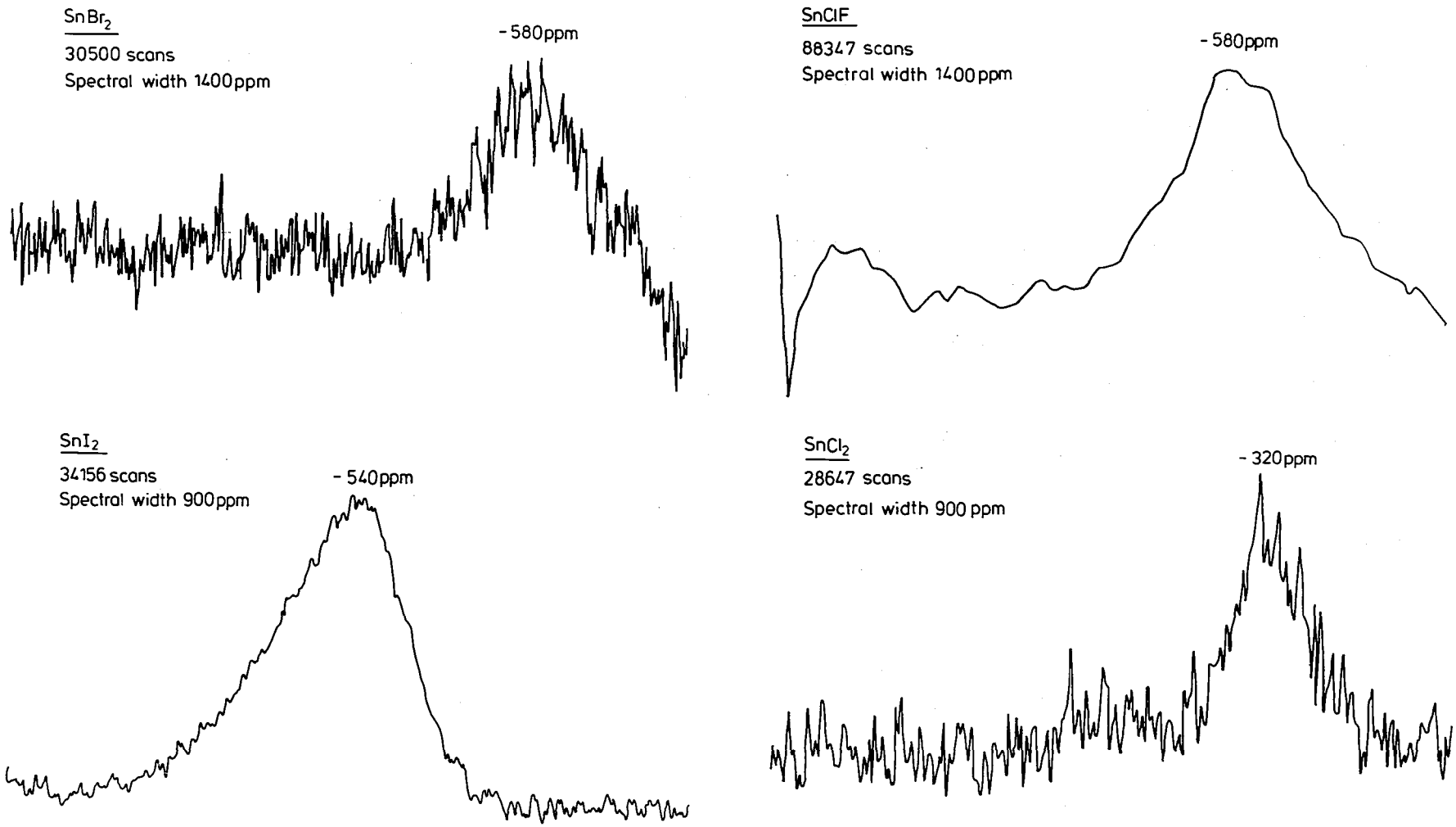


repeated.

$SnBr_2$ with BrCN in CH_2Cl_2 showed one signal at -641.3 ppm which corresponds to $SnBr_4$ in CH_2Cl_2, but no trace of signals due to cyanide-containing species could be found. The same reactants in CH_3CN gave no ^{119}Sn n.m.r. signals since a white, insoluble precipitate (presumably tin (IV) adducts with CH_3CN) was formed in the reaction. $SnBr_2$ with BrCN in EtOH proved more interesting. The spectra for this compound over a period of 9 days are shown in Figure 5.12. These show no indication of a peak at -1379 ppm corresponding to $SnBr_4$ in EtOH, or of peaks at lower field from $SnBr_2$ in EtOH. The resonances seen are therefore most probably due to cyanide-containing species of the type $SnBr_3CN$ and $SnBr_2(CN)_2$. The spectrum after one day shows one signal only at -932 ppm and this may well be the product of a simple addition reaction between $SnBr_2$ and BrCN to produce $SnBr_3CN$. The growing resonances A and B would then be produced by inter-molecular exchange possibly involving any unreacted BrCN to give $SnBr_2(CN)_2$. The observation of two resonances assigned to each species can be rationalised since 2 moles of EtOH probably co-ordinate to the tin to give it an octahedral configuration of ligands. If the two EtOH molecules co-ordinate in a cis-fashion (as they do for solid $SnCl_4.2EtOH$, the structure of which has been found by ^{35}Cl n.q.r.[65]) then there would be two possible isomers for $SnBr_3(CN).2EtOH$ (corresponding to C and D) and three possible isomers for $SnBr_2(CN)_2.2EtOH$ (corresponding to A and B). If the EtOH molecules co-ordinate in a trans-fashion, however, there would be one fewer isomer for each complex. It is therefore possible for each species to give more than one n.m.r. resonance due to different isomers, though any assignment must remain speculative until further work has been done in this area.

Figure 5.13

Solid State ^{119}Sn n.m.r. Spectra of Stannous Halides



(e) Solid State ^{119}Sn N.m.r. Spectra of Stannous Halides

The spectra obtained from solid, powdered samples of SnClF, $SnCl_2$, $SnBr_2$ and SnI_2 are shown in Figure 5.13. As can be seen from the figure each of the samples gave very broad n.m.r. resonances. The extreme example, obtained for SnF_2, appears to be a very broad shallow signal at about -870 ppm but this spectrum is not shown as it is not sufficiently conclusive. The estimated shifts from the broad resonances in Figure 5.13. are for SnClF -580 ppm, for $SnCl_2$ -320 ppm, for $SnBr_2$ -580 ppm and for SnI_2 -540 ppm. These values are all visual estimates of the centres of each broad band and must necessarily be subject to fairly large error bounds, possibly up to $\pm$50 ppm for the broadest lines, especially since manipulation of the phase correction facility of the spectrometer to obtain a good baseline could sometimes alter the position of the peaks. In view of these errors, discussion of the shifts must be guarded. The only point made here is that the δ values for solid stannous halides in the order of $SnCl_2 > SnI_2 > SnBr_2 \simeq SnClF (> SnF_2)$ do not follow the same pattern as the δ values for these compounds in solution.

(f) Experimental

The quantities of reactants and solvents used for the experiments in this chapter were determined by weighing on a balance, to an accuracy of $\pm$ 0.0005 g. Cyanogen chloride was the exception to this and its quantity was determined from the volume used as measured by a graduated cold finger on the vacuum line.

Owing to the sensitivity of stannous compounds to atmospheric oxidation every attempt was made to exclude oxygen from the n.m.r. tubes. The tubes were purged with nitrogen and charged with solids in the glove box. Solvents undesirable in the glove box (virtually any good co-ordinating

solvent e.g. H_2O, MeOH, EtOH, acetone, CH_3CN) were added in the laboratory atmosphere from nitrogen-filled vessels while blowing a stream of nitrogen over the end of the open n.m.r. tube. The solvents were first degassed. Sealed tube reactions were used when cyanogen chloride was employed. These tubes were purged simply by applying a vacuum and then letting them down to atmospheric pressure with nitrogen before sealing.

For the systems in which temperature sensitivity was noticed, the n.m.r. tubes were placed in the probe of the magnet and allowed to warm up with the spectrometer operating, or partially preheated by a hair dryer or by using a special chamber provided for the purpose situated next to the n.m.r. magnet. The spectrometer was then set up so as to run for 50 scans, take the power spectrum, measure the largest resonance produced and restart itself in a continuous cycle. Thermal equilibrium was then adjudged to have been reached when 3 such successive measurements of a shift gave the same value. Typically there would be only 0.37 ppm between the channels in the spectral display so 3 successive, identical readings were considered a sufficient condition. The spectra were then run manually to see if more than one peak was occurring for any particular system.

Several variations of spectrometer settings were tried in an effort to obtain better solid state spectra. Delay times of 0.5, 2.0, 5.0 and 10.0 secs. were used, together with varying pulse lengths from 10 to 25μ secs. No substantial improvement on the quality of the spectra obtained was noted for any combination of settings.

Cyanide wastes were destroyed by reaction with hypochlorite solution.

CHAPTER 6

^{119}Sn N.m.r. Studies of Some Inorganic Tin (IV) Compounds

(a) Introduction

The literature[81,83-85] contains several reports of measurements of ^{119}Sn n.m.r. shifts of tin (IV) halides in solution. $SnCl_4$ is reported to give shifts of -147.8[85] or -150 ppm as a neat liquid, or -673 ppm in water.[84] Various shifts between -631 and -967 ppm were also observed for $SnCl_4$ in solutions of acetone and water when the ratio of the two solvents was varied.[84] $SnBr_4$ as a neat liquid gave shifts of -638[83] or -640[84] ppm, while in H_2O a value for δ of -1210 ppm was recorded.[84] In CS_2 solution, tin (IV) bromide has given[83,85] δ values between -629 and -635 ppm. SnI_4 in CS_2 has exhibited various shifts between -1698 and -1712 ppm.[83,85] Furthermore various mixed tin (IV) tetrahalides of the type $SnCl_xBr_yI_z$ ($x + y + z = 4$) have been identified in solution by ^{119}Sn n.m.r.; all fifteen isomers and their ^{119}Sn n.m.r. shifts were quoted.[83]

Six-coordinate tin (IV) compounds studied via ^{119}Sn n.m.r. include $Na_2Sn(OH)_6$ in H_2O (δ -592 ppm) and $K_2Sn(OH)_6$ in H_2O (δ -590 ppm).[83] A shift of -888 ppm has also been obtained for SnF_6^{2-} in H_2O[82] while $SnCl_6^{2-}$ in 25-oleum and 100% H_2SO_4 gives δ values of -725.5 ppm and -740.9 ppm respectively.[121] A large number of six co-ordinate inorganic tin (IV) fluoro-complexes has also been studied by means of ^{19}F n.m.r. in which the ^{19}F chemical shifts and ^{19}F-^{119}Sn coupling constants for many of the compounds have been given.[146] This study identified various mixed halostannates (IV) containing Cl, Br, F and I, as well as their solvolysis products, dissolved in H_2O, MeOH, and $CHCl_3$; several complexes containing N_3^-, NCO^- and F^- ligands were also observed.[146]

(b) Prediction of Chemical Shifts Using the Pairwise Interaction Model[147]

The theory of pairwise interactions for the prediction of n.m.r. chemical shifts was introduced in 1967 by Vladimiroff and Malinowski[147] in the discussion of ^{13}C chemical shifts. This model has been extended by other workers for use with various complexes and successfully predicts the chemical shifts in various niobium,[148,150] antimony,[149] boron and phosphorous systems.[157-160] In this method, the shifts are calculated for metal complexes by summing all the contributions from adjacent pairs of ligands around the central metal. Thus an octahedral complex has 12 such pairs, while a tetrahedral complex would only have 6. Each pair of ligands provides a definite contribution to the overall chemical shift of the complex, and the sum of all of the pairs gives this value. Vladimiroff and Malinowski[147] state that the chemical shifts of the nuclei are pairwise additive when Fermi contact interactions do not dominate.

The pairwise model is used to aid the assignment of chemical shifts in this chapter. Some of the work was unfortunately duplicated by a very recent publication[151] while writing of this thesis was taking place. This work was the study of stannic halide exchange products, $SnCl_xBr_yI_z$ ($x + y + z = 4$) in CS_2, and hexachlorobromostannates, $SnCl_nBr_{6-n}^{2-}$ ($n = 0 - 6$) in CH_2Cl_2. The literature values[151] of the shifts of these compounds were in good agreement with the pairwise theory, although the actual figures differed marginally from those obtained in this thesis due to a measurement temperature of 243K for the former. The lower temperature was reported to narrow the observed lines.

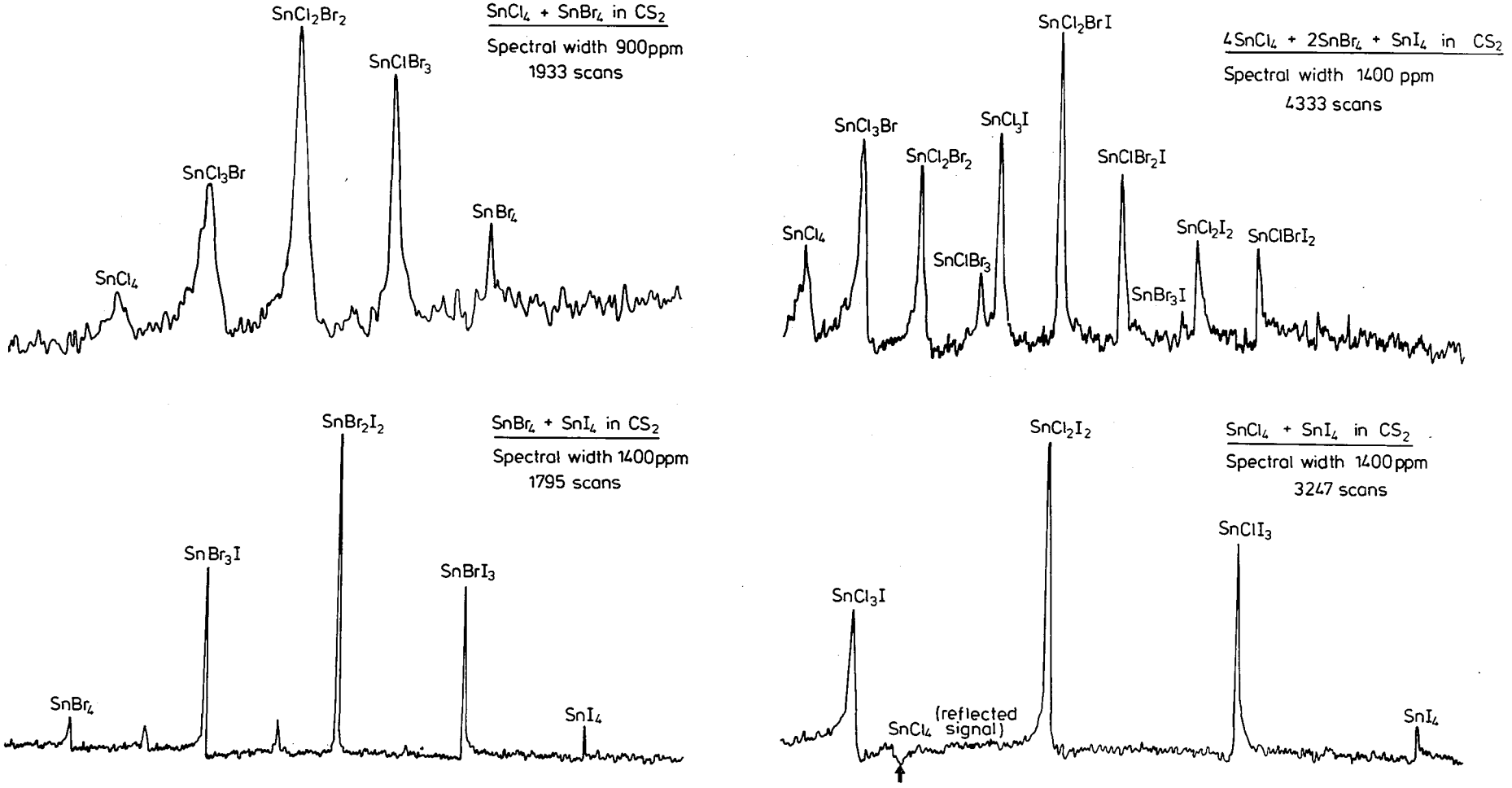
(c) Stannic Halides

(i) Exchange Between $SnCl_4$, $SnBr_4$ and SnI_4 in CS_2

The reaction between these stannic halides was studied to test the applicability of the pairwise interactions theory to them, and to confirm

Figure 6.1

Sample ^{119}Sn n.m.r. Spectra



the early δ values[83] obtained on more primitive equipment. CS_2 was used as the solvent since although the $SnCl_4/SnBr_4$ and $SnCl_4/SnI_4$ systems can be studied in neat mixtures, the $SnBr_4/SnI_4$ system is solid on its own, and CS_2 is a good solvent for SnI_4 (and $SnBr_4$). CS_2 is a fairly weak co-ordinator, and little difference between the chemical shifts from spectra obtained with or without it was seen for the $SnCl_4/SnBr_4$ or $SnCl_4/SnI_4$ systems.

Sample spectra of the various systems are shown in Figure 6.1. and the chemical shifts, together with their assignments are shown in Table 6.1. The table also shows the shifts calculated for all the $SnCl_xBr_yI_z$ $(x + y + z)$ isomers from a pairwise treatment. In calculating these figures the contributions from pairs of identical halides (i.e. the Cl:Cl, Br:Br and I:I terms) were obtained from the chemical shifts of the appropriate pure stannic halides [e.g. Cl:Cl = $^1/_6$ (δ for $SnCl_4$)] as the mean of several measurements obtained from the various systems. This method leads to some error since slight but consistent differences for δ were noted for SnI_4 with $SnBr_4$ or $SnCl_4$, the shift with $SnBr_4$ occurring at ca. -1706 ppm while with $SnCl_4$ the average value was about -1698 ppm. Also the shift of $SnCl_4$ in the presence of SnI_4 was around -148 ppm, whereas with $SnBr_4$ a value of approximately -152 ppm was found. The shift of $SnBr_4$, however, remained roughly constant. These slight differences are probably indicative of minor interactions between the various species in solution. The mixed halide terms (i.e. Cl:Br, Cl:I and I:Br) were obtained as the mean of three figures calculated from each of the SnX_nY_{4-n} (X, Y = Cl/Br/I; n = 1, 2, 3) species after these were assigned to the observed peaks on the assumption that the contributions to the shifts increase in the order Cl > Br > I. The values calculated for $SnCl_2BrI$, $SnClBr_2I$ and $SnClBrI_2$ were then obtained using these parameters.

Table 6.1.

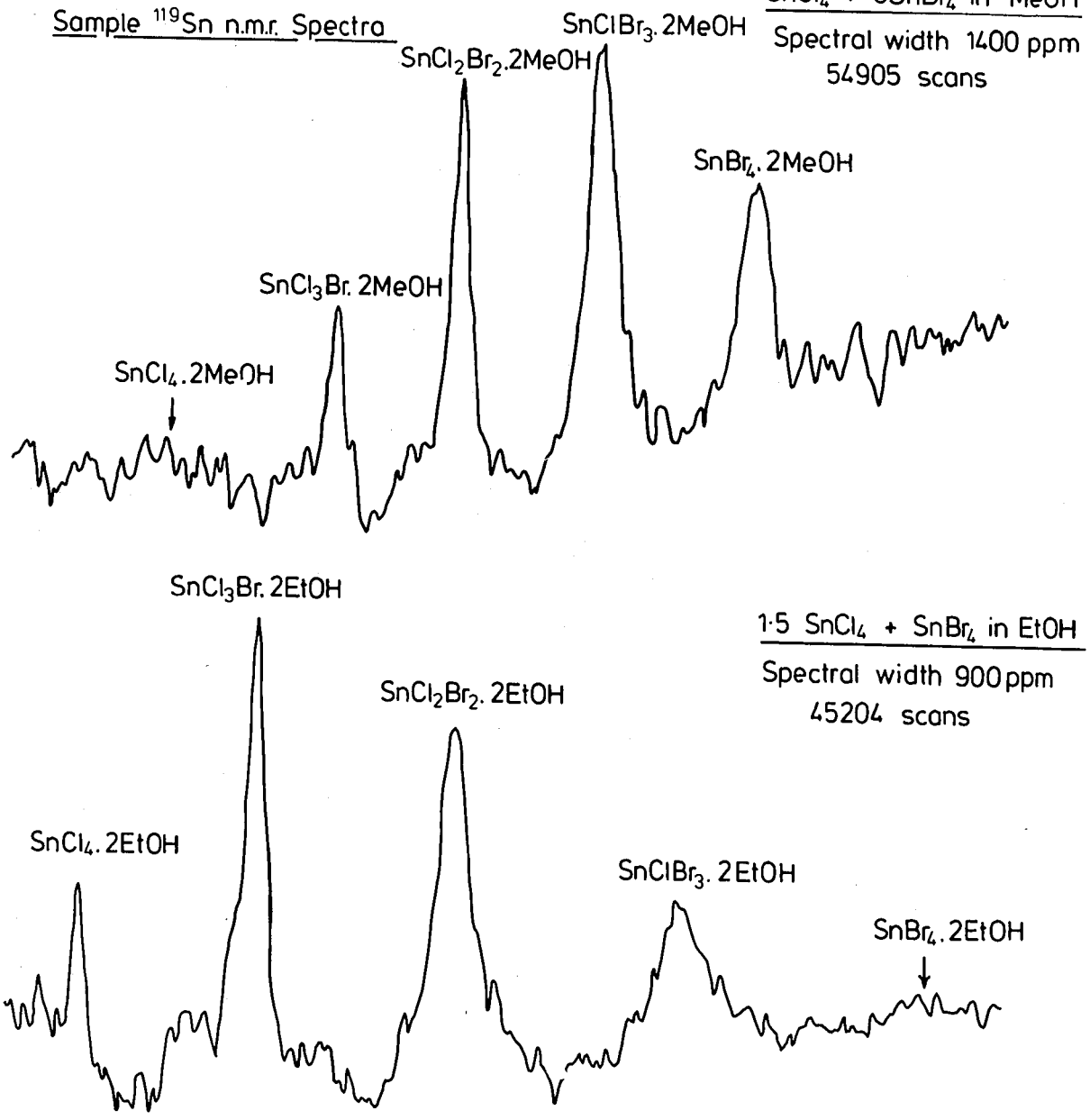
The ^{119}Sn Chemical Shifts of the Mixed Stannic Halides in CS_2

Compound	$-\delta/\pm 2$ ppm (observed)	$-\delta$ calculated from pairwise interactions[a]
$SnCl_4$	149.9	6Cl:Cl = 149.9
$SnCl_3Br$	267.3	3Cl:Cl + 3Cl:Br = 267.0
$SnCl_2Br_2$	387.3	Cl:Cl + 44Cl:Br + Br:Br = 387.2
$SnCl_3Br$	510.1	3Cl:Br + 3Br:Br = 510.5
$SnCl_3I$	549.6	3Cl:Cl + 3Cl:I = 554.0
$SnBr_4$	636.7	6Br:Br = 636.7
$SnCl_2BrI$	672.4	Cl:Cl + 2Cl:Br + 2Cl:I + Br:I = 671.3
$SnClBr_2I$	796.5	Br:Br + 2Cl:Br + Cl:I + 2Br:I = 791.6
$SnBr_3I$	915.1	3Br:Br + 3Br:I = 914.9
$SnCl_2I_2$	947.9	Cl:Cl + 4Cl:I + I:I = 947.6
$SnClBrI_2$	1073.3	I:I + Cl:Br + 2Cl:I + 2Br:I = 1065.0
$SnBr_2I_2$	1186.6	Br:Br + 4Br:I + I:I = 1185.4
$SnClI_3$	1335.0	3Cl:I + 3I:I = 1330.7
$SnBrI_3$	1447.0	3Br:I + 3I:I = 1448.1
SnI_4	1703.2	6I:I = 1703.2

(a) Parameters used in the calculations: Cl:Cl = -24.98, Cl:Br = -64.03, Br:Br = -106.12, Cl:I = -159.70, Br:I = -198.84, I:I = -283.87 ppm.

The results show a fairly good agreement between the experimentally determined and the calculated values. A better fit might be obtained using a rigorous statistical treatment. Furthermore on varying the relative proportions of the stannic halides it was found that the distributions of the mixed halide compounds in solution changed according to purely

Figure 6.2.
Sample ^{119}Sn n.m.r. Spectra



statistical preference. It appears, therefore, that there is little difference in the stabilities of the Sn-X bonds (X = Cl, Br, I) towards exchange in this system.

It was noticed that for $SnCl_nBr_{4-n}$ (n = 0 - 4) the linewidths of the various compounds decreased as n decreased. This is perhaps attributable to the greater quadrupole moment of Cl compared with Br nuclei, hence causing more quadrupolar broadening of the lines when more Cl is present. Another possibility is that the Cl^- ions exchange more rapidly than Br^-, so that the peaks with more Cl suffer more exchange broadening.

(ii) Exchange Between $SnCl_4$ and $SnBr_4$ in Methanol or Ethanol

Sample spectra of mixtures of $SnCl_4$ and $SnBr_4$ in methanol or ethanol are shown in Figure 6.2. As can be seen, each gives a number of broad peaks, and by varying the ratio of $SnCl_4$:$SnBr_4$ it was possible to observe 5 peaks for each system. This at first sight is the expected number of resonances for an $SnCl_nBr_{4-n}$ (n = 0 - 4) system as found in the previous section. MeOH and EtOH are good co-ordinating solvents, however, and both $SnCl_4$ and $SnBr_4$ are good acceptors capable of bonding to obtain six-coordination. Evidence for this co-ordination is given from the ^{119}Sn n.m.r. spectra by the shift of the peaks to higher field than for $SnCl_4$/$SnBr_4$ in CS_2. Similar movement of Sn IV n.m.r. shifts to higher field on co-ordination has been observed for acetone, dimethylsulphoxide and pyridine.[81] The system containing compounds of the type $SnCl_nBr_{4-n}.2S$ (n = 0 - 4; S = MeOH or EtOH) is considerably more complicated. There are 6 species possible if the solvent molecules co-ordinate in a trans-fashion while 9 species are possible if these co-ordinate in a cis-configuration. Table 6.2. shows the species possible and assigns the chemical shifts of the broad peaks to groups of isomers on the assumption that the difference in

Table 6.2.

Exchange Products from $SnCl_4$ and $SnBr_4$ in MeOH or EtOH

Empirical Formula	$-\delta/\pm$ ppm (observed)		Isomers	Pairwise interaction terms					
	S = MeOH	S = EtOH		S:S	Cl:Cl	Br:Br	Cl:Br	S:Cl	S:Br
$SnCl_4.2S$	604.8	614.9	cis S	1	5			6	
			trans-S		4			8	
$SnCl_3Br.2S$	759.5	775.6	cis-S: Br cis to S	1	3		2	4	2
			cis-S: Br trans to S	1	2		3	5	1
			trans-S		2		2	6	2
$SnCl_2Br_2.2S$	927.1	953.6	cis-S: 2Br cis to S	1	1		4	2	4
			cis-S: Br cis & trans to S	1	1	1	3	3	3
			cis-S: 2Br trans to S	1		1	4	4	2
			trans-S: cis Br		1	1	2	4	4
			trans-S: trans Br				4	4	4
$SnClBr_3.2S$	1125.5	1160.6	cis-S: Cl cis to S	1		3	2	2	4
			cis-S: Cl trans to S	1		2	3	1	5
			trans-S			2	2	2	6
$SnBr_4.2S$	1343.4	1378.7	cis-S	1		5			6
			trans-S			4			8

δ ought to be less between isomers than between different molecular species.

The broad linewidths of the resonances seen in Figure 6.2. means that if each peak contains more than one signal, then they are not resolved. This situation makes application of pairwise theory difficult. The adducts $SnCl_4.2S$ (S = MeOH, EtOH) have been studied by ^{35}Cl n.q.r.[152] and have been shown to have a cis-configuration of the solvent molecules in the solid state. The high dipole moment of solid $SnCl_4.2MeOH$ has also been attributed to a cis-configuration of MeOH molecules.[65] It might seem reasonable, therefore, to assume that the cis-configuration would be prevalent in solution. The mixed chlorobromostannates, $SnCl_{6-n}Br_n^{2-}$ (n = 2, 4), however, were reported to show a cis-configuration only in the solid state,[50] whereas in solution both cis- and trans-isomers are present (see section 6(d)(i)). Nevertheless it is likely that there would be more stannic halides cis- than trans-co-ordinated by the solvents, so the maxima of the peaks in the n.m.r. spectra are likely to correspond to the cis-species. On statistical grounds, $SnCl_3Br.2S$ and $SnClBr_3.2S$ with cis-S should each have two isomers of equal abundance, while $SnCl_2Br_2.2S$ should have three isomers of relative intensities 1:4:1 for the cis-S species; the particular isomer of relative intensity 4 is the one which has one Br only trans- to an S molecule. A statistical distribution is probably followed since the relative intensities of the peaks appeared (from a visual estimate) to vary freely according to the relative quantities of $SnCl_4$ or $SnBr_4$ added, without bias towards either stannic halide. The peaks measured in Table 6.2. therefore probably correspond to averages of the two cis-S isomers for each of $SnCl_3Br.2S$ and $SnClBr_3.2S$, $SnCl_4.2S$, $SnBr_4.2S$ and $SnCl_2Br_2.2S$ (only one Br trans- to S), each with the solvent molecules cis- to each other.

Using the above assignments, however, it still proved impossible to solve the equations obtained from the pairwise terms, thus making theoretical predictions of the shifts unobtainable. An attempt was made to utilise the Cl:Cl, Cl:Br and Br:Br terms obtained from the $SnCl_4/SnBr_4$ system in CS_2. These terms were corrected to account for the difference in tetrahedral and octahedral co-ordination (via the estimated change in the inter-halogen distances) according to the method of Colton et al.[151] With these assumptions, however, the equations proved insoluble, if not contradictory, so they were used no further. More information was therefore found to be required before the full nature of the MeOH and EtOH solutions of $SnBr_4$ and $SnCl_4$ can be elucidated.

The observation of chemical shifts to higher field for the EtOH adducts than for the MeOH ones is consistent with the greater inductive effect of the ethyl group. This means more electronic charge would be released onto the O atom co-ordinated to the tin for EtOH than MeOH and enable EtOH to donate slightly more charge to the Sn atom in its bonding than MeOH. The extra electron density around the tin nucleus would then increase the shielding of the nucleus and move its observed chemical shift to higher field.

(iii) Aqueous Studies of $SnCl_4$

The effect of chloride ion concentration on the ^{119}Sn n.m.r. of $SnCl_4$ in water was studied from two approaches, producing somewhat different results. Firstly a solution of $SnCl_4.5H_2O$ in excess cHCl was prepared and its shift monitored after successive additions of $SnCl_4.5H_2O$, thus effectively decreasing the chloride ion concentration. This system showed one signal only in each spectrum and its results are given in Table 6.3. The table reveals a steady increase in shift as more chloride is added until sufficient is present to give a constant shift at about -711 ppm,

corresponding presumably to the $SnCl_6^{2-}$ ion. The results are consistent with equilibria occurring of the type:

$$SnCl_4\ (aq) + Cl^-\ (aq) \rightleftharpoons SnCl_5^-\ (aq) \qquad \text{eq. 6.1.(a)}$$

$$SnCl_5^-\ (aq) + Cl^-\ (aq) \rightleftharpoons SnCl_6^{2-}\ (aq) \qquad \text{(b)}$$

Table 6.3.

Addition of $SnCl_4.5H_2O$ to $SnCl_4.5H_2O$ in Concentrated Hydrochloric Acid

Relative molar ratios			$-\delta/\pm 2$ ppm
Cl^-	$SnCl_4$	H_2O	
7.40	1.00	31.1	711.4
3.71	1.00	18.1	711.4
2.14	1.00	12.6	704.4
1.33	1.00	9.7	693.9
1.05	1.00	8.7	683.4
0.66	1.00	7.4	665.9

A steady broadening of the observed resonances was noticed as the $Cl^-:SnCl_4$ ratio decreased which indicates that at lower Cl^- concentrations, either a slower exchange between the species present is taking place, or there are more species involved in the exchange.

The second method of study involved successive additions of cHCl to a solution of $SnCl_4.5H_2O$ in H_2O. The spectra obtained at comparable $Cl^-:SnCl_4$ ratios showed extra peaks relative to their counterparts from the first method of study. Sample spectra of this system are shown in Figure 6.3(a) and the results are tabulated in Table 6.4. The table and the spectra show that there are essentially four peaks in each spectrum, and that the relative

Fig. 6.3a

Addition of Concentrated Hydrochloric Acid to $SnCl_4 . 5H_2O$ in H_2O

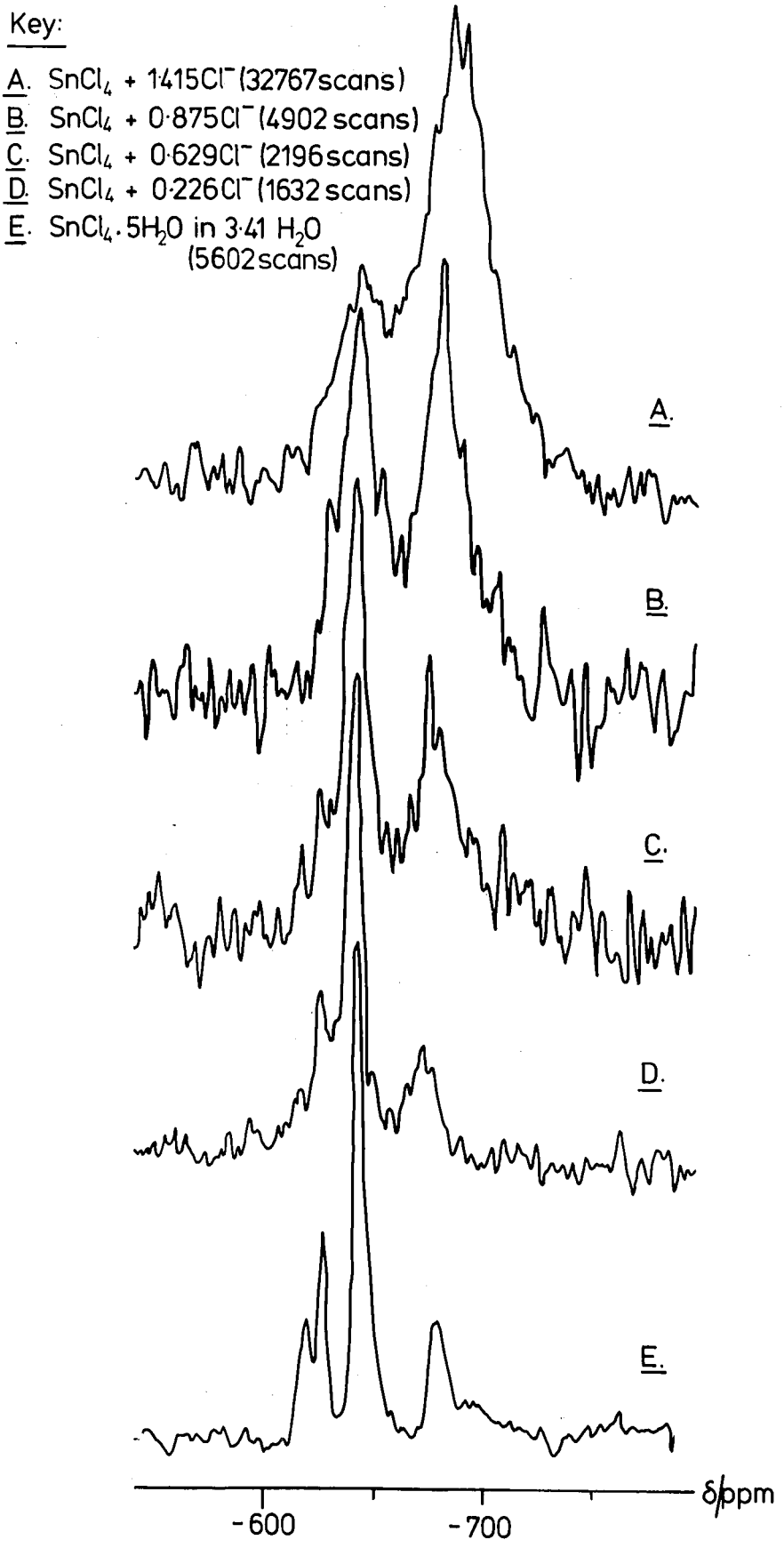


Table 6.4.

Addition of Concentrated Hydrochloric Acid to $SnCl_4.5H_2O$ in H_2O

Relative molar ratios			-δ/±1 ppm, with relative signal heights in brackets			
Cl^-	$SnCl_4$	H_2O				
0	1.00	8.41	622.2 (0.24)	629.2 (0.42)	644.9 (1.0)	676.3 (0.24)
0.126	1.00	8.83	620.4 (0.08)	629.2 (0.31)	643.1 (1.0)	674.6 (0.13)
0.226	1.00	9.21	622.8 (0.05)	630.6 (0.27)	644.6 (1.0)	673.4 (0.15)
0.437	1.00	9.94		631.2 (0.14)	644.3 (1.0)	675.7 (0.24)
0.629	1.00	10.63	619.8 (0.14)	626.9 (0.24)	643.5 (1.0)	674.0 (0.52)
0.875	1.00	11.51			642.6 (0.82)	677.5 (1.0)
1.415	1.00	13.41			644.3 (0.36)	683.6 (1.0)

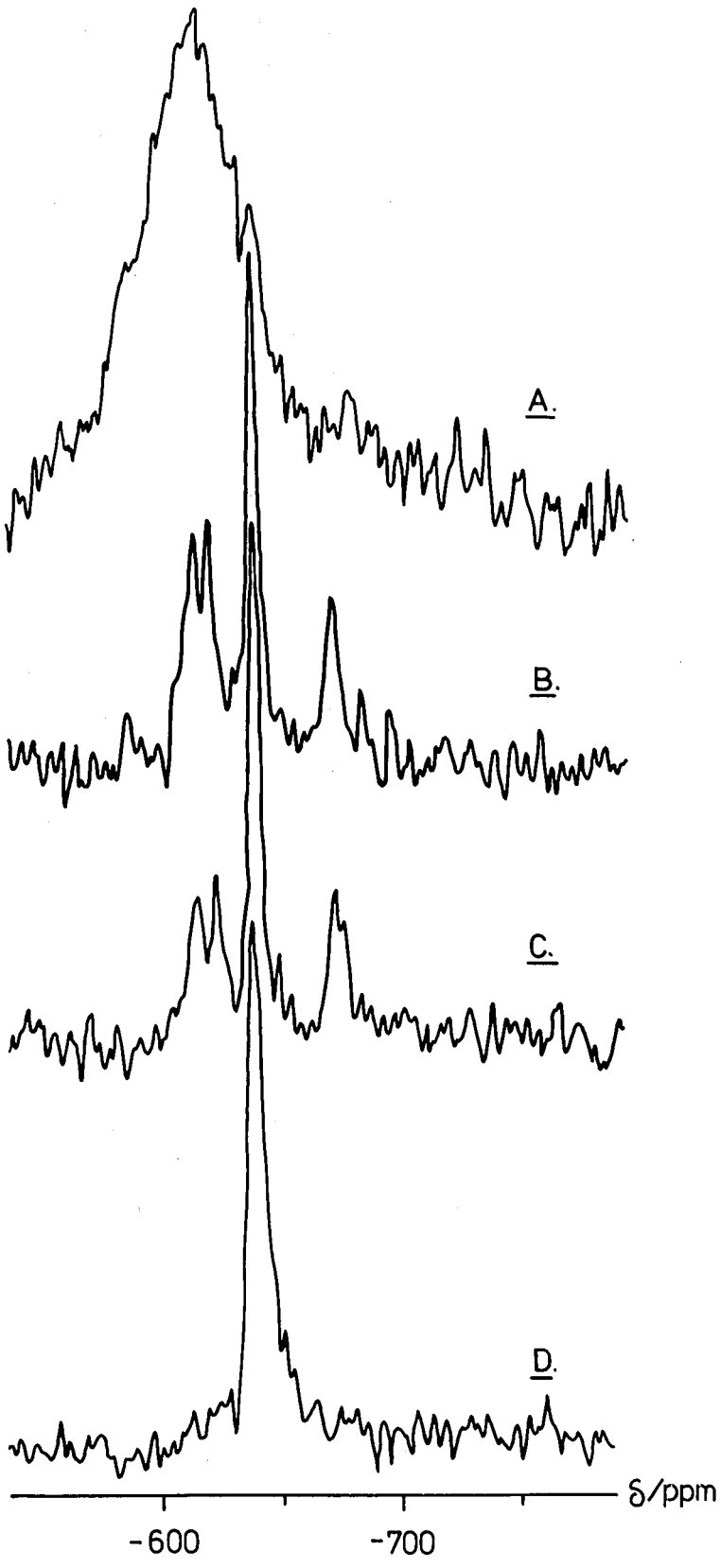
intensities of each peak change as HCl is added. The peak at about -644 ppm is attributed to $SnCl_4.2H_2O$ since a shift of -644.3 ppm (only) was obtained for a melt of $SnCl_4.5H_2O$, and the crystal structure of $SnCl_4.5H_2O$ has been shown to be made up of octahedrally co-ordinated $SnCl_4.2H_2O$ complexes.[153] The H_2O molecules in $SnCl_4.2H_2O$ co-ordinate in a cis-fashion.[153] The growth of the broad peak between -673 and -683 ppm is accompanied by a decrease in the peak assigned to $SnCl_4.2H_2O$. This is consistent with a shift in the equilibria shown in eq. 6.1. to species such as $SnCl_5^-.H_2O$ and $SnCl_6^{2-}$ at higher field. The extra electronic charge present in the anionic complexes probably creates a greater screening effect around the Sn nucleus than occurs for the neutral species. The large, broad peak which dominates the spectra for $Cl^-:SnCl_4$ ratios of more than 0.875 is probably therefore the same exchange peak observed in the $SnCl_4.5H_2O$ in cHCl system as studied in the first instance. The two peaks around -621 and -630 ppm are assigned to OH^--containing complexes since both these peaks increased progressively as

Fig. 6.3b

Addition of Aqueous KOH to a melt of $SnCl_4.5H_2O$

Key.

A. $SnCl_4$ + 3·0 KOH (8585 scans)
B. $SnCl_4$ + 1·0 KOH (1764 scans)
C. $SnCl_4$ + 0·5 KOH (674 scans)
D. Melted $SnCl_4.5H_2O$ (372 scans)



aqueous KOH solution was added to a melt of $SnCl_4.5H_2O$ (Figure 6.3(b)). One (or perhaps both) of these peaks is possibly due to species of the type $[Sn_2Cl_6(OH)_2(OH_2)_2]$ which has been isolated, as a solid tetrahydrate, from a commercial sample of $SnCl_4.5H_2O$, and identified by x-ray diffraction.[153] This complex contains octahedrally co-ordinated tin atoms in a dimeric structure containing hydroxy-bridges.[153] Alternatively, monomeric species such as $SnCl_3(OH).2H_2O$ might be present, although this must remain as speculation.

The four peak spectrum of $SnCl_4.5H_2O$ in H_2O (Figure 6.3(a)) therefore contains mostly $SnCl_4.5H_2O$ with some hydrolysis products: some $SnCl_5^-.H_2O$ or $SnCl_6^{2-}$ ions together with $SnCl_3(OH)$ type complexes. It would seem then that the results in Table 6.3. show no evidence of hydrolysis since these measurements were performed in solutions of sufficient acidity to prevent appreciable hydroxide ion formation. The results in Table 6.4., however, were from less acidic systems (for the lower $Cl^-:SnCl_4$ ratios at least) where some hydrolysis products were formed.

(iv) Aqueous Solutions of $SnBr_4$

The spectra obtained from solutions of $SnBr_4$ in water, with varying amounts of concentrated hydrobromic acid, were studied and the results are shown in Table 6.5. These show that there are essentially two features only in the ^{119}Sn n.m.r. spectra: a static peak at about -1100 ppm which diminishes with the addition of Br^-, and a broad peak (typically 60 - 70 ppm wide at half peak height) which moves from -1480 to -1820 ppm. The peak at -1100 is the only one obvious in the spectra of $SnBr_4$ in H_2O only, and is therefore assigned to solvated $SnBr_4$, probably as $SnBr_4.2H_2O$. There was some evidence for a weak, broad peak around -1440 ppm for $SnBr_4$ in H_2O only.

Table 6.5.

Addition of Concentrated Hydrobromic Acid to $SnBr_4$ in H_2O

Relative molar ratios			$-\delta/\pm 5$ ppm, with relative signal heights in brackets	
Br^-	$SnBr_4$	H_2O		
0.00	1.00	13.47	1095.0 (1.0)	
0.00	1.00	7.52	1108.5 (1.0)	
0.25	1.00	8.80	1096.5 (0.4)	1478.4 (1.0)
0.58	1.00	10.45	1094.2 (0.1)	1557.9 (1.0)
1.48	1.00	15.01		1659.1 (1.0)
1.88	1.00	17.04		1720.7 (1.0)
2.25	1.00	18.96		1760.0 (1.0)
2.82	1.00	22.01		1780.0 (1.0)
3.22	1.00	24.02		1821.2 (1.0)

A stronger peak at -1478.4 ppm appeared with the first addition of Br^- to $SnBr_4$ and its shift decreased with subsequent additions of Br^-; concurrently the peak at -1100 ppm decreased in intensity. This is explained by the presence of a dynamic equilibrium between $SnBr_4$, $SnBr_5^-$, $SnBr_6^{2-}$ and Br^- ions, similar to those shown in eq. 6.1. for the $SnCl_4$/HCl system, which gives an average chemical shift in the n.m.r. from the species present. The value of -1812.0 ppm with $3.22Br^-/SnBr_4$, however, is still somewhat higher than the shift of -2074.0 ppm obtained for $(But_4P)_2SnBr_6$ in CH_2Cl_2. This indicates that a large excess of Br^- ions is necessary to push the equilibrium far enough so all the tin is present as $SnBr_6^{2-}$; it is possible, however, that the acidic nature of the system also has an effect, though this was not investigated.

Addition of aqueous KOH to $SnBr_4$ in H_2O produced a spectrum with the strongest peak at -1087.4 ppm as for the solution without the base. The broad peak at -1440 ppm disappeared however, and a new strong resonance at -874.7 ppm was seen. This new signal is probably due to $SnBr_3OH$ or a similar hydroxy-containing species. The absence of observable resonances around -870 ppm for $SnBr_4$ in H_2O only therefore indicates that little hydrolysis takes place in this system.

(v) SnF_4 in H_2O

The ^{119}Sn n.m.r. spectrum of SnF_4 in H_2O showed a pentet: δ = -761.8 ppm, $J^{19}F-^{119}Sn$ = 1710 Hz. This implies that all the fluorines are equivalent in the stannic fluoride molecule and hence a trans-configuration of H_2O ligands would be inferred, if it is assumed that the compound exists as $SnF_4.2H_2O$ in solution i.e. as a dihydrate similar to stannic chloride and stannic bromide. A triplet of triplets would have been expected if a cis-configuration of H_2O ligands was present, but the pentet was the dominant feature of the spectrum. Another way in which a pentet would have been produced is if the ligands were fluxional so that previously inequivalent fluorines would be averaged to equivalence through a rapid interchange of positions. Several smaller peaks were evident at -753.1, -825.5 and -911.1 ppm. These are possibly hydrolysis products though no assignment was attempted since the resolution of the spectrum was not very good.

(d) Hexahalostannates and Halide Complexes

(i) Exchange Between $SnCl_6^{2-}$ and $SnBr_6^{2-}$

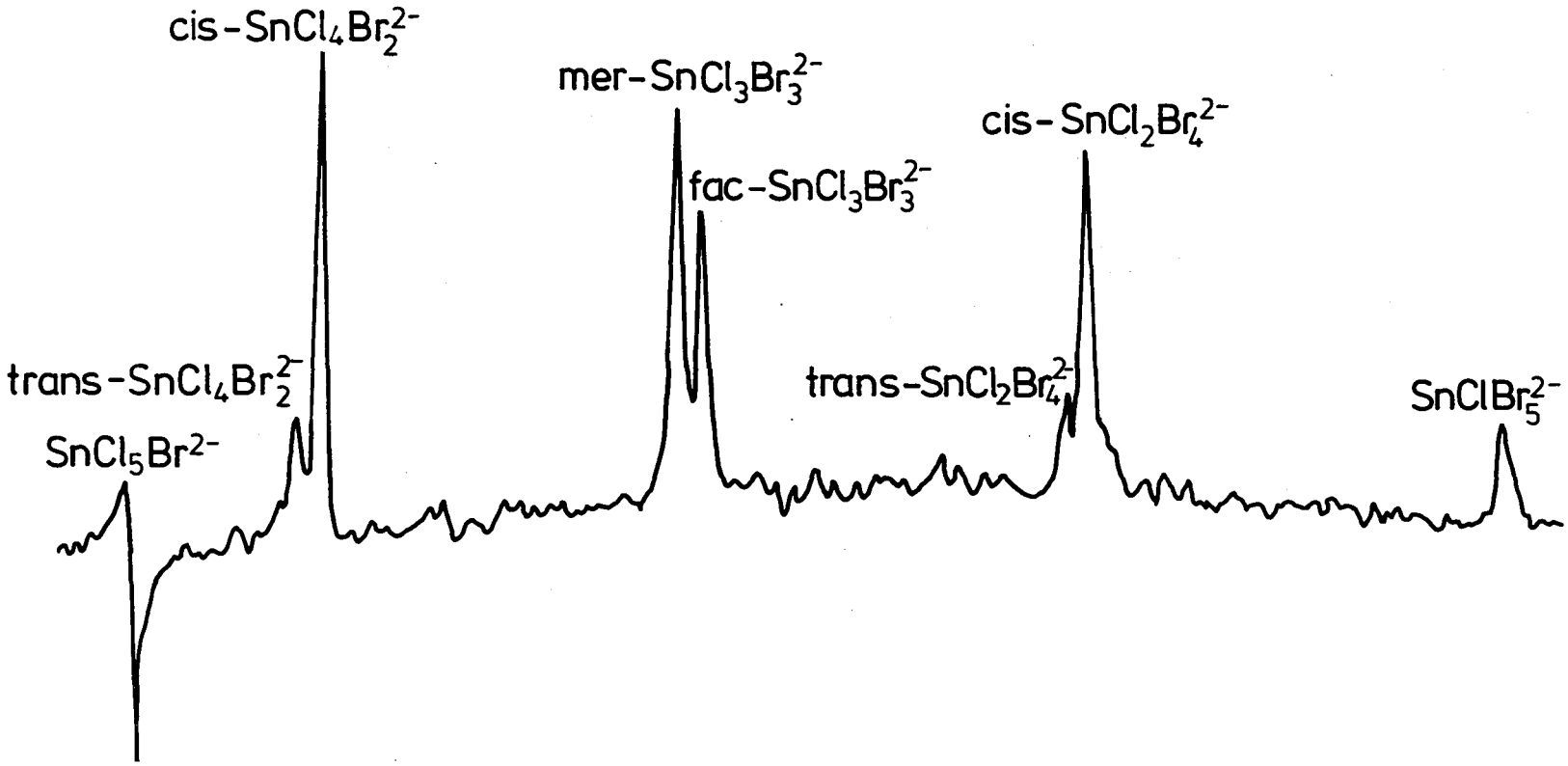
The exchange of ligands between $SnCl_6^{2-}$ and $SnBr_6^{2-}$ was studied via their tetrabutylphosphonium salts in CH_2Cl_2. Both compounds and their exchange products were found to be very soluble in this solvent. The ^{119}Sn

Figure 6.4

Exchange Between $SnCl_6^{2-}$ and $SnBr_6^{2-}$ in CH_2Cl_2

Spectral width 900ppm

77461 scans



n.m.r. spectra revealed that halide exchange occurs freely in this system and that all ten ions [$SnCl_{6-n}Br_n^{2-}$ (n = 0 - 6) including two isomers for n = 2, 3 or 4] of the hexachlorobromostannates were observed. A sample of the type of spectra obtained is shown in Figure 6.4. This includes one signal, for $SnCl_5Br^{2-}$, which is reflected back from outside the range covered in the Fourier transform and is a typical example of this phenomenon. Such reflections can be troublesome, when the interpretation of spectra is attempted, if they are not recognised.

It was found that the intensities of the various signals varied according to the statistically expected way for random exchange, depending on the initial $SnCl_6^{2-}$:$SnBr_6^{2-}$ ratio. Furthermore the cis:trans ratios were found to be roughly 4:1, and the fac:mer ratio 2:3, for the respective isomers, which are also in the correct order for random exchange. No preference was therefore noted for any of the ions or isomers.

Table 6.5.

Chemical Shifts of the $SnCl_{6-n}Br_n^{2-}$ Ions in CH_2Cl_2

Ion	-δ/±2 ppm (observed)	-δ/ppm (calculated from pairwise interactions)[a]
$SnCl_6^{2-}$	729.3	12ClCl = 729.3
$SnCl_5Br^{2-}$	916.1	8ClCl + 4ClBr = 917.4
trans-$SnCl_4Br_2^{2-}$	1106.6	4ClCl + 8ClBr = 1105.4
cis-$SnCl_4Br_2^{2-}$	1120.5	5ClCl + 6ClBr + BrBr = 1123.4
mer-$SnCl_3Br_3^{2-}$	1330.1	2ClCl + 8ClBr + 2BrBr = 1329.5
fac-$SnCl_3Br_3^{2-}$	1344.0	3ClCl + 6ClBr + 3BrBr = 1347.6
trans-$SnCl_2Br_4^{2-}$	1560.6	8ClBr + 4BrBr = 1553.6
cis-$SnCl_2Br_4^{2-}$	1571.0	ClCl + 6ClBr + 5BrBr = 1571.7
$SnClBr_5^{2-}$	1815.5	4ClBr + 8BrBr = 1813.8
$SnBr_6^{2-}$	2074.0	12BrBr = 2074.0

(a) Calculated using ClCl = -60.78, ClBr = -107.79, BrBr = -172.83 ppm.

Table 6.5. shows the observed shifts for the various species in solution and also the calculated values for these ions which were derived from pairwise interactions. The assignments of the individual isomers in the three isomeric pairs was achieved by roughly calculating their shifts from the pairwise terms obtained from $SnCl_6^{2-}$, $SnBr_6^{2-}$ and $SnCl_5Br^{2-}$ (this ion was taken to give the nearest peak to $SnCl_6^{2-}$) and also by reference to their expected intensities from statistical grounds. The final pairwise terms used were calculated by assuming the ClCl and BrBr terms to be correct in $SnCl_6^{2-}$ and $SnBr_6^{2-}$ respectively (since each of these could be measured independently) and then by using these values to calculate the ClBr term for each of the remaining isomers. The mean of all the ClBr terms thus calculated was the value used for predicting the various shifts in Table 6.5. It can be seen from these results that the pairwise interaction theory works well for the hexachlorobromostannates.

(ii) Exchange Between $SnCl_6^{2-}$ and SnF_6^{2-}

This system was studied in CH_2Cl_2 by preparing solutions containing $SnCl_xF_y^{2-}$ $(x + y = 6)$"in situ" with tetrabutylammonium or phosphonium cations. The ^{119}Sn n.m.r. results obtained are shown in Table 6.6. together with pairwise interaction calculations for predicting δ (the actual equations are not shown but are essentially the same as those in Table 6.5.). The interpretation of the spectra was particularly difficult due to the ^{119}Sn-^{19}F coupling producing fifty lines (in theory) for the ten different ions possible in the $SnCl_{6-n}F_n^{2-}$ $(n= 0-6)$ series. Several of these lines overlapped while others were so small as to make them virtually indeterminate from the spectra noise (even after several tens of thousand scans). Identification of the ions was however facilitated to some extent by a knowledge of some of the ^{119}Sn-^{19}F coupling constants from a previous ^{19}F

Table 6.6.

Chemical Shifts of the $SnCl_{6-n}F_n^{2-}$ Ions in CH_2Cl_2

Ion	Description of n.m.r. spectrum	$-\delta/\pm 2$ ppm observed	$-\delta$/ppm calculated	$J^{19}_{F-}{}^{119}_{Sn}$/Hz this work	$J^{19}_{F-}{}^{119}_{Sn}$/Hz ref. 146
$SnCl_6^{2-}$	Singlet	733.0	733.0	-	-
$SnCl_5F^{2-}$	Doublet	695.5	698.4	2430	-
trans-$SnCl_4F_2^{2-}$	Triplet	666.7(?)[d]	663.9	1943(?)[d]	-
cis-$SnCl_4F_2^{2-}$	Triplet	685.5	687.7	2263	-
mer-$SnCl_3F_3^{2-}$	Doublet of triplets	-	676.9	-	-
				-	-
fac-$SnCl_3F_3^{2-}$	Quartet	697.0	700.6	2056	2033[a]
trans-$SnCl_2F_4^{2-}$	Pentet	688.5(?)[d]	689.9	-	2240[a]
cis-$SnCl_2F_4^{2-}$	Triplet of triplets	716.8	713.6	1821	1809[b]
				2132	2122[b]
$SnClF_5^{2-}$	Doublet of pentets	755.3	750.4	1528	1529[b]
				1875	1899[b]
SnF_6^{2-}	Septet	810.8	810.8	1579	1601[b]

(a) In MeOH; (b) in $CHCl_3$; (c) pairwise interaction terms: ClCl = -61.08, ClF = -52.45, FF = -67.57 ppm; (d) poorly resolved, weak peaks.

study.[146] The J values obtained in this work[146] are included in Table 6.6. and though they were derived from the ions in different solvents, they still suffice as a rough guide for present study in CH_2Cl_2. The general method of identification involved preparing solutions containing either mostly Cl^- or F^- containing species and running their n.m.r. spectra so that certain ions could be identified before more complex spectra were studied

Fig. 6.5.

"In situ" $SnCl_{2.9}F_{3.1}^{2-}$ in CH_2Cl_2

Spectral width 447ppm

70000 scans

Key:

A. $SnCl_6^{2-}$

B. $SnCl_5F^{2-}$

C. cis-$SnCl_4F_2^{2-}$

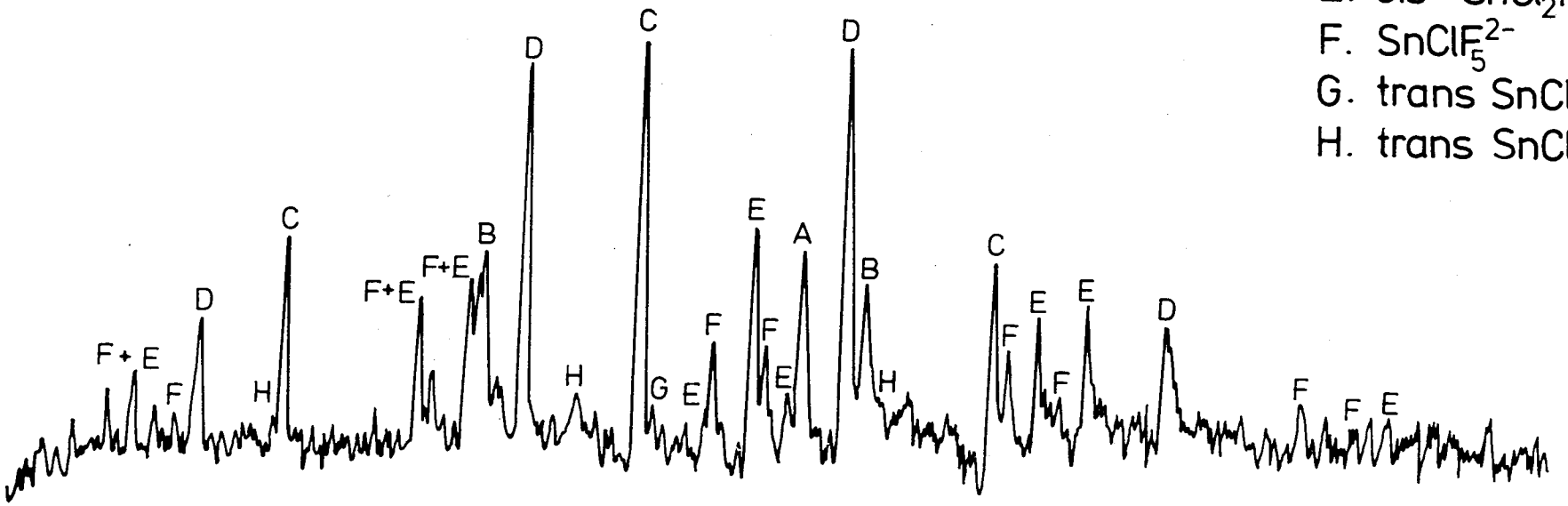
D. fac-$SnCl_3F_3^{2-}$

E. cis-$SnCl_2F_4^{2-}$

F. $SnClF_5^{2-}$

G. trans $SnCl_2F_4^{2-}$?

H. trans $SnCl_4F_2^{2-}$?



with Cl:F ratios approximately 1:1. A sample of one of the more complex spectra is shown in Figure 6.5.

Seven of the ten ions were successfully identified through their characteristic splitting patterns. The assignment of these to various chemical shifts (Table 6.6.) led to their pairwise interaction terms being calculated in a similar manner to those for the hexachlorobromostannates in the previous section with the ClF term determined as an average of several values. On comparing the calculated and observed values of δ in Table 6.6. it can be seen that the pairwise theory gives a reasonable correlation.

A systematic increase in the ClF terms calculated from individual isomers, on increasing the amount of F in each, was noted before the average value of the ClF term was obtained for use in the final calculations. This trend indicates that extra fluorines complement each other in shielding the tin nucleus and that the simple pairwise additive model is insufficient to cope with this detail.

The model does however give agreement within 5 ppm and from the predicted figures weak peaks from trans-$SnCl_4F_2^{2-}$ and trans-$SnCl_2F_4^{2-}$ were located in the n.m.r. spectra. The mer-isomer of $SnCl_3F_3^{2-}$ could not be located which was surprising since, on statistical grounds, its largest peaks (of the doublet of triplets) should be the second largest in Figure 6.5. This lack of signal for the mer-isomer together with the weak signals obtained for the trans-isomers argues that a trans configuration for the fluorines may be less stable than a cis arrangement. One way in which this could be accounted for would be if some Sn-F π-bonding was occurring by back donation from the F p-orbitals into vacant d-orbitals around the tin atom. Once one such bond had been formed, then further substitution would be

preferred in a perpendicular plane to the existing Sn-F bond to maximise the π-bonding interactions (partially filled d-orbitals would less readily accept further electronic charge due to electronic repulsion).

(iii) Exchange Between SnF_6^{2-} and $SnBr_6^{2-}$

Similar experiments to those used in the study of $SnCl_6^{2-}/SnF_6^{2-}$ exchange were employed in an attempt to identify the ions $SnBr_{6-n}F_n^{2-}$ (n = 0 - 6) through ^{119}Sn n.m.r. spectroscopy. Unfortunately, however, the spectra produced had signal to noise ratios of such a magnitude that few peaks, bar that for $SnBr_6^{2-}$ at -2071 ppm, could be identified even after 30,000 or more scans. For this reason no data are reported; no consistent set of results was obtained. The difficulty in observing signals may be attributable to broader lines than obtained for the $SnCl_6^{2-}/SnF_6^{2-}$ system, although the reason for this is not apparent.

(iv) Exchange Between SnI_6^{2-} and Other Hexahalostannates

Very little information could be gained on six-co-ordinate iodide-containing halogeno-complexes of tin (IV) since no signal for SnI_6^{2-} could be found. In fact virtually the only feature present in any spectrum of SnI_6^{2-}/SnX_6^{2-} (X = Cl or Br) was the SnX_6^{2-} peak, and even this faded out on adding sufficient SnI_6^{2-}. There are two possible reasons for this behaviour: the iodide may induce very fast relaxation of the tin nuclei, so broadening the lines to obscurity, or may be involved in very rapid exchange between all the species present, which would give one very broad exchange peak which might be very difficult to detect. The only (presumed) observation of iodide-containing complexes came from adding I^- to SnX_6^{2-} (X = Cl or Br) in CH_2Cl_2. In each case the SnX_6^{2-} peak was seen together with a second peak at higher field: for $SnCl_6^{2-}$ + Pe_4NI, two peaks were observed at -729.9

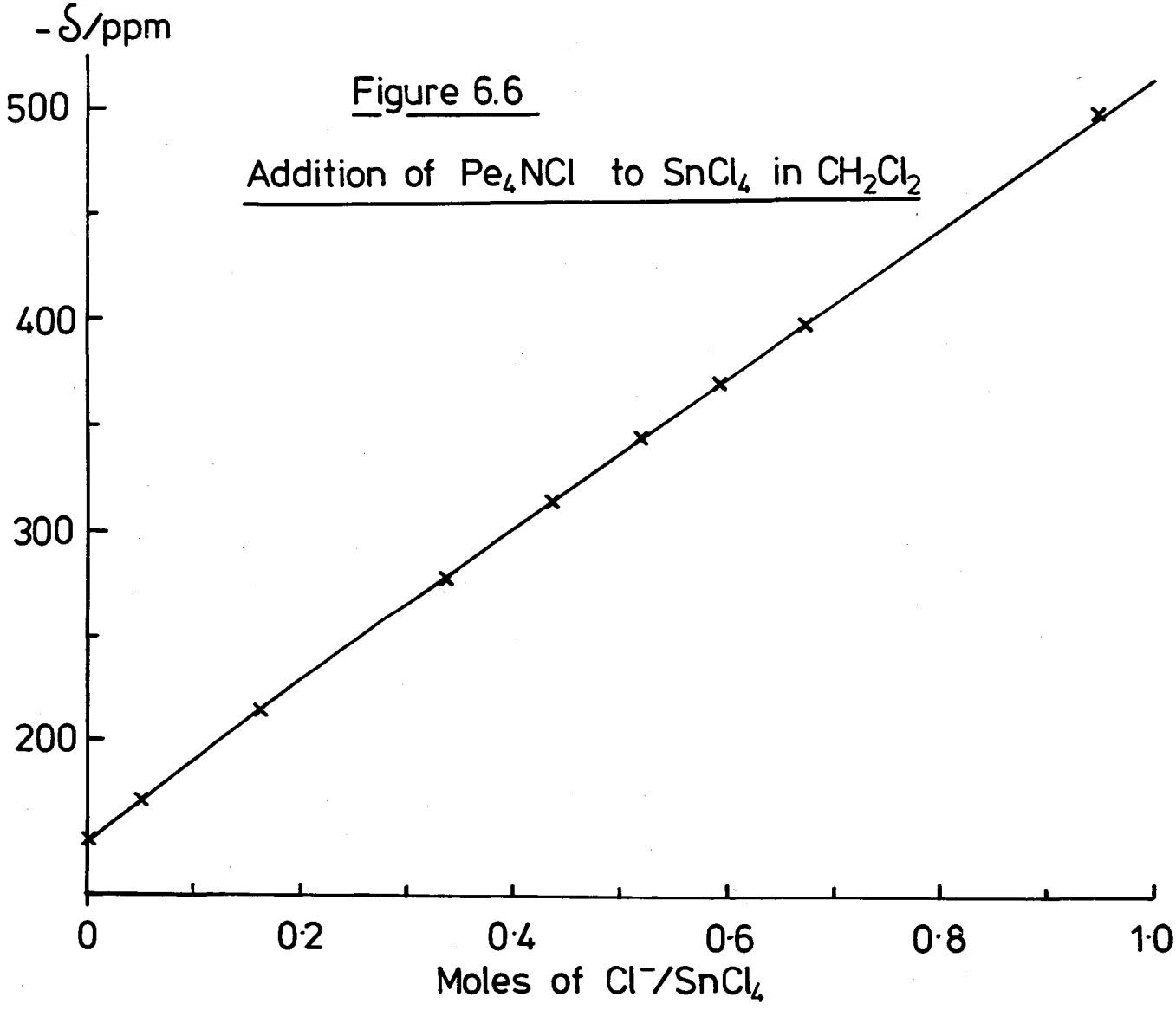


Figure 6.6

Addition of Pe_4NCl to $SnCl_4$ in CH_2Cl_2

($SnCl_6^{2-}$) and -813.7 ppm, while for $SnBr_6^{2-}$ + $Prop_4NI$ the two peaks came at -2074.8 ($SnBr_6^{2-}$) and -2179.6 ppm. No attempt at assigning the resonances at higher field has been made, however, since no additional information is available.

(v) Addition of Halide Ions to Stannic Halides

The effect of adding Cl^- to $SnCl_4$ was studied in CH_2Cl_2 as solvent and the results are shown in Figure 6.6. and Table 6.7. The figure clearly shows a steady decrease in δ on adding more Cl^-, as expected from the difference in shifts for $SnCl_4$ and $SnCl_6^{2-}$. No signals could be detected, however, for ratios of Cl^-:$SnCl_4$ between 1 and 2, due to considerable line-broadening. After a ratio of more than 2 moles of Cl^- to one of $SnCl_4$ had been reached, the characteristic peak at -730 ppm was observable for $SnCl_6^{2-}$. The regions from 0 to 1 and 1 to 2 ratios of Cl^-:$SnCl_4$ therefore show evidence of exchange between different species: probably $SnCl_4/SnCl_5^-/Cl^-$ exchange in the first instance, and $SnCl_5^-/SnCl_6^{2-}/Cl^-$ exchange in the second case. The first exchange occurs much more quickly than the second since sharp, single resonances are seen in this instance, whereas broad exchange peaks (presumed) are produced for the latter. The measurement of δ =

Table 6.7.

Addition of Pe_4NCl to $SnCl_4$ in CH_2Cl_2

Moles Cl^-/mole $SnCl_4$	-δ/±1 ppm	Moles Cl^-/mole $SnCl_4$	-δ/±1 ppm
0.000[a]	152.6	0.522	342.9
0.048	171.8	0.597	367.2
0.164	213.7	0.675	396.3
0.336	276.7	0.947	494.9[b]
0.438	311.9		

(a) Broadish line about 10 ppm wide at half signal height, all other lines less than 4 ppm wide; (b) very weak, broad signal, 20 ppm wide.

-494.9 ppm for $SnCl_4$ with 0.947 moles Cl^- compares well with a figure of -501.7 ppm for $Et_4N^+SnCl_5^-$ in $MeNO_2$ [121] and indicates that $SnCl_5^-$ may be the dominant contributor to the exchange peak for this chloride ion concentration. Colton et al[151] failed to observe signals from a 1:1 mixture of But_4NCl and $SnCl_4$ in CH_2Cl_2 at room temperature, however they obtained a comparable shift of -479 ppm at 243K.

Further attempts to detect iodide-containing tin (IV) complexes proceeded via addition of Pe_4NCl or Pe_4NBr to SnI_4 in CS_2. The chloride produced no change in the shift of SnI_4 at -1698.7 ppm with 0.19 equivalents added, though when a ratio of 0.99 moles of Cl^-/mole SnI_4 was reached no signals at all could be found in the ^{119}Sn n.m.r. spectrum. With bromide, however, exchange peaks were visible at -1709 (with 0.495 equivalents of Br^-) and -2530 ppm (with 0.82 equivalents of Br^-). Both peaks were rather broad and required several thousand scans for detection. The peaks were presumably due to tin (IV) halide complexes containing some iodide with rapid exchange occurring. The large shift of over 800 ppm upfield on adding 0.82 moles of Br^- to SnI_4 (a shift of $\sim$ 275 ppm was seen for $0.8Cl^- + 1.0SnCl_4$) indicates that SnI_6^{2-} (or $SnI_4Br_2^{2-}$) signals occur at very high field. No signals could be obtained on adding Pe_4NI to SnI_4 in CS_2.

(e) Pseudohalide Complexes of Tin (IV)

(i) Cyanide Complexes

Attempts at the preparation of hexacyanostannate (IV) compounds proved unsuccessful (see experimental section) so studies of six-co-ordinate tin (IV) complexes of halide (Cl or Br) and cyanide were made by preparing these "in situ". Two methods were used:

$$SnX_4 + xBut_4NCN + yPent_4NX \longrightarrow SnX_{4+y}(CN)_x^{2-} + \text{cations} \qquad \text{eq. 6.2.}$$

$$SnX_2 + CNX + 2But_4NCN \longrightarrow SnX_3(CN)_3^{2-} + \text{cations} \qquad \text{eq. 6.3.}$$

X = Cl or Br.

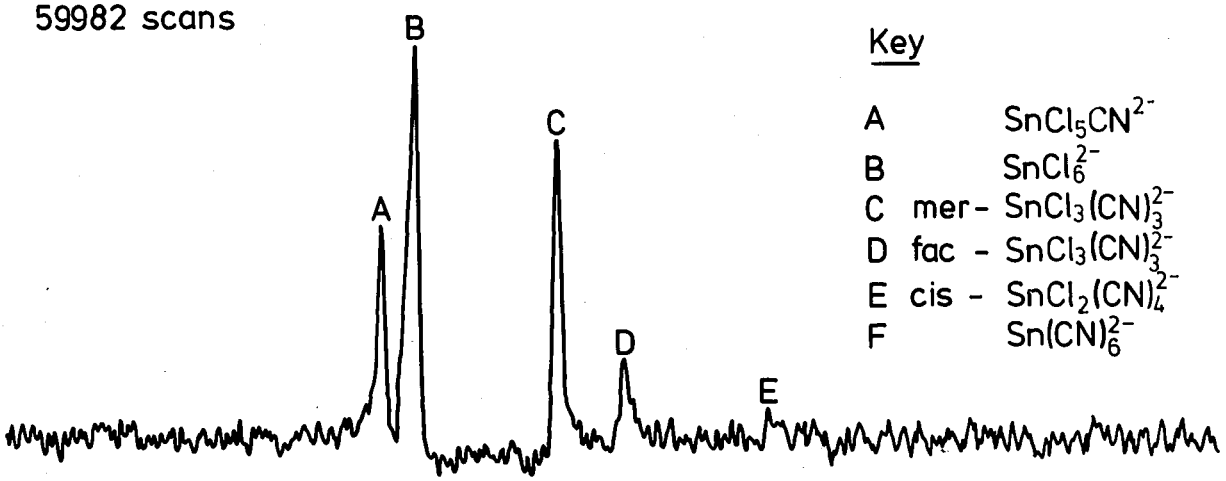
Figure 6.7

Sample ^{119}Sn n.m.r. Spectra from the Chlorocyanostannates (IV)

$SnCl_4$ + $Pent_4NCl$ + But_4NCN in CH_2Cl_2

Spectral width 223 ppm

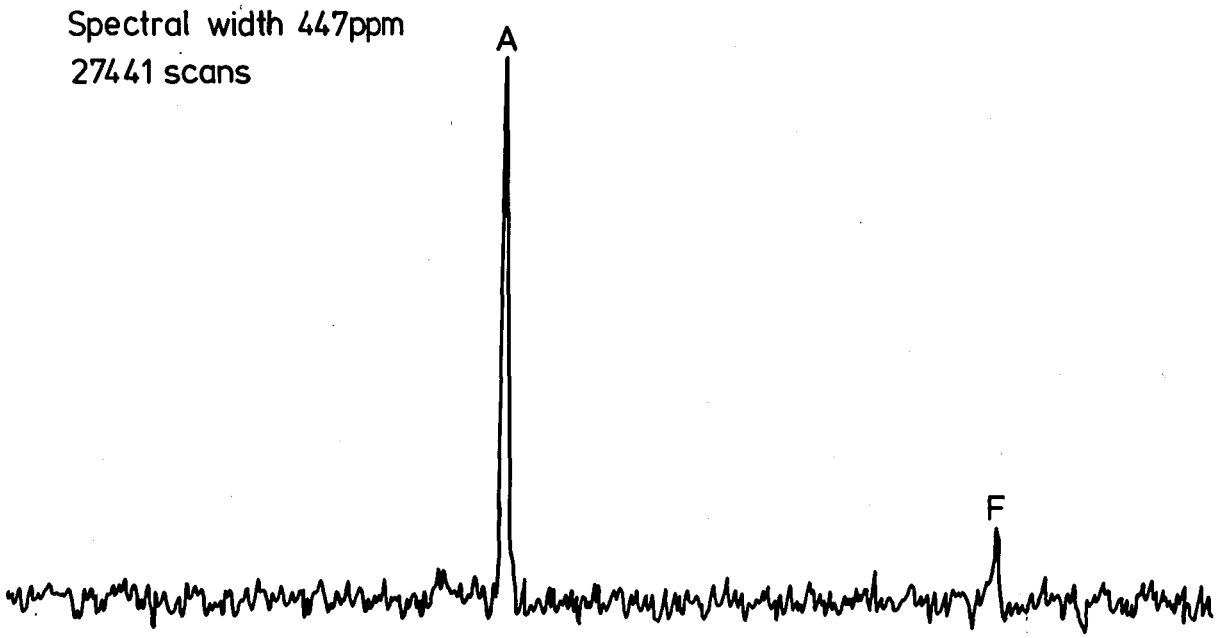
59982 scans



$SnCl_2$ + ClCN + 2$Pent_4NCl$ in CH_2Cl_2

Spectral width 447ppm

27441 scans



Furthermore in order to obtain complexes containing more CN than halide some AgCN was added to selected samples.

The ^{119}Sn n.m.r. spectra of each cyanohalostannate (IV) system (Figures 6.7. and 6.8.) showed several peaks and attempts were made to interpret these through application of pairwise interaction theory. Though $Sn(CN)_6^{2-}$ could not be isolated as a solid compound, the same peak at about -916 ppm appeared in both the chloro- and bromo-cyanide systems and was therefore thought to correspond to this moiety. The shifts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ were known from earlier work (section 6(d)(i)) so the ClCl, BrBr and CNCN pairwise terms were easily obtained. Correct assignment of one resonance to a particular cyanohalostannate (IV) from each system should therefore have been sufficient to obtain the ClCN and BrCN pairwise terms, and allow prediction of the shifts of the other possible species in each case. Such assignments were made by preparing solutions of $SnX_n(CN)_{6-n}^{2-}$ (X = Cl/Br) with n near to six so that complexes with preponderances of either halide were formed. The first substitution products (i.e. n = 5) could then be identified, especially since the overall intensities of the peaks should average out to correspond to the initial, known stoichiometry of the sample under study. (For example, if three peaks $SnCl_6^{2-}$, $SnCl_5CN^{2-}$ and $SnCl_4(CN)_2^{2-}$ have intensities of 1:2:1 then the initial stoichiometry of the mixture must be $SnCl_5CN^{2-}$; clearly in such a system if the peak of intensity 2 was assigned to any species other than $SnCl_5CN^{2-}$ then an incorrect estimate of the stoichiometry would be obtained). From the shifts of the first substitution products the ClCN and BrCN terms were calculated and the pairwise predictions from them obtained. These predictions then enabled further assignments of the peaks to be made. This method worked fairly well for the chloro-cyanide system but poorly for the

Table 6.8.

Chemical Shifts of Cyanohalostannates (IV) in CH_2Cl_2

Ion	$-\delta$/ppm[a]			
	X=Cl		X=Br	
	Observed	Calculated[b]	Observed	Calculated[c]
SnX_6^{2-}	734.2	-	2075.7	-
SnX_5CN^{2-}	728.1	729.5	1690.7	1767.2
trans-$SnX_4(CN)_2^{2-}$	-	724.9	1453.1	1458.6
cis-$SnX_4(CN)_2^{2-}$	-	742.4	1482.0	1516.6
mer-$SnX_3(CN)_3^{2-}$	760.3	755.2	1285.1	1266.0
fac-$SnX_3(CN)_3^{2-}$	773.4	772.7	1308.3	1323.9
trans-$SnX_2(CN)_4^{2-}$	-	785.5	1093.7	1073.3
cis-$SnX_2(CN)_4^{2-}$	800.1	803.0	1168.3	1131.2
$SnX(CN)_5^{2-}$	-	850.8	1052.5	996.5
$Sn(CN)_6^{2-}$	916.2	-	919.7	-

(a) $\pm$2 ppm for observed values; (b) ClCl = -61.183, ClCN = -60.018, CNCN = -76.347 ppm; (c) BrBr = -172.975, BrCN = -95.841, CNCN = -76.642 ppm.

bromo-cyanides. The spectra from the bromo-compounds were therefore studied again with the recognition that trans-isomers normally occur at lower field than cis- and similarly mer- at lower field than fac-, and also that the splitting of the shifts of isomeric pairs should not be as great as the separation between ions of different stoichiometries. On this basis the ions $SnBr_{6-n}(CN)_n^{2-}$ (n = 1, 2, 3) were assigned to various observed shifts. From these assignments a value for the BrCN term was obtained from each

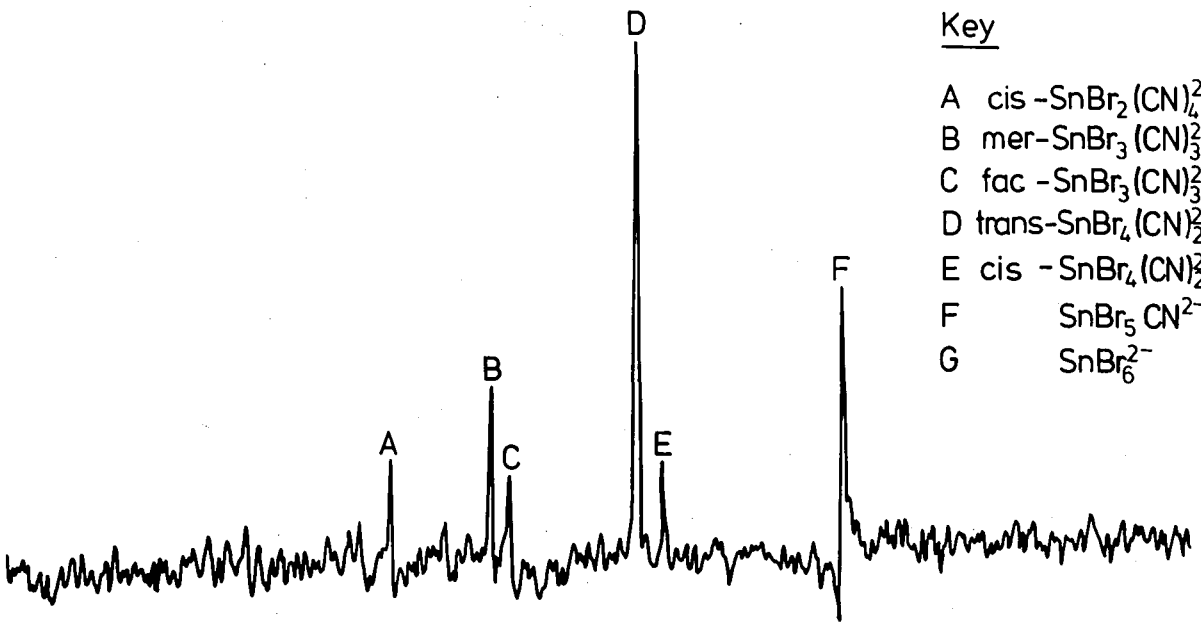
Figure 6.8

Sample ^{119}Sn n.m.r. Spectra from the Bromocyanostannates (IV)

$SnBr_4$ + 2·3But_4NCN in CH_2Cl_2

Spectral width 1400 ppm

29761 scans



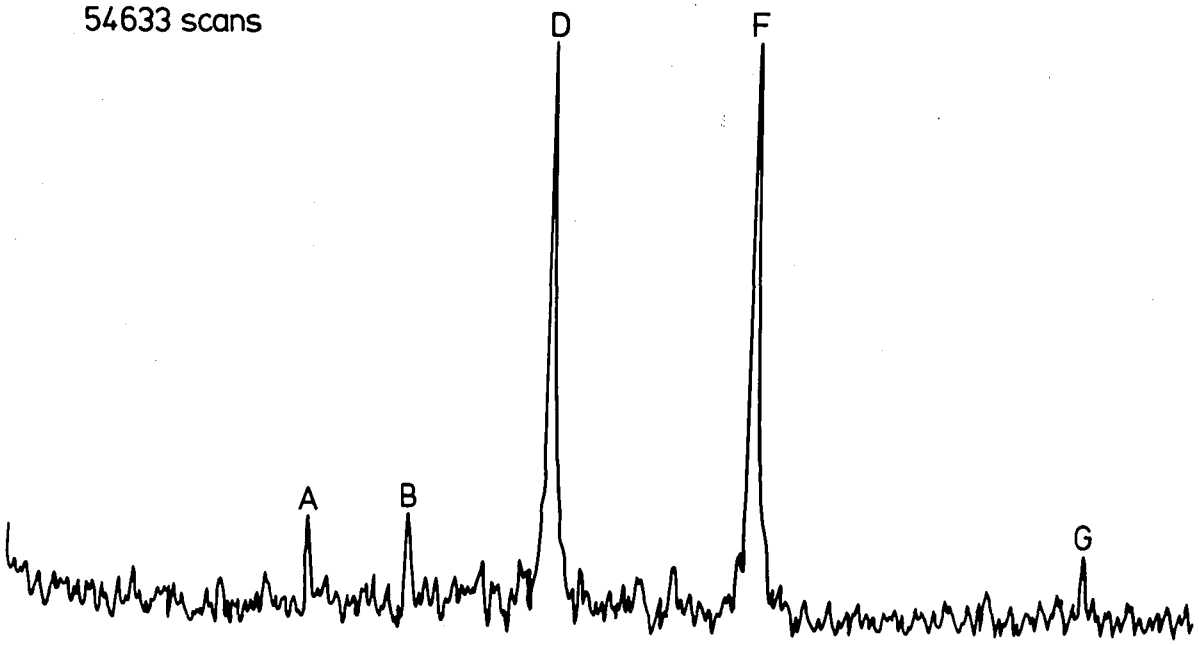
Key

A cis-$SnBr_2(CN)_4^{2-}$
B mer-$SnBr_3(CN)_3^{2-}$
C fac-$SnBr_3(CN)_3^{2-}$
D trans-$SnBr_4(CN)_2^{2-}$
E cis-$SnBr_4(CN)_2^{2-}$
F $SnBr_5CN^{2-}$
G $SnBr_6^{2-}$

$SnBr_2$ + BrCN + 2But_4NCN in CH_2Cl_2

Spectral width 1400 ppm

54633 scans



isomer and the weighted average (depending on the number of BrCN terms in each pairwise equation) of this parameter was calculated. This new value enabled a better fit to the experimental to be obtained and approximate assignment of the rest of the ions was performed. The parameters used for the calculations in Table 6.8. were finally obtained by calculating the ClCN and BrCN pairwise terms from each assigned ion, followed by the calculation of their respective weighted averages.

It is interesting to note that there was a systematic increase in the BrCN term calculated from each assignment as the amount of cyanide in the sample decreased (cf. the ClF term for $SnCl_{6-n}F_n^{2-}$). Table 6.9. shows the values obtained. This variation is demonstrated in Table 6.8. by the mediocre correlation between the experimental and calculated shifts for the $SnBr_{6-n}(CN)_n^{2-}$ series. It should also be noted that the BrBr and CNCN terms, though assumed to be constant, may also vary. Nevertheless these two terms were calculated from the regular octahedral species and may well therefore represent the best average values. The change in the calculated BrCN terms probably reflects a deviation from the pairwise theory by the cyanide ligands (since the $SnCl_{6-n}Br_n^{2-}$ series, for example gave good

Table 6.9.

Calculated BrCN Pairwise Interaction Parameters

Ion	BrCN[a]/ppm
$SnBr_5CN^{2-}$	-76.725
$SnBr_4(CN)_2^{2-}$	-93.081 (cis) -95.150 (trans)
$SnBr_3(CN)_3^{2-}$	-93.242 (fac) -98.233 (mer)
$SnBr_2(CN)_4^{2-}$	-102.019 (cis) -98.392 (trans)
$SnBr(CN)_5^{2-}$	-109.842

(a) Calculated from BrBr = -172.975, CNCN = -76.642 ppm.

agreement). The nature of this deviation is not clear but may be due to either one or both of two effects: distortion from a regular octahedral configuration of ligands, or π-bonding interactions between Sn and CN. It has been found elsewhere that CN also gives poorer agreement than other ligands for the $PCl_{6-n}(CN)_n^-$ series.[160]

Table 6.8. reveals that several ions of the $SnCl_{6-n}(CN)_n^{2-}$ series were not located. In particular neither isomer of $SnCl_4(CN)_2^{2-}$ could be found, despite the observation of their two neighbours (i.e. n = 1 and 3). This is perhaps attributable to increased reactivity of $SnCl_4(CN)_2^{2-}$ compared to the other members of the series such that any formed is either immediately substituted to form other species, or else possibly disproportionates. The failure to observe $SnCl(CN)_5^{2-}$ on the other hand probably arises because no solutions could be prepared with a high enough CN:Cl ratio, since AgCN appeared not to react with $SnCl_6^{2-}$ and thus the highest stoichiometry attainable was $SnCl_3(CN)_3^{2-}$. The spectra show that mer-$SnCl_3(CN)_3^{2-}$ and cis-$SnCl_2(CN)_4^{2-}$ are the favoured isomers of their respective stoichiometries, and this is in accordance with statistical expectations for random exchange, although the absence of trans-$SnCl_2(CN)_4^{2-}$ indicates that the cis-isomer may have extra stability. The fac:mer ratio was found to vary between 1:2 and 1:4, the reason for which is not obvious.

Oxidation of $SnCl_2$ by cyanogen chloride in the presence of Cl^- or CN^- generally gave two peak spectra showing $SnCl_6^{2-}$ and $Sn(CN)_6^{2-}$ resonances only, without any sign of the intermediate exchange products (see Figure 6.7.). A disproportionation reaction is therefore indicated and hence this method of preparation of n.m.r. samples was of little use for increasing the CN:Cl ratio. The quantities of $SnCl_6^{2-}$ and $Sn(CN)_6^{2-}$ present varied according to the amounts of Cl^- and CN^- added. If the cyanogen chloride was in excess,

however, $SnCl_6^{2-}$ became the exclusive product. This may well arise from reactions of the type:

$$SnCl_5CN^{2-} + ClCN \rightleftharpoons SnCl_6^{2-} + (CN)_2 \qquad \text{eq. 6.4.}$$

The cyanogen shown in equation 6.4. then probably reacts further, possibly to form polymeric species, since the samples were typically dark brown in colour. Should such polymeric species be formed, the back reaction away from $SnCl_6^{2-}$ would become more difficult and might not occur at all.

The $SnBr_{6-n}(CN)_n^{2-}$ series showed the presence of all ten possible species in its n.m.r. spectra. The preferred isomers for n = 2, 3 and 4 are trans-$SnBr_4(CN)_2^{2-}$, mer-$SnBr_3(CN)_3^{2-}$ and cis-$SnBr_2(CN)_4^{2-}$. The trans-isomer in this sequence is contrary to the statistical prediction of cis-$SnBr_4(CN)_2^{2-}$ as the preferred isomer, and implies that a particular stability may exist for two trans cyano-groups. This may be due to a type of trans-effect in the octahedral system, similar to that seen in chloro-cyano square planar complexes,[161] such that the CN group in Sn $CNCl_5^{2-}$ labilises substitution of the Cl group trans to it. It is strange, however, that if this is the case then trans-$SnBr_2(CN)_4^{2-}$ is not also favoured, although statistics again predict that cis-$SnBr_2(CN)_4^{2-}$ should be formed preferentially.

Preparation of the $SnBr_{6-n}(CN)_n^{2-}$ complexes by oxidation yielded spectra which initially showed no sign of the less favoured isomers (see Figure 6.8.). After the solutions had been left to stand for a period of several weeks, however, these peaks were also observable. The oxidation reaction therefore favours the formation of trans-$SnBr_4(CN)_2^{2-}$, and from this isomer further substitution by cyanide can only produce mer-$SnBr_3(CN)_3^{2-}$. This in turn can give cis- or trans-$SnBr_2(CN)_4^{2-}$, but the cis-isomer is statistically favoured by a 2:1 ratio.

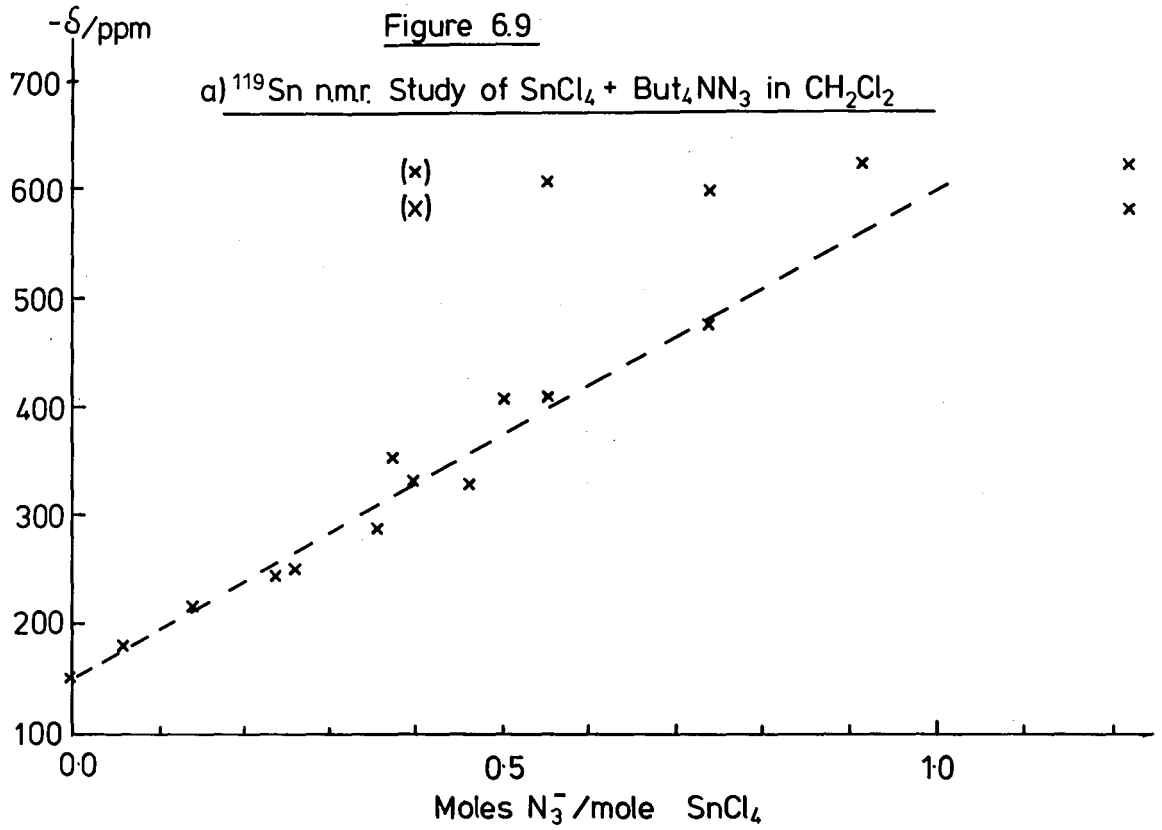
(ii) Azide Complexes

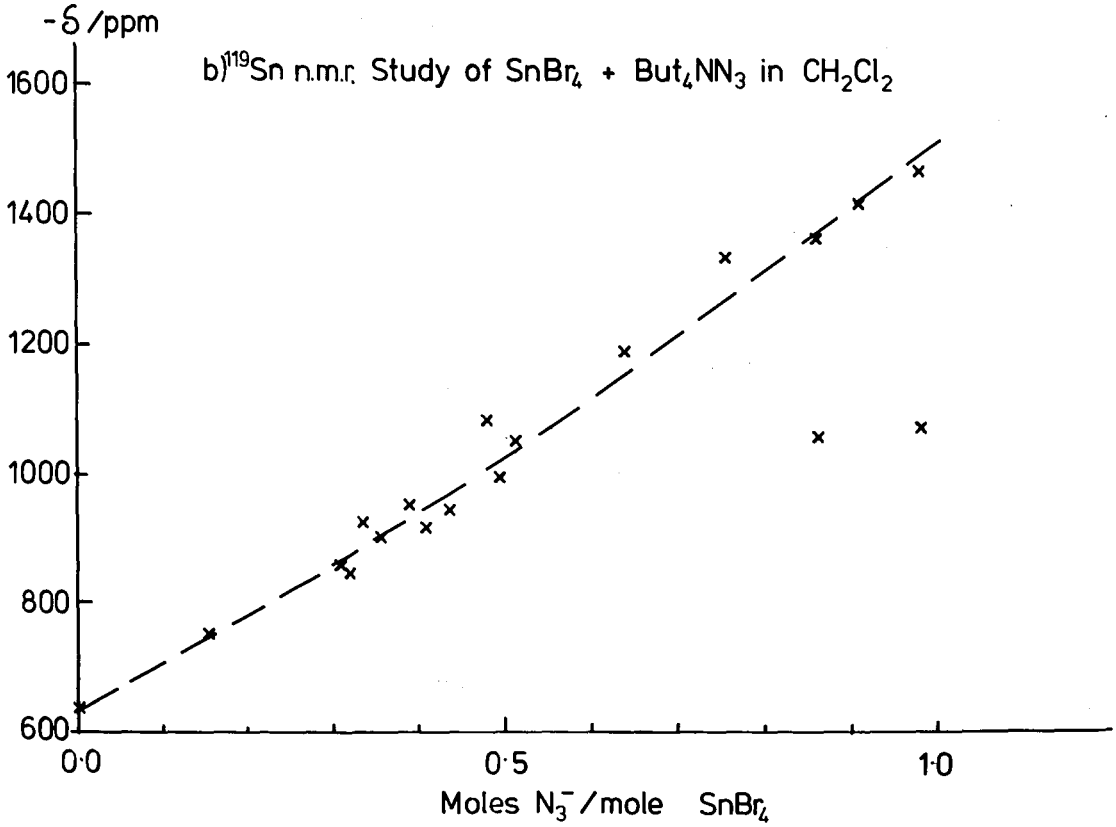
Six co-ordinate complexes of tin containing azide with either chloride or bromide were obtained in solution by mixing tetrabutylphosphonium hexaazidostannate with an appropriate hexahalostannate in dichloromethane. The ^{119}Sn n.m.r. spectra of such samples typically showed several peaks, the intensities of which could be varied by control of the ratio of azide to halide ions. Further n.m.r. samples were prepared using tetrabutylammonium azide in a 2:1 ratio with the appropriate stannic halide, but these samples showed similar spectra to those prepared by the first method. The chemical shifts from a number of spectra were then collected and compared with each other, so that minor resonances could be checked for reproducibility and that average values of the shifts corresponding to each species could be evaluated. The results are shown in Table 6.12.

It quickly became apparent from the number of resonances observed in the azidobromostannate (IV) system that more species were present than the ten expected (including isomers) in the $SnBr_{6-n}(N_3)_n^{2-}$ (n = 0 - 6) series. These extra resonances are possibly N_3-bridged dimers, since $(Me_4N)_2(SnCl_4\mu\text{-}N_3)_2$ has been prepared and has been shown by Raman and Mössbauer spectroscopy to have such a structure.[95] There was also some evidence of extra peaks in the azidochlorostannate (IV) system, but this was less clear cut than for the bromo-analogues; nevertheless bridged species are also expected to be present here. No attempt was made to assign any peaks to specific bridged species from these spectra because of the large number of possible species.

The existence of the bridged ions was implied, however, from the results of adding But_4NN_3 to $SnCl_4$ or $SnBr_4$ in CH_2Cl_2, since in both cases by the time a 1:1 ratio of reactants was achieved, (after using progressively increasing amounts of azide until this ratio was reached),

Figure 6.9


a) ^{119}Sn n.m.r. Study of $SnCl_4$ + But_4NN_3 in CH_2Cl_2
-δ/ppm
700
600
500
400
300
200
100
(x)
(x)
0·0
0·5
1·0
Moles N_3^-/mole $SnCl_4$


b) ^{119}Sn n.m.r. Study of $SnBr_4$ + But_4NN_3 in CH_2Cl_2
-δ/ppm
1600
1400
1200
1000
800
600
0·0
0·5
1·0
Moles N_3^-/mole $SnBr_4$

several peaks became visible in the ^{119}Sn n.m.r. spectra. This is unlike adding Br^- to $SnCl_4$ in CH_2Cl_2 - separate experiments here showed one broad exchange peak only at a 1:1 ratio of $SnCl_4$:Br^-, i.e. no evidence of any of the $SnCl_{6-n}Br_n^{2-}$ series. A 1:0.98 ratio of $SnBr_4$:N_3^- showed a major peak at -1068.5 ppm together with a second peak at -1012.6 ppm, corresponding to the average shifts of -1075.4 and -1011.0 ppm found in the spectra of the $SnBr_6^{2-}/Sn(N_3)_6^{2-}$ exchange system. The dominant feature in a spectrum of $SnCl_4$ with 1.23 equivalents of azide was a peak at -620.7 ppm, which also corresponds to a weak average shift of -622.6 ppm from the spectra of the $SnCl_6^{2-}/Sn(N_3)_6^{2-}$ exchange system. The results of these studies are shown in Tables 6.10. and 6.11. and in Figure 6.9. Both with $SnCl_4$ and $SnBr_4$ the

Table 6.10.

Addition of But_4NN_3 to $SnCl_4$ in CH_2Cl_2

Moles N_3^-/mole $SnCl_4$	-δ/±5 ppm	
0.000	149.5	
0.057	180.1[a]	
0.139	215.2[a]	
0.237	245.5[a]	
0.260	250.0[a]	
0.357	288.0[a]	
0.376	354.0[a]	
0.400	332.7[a]	584.1[b], 615.5[b]
0.462	330.0[a]	
0.503	406.9[a]	
0.556	409.7[a]	606.1[a]
0.739	474.1	597.2[a]
0.915		620.4
1.230	580.2	620.7

(a) Resonances at least 40 ppm wide at half signal height; (b) weak lines.

Table 6.11.

Addition of But_4NN_3 to $SnBr_4$ in CH_2Cl_2

Moles N_3^-/ mole $SnBr_4$	$-\delta/\pm 5$ ppm	Moles N_3^-/ mole $SnBr_4$	$-\delta$		
0.000	634.2	0.495	992.6		
0.154	750.1	0.514	1049.2		
0.309	859.2	0.611	1121.6		
		0.640	1184.9		
0.320	844.6	0.757	1330.1		
0.338	921.7	0.859	1360.0		1056.2[a]
0.360	899.6	0.910	1411.0		
0.391	950.9				
0.408	915.6	0.980	1459.6	1012.6	1068.5[a]
0.436	937.1				
0.456	1078.3				

(a) identified in spectra from ∿ 30,000 scans.

azide ion produces a steady increase in shift as its proportion increases. This increase is shown by the dotted lines in Figure 6.9. and the points around the line are thought to come from exchange peaks in a similar manner to those found in the $SnCl_4/Cl^-$ system (section 6(d)(v)). The exchange in these systems is probably more complicated because of the possible existence of azido-derivatives of SnX_4, SnX_5^- and SnX_6^{2-} (X = halogen) (cf. eq. 6.1.), as well as azide-bridged dimers. The points away from the dotted lines probably represent the resonances of single species (although some of these may coalesce to give broad peaks, e.g. the signals at -606.1 and -597.2 ppm for the $SnCl_4/N_3^-$ system) since the position of these are

relatively invariant with different amounts of azide. Furthermore, as these resonances are observable (and indeed dominate the spectra) at a ca. 1:1 ratio of $SnX_4:N_3^-$, when the stoichiometry is correct for dimer formation, it is very probable that they correspond to azide-bridged dimers since such ions contain tin in its more favoured six-co-ordinate form. The observation of evidence for the dimers below the 1:1 ratio suggests that they may possess a particular stability, i.e. when formed they take little or no part in the exchange reactions which give the peaks near the dotted lines in Figure 6.9.

Table 6.12. shows the average chemical shifts and pairwise interaction predictions from the $SnX_6^{2-}/Sn(N_3)_6^{2-}$ exchange reactions. The N_3N_3, ClCl and BrBr pairwise terms were easily obtained since $Sn(N_3)_6^{2-}$, $SnCl_6^{2-}$ and $SnBr_6^{2-}$ had all been prepared and their shifts measured independently, though the actual values used were those calculated from their shifts in solutions with the various other mixed azido-halo anions also present. This was because their positions varied slightly, depending on the system under investigation. $(Et_4N)_2Sn(N_3)_6$ in CH_3CN gave a figure of -605.2 ppm, while $(But_4P)_2Sn(N_3)_6$ in CH_2Cl_2 showed a peak at -603.5 ppm with a shoulder at -594 ppm, possibly due to some impurity. This sample was prepared by the reaction of $SnBr_6^{2-}$ with NaN_3, while a solution containing $SnCl_6^{2-}$ with 6 moles of NaN_3 in CH_2Cl_2 gave an almost identical spectrum, so the nature of this impurity is not clear. The shoulder was observed to grow on the addition of extra $SnCl_6^{2-}$ to the solution of $SnCl_6^{2-}$ with $6NaN_3$ so in this case it probably is due to a chloro-containing species, possibly $Sn(N_3)_5Cl^{2-}$, though this does not explain the presence of the chloride in the compound prepared from $SnBr_6^{2-}$. The peak at -605.0 ppm was thus assigned to $Sn(N_3)_6^{2-}$ for the chloro-system, while a shift of -593.7 ppm was designated

Table 6.12.

Chemical Shifts of Azidohalostannates (IV) in CH_2Cl_2

Ion	-δ/ppm[a]			
	X=Cl		X=Br	
	Observed	Calculated[c]	Observed	Calculated[d]
$Sn(N_3)_6^{2-}$	605.0[b]	-	593.7[b]	-
			642.4[b]	
			670.3	
$Sn(N_3)_5X^{2-}$	598.2[b]	589.5	749.2[b]	741.1
trans-$Sn(N_3)_4X_2^{2-}$	578.0	574.1	874.4[b]	888.6
cis-$Sn(N_3)_4X_2^{2-}$	590.6	592.4	951.1[b]	938.6
			1011.0	
			1045.5	
mer-$Sn(N_3)_3X_3^{2-}$		595.3	1075.5	1136.1
fac-$Sn(N_3)_3X_3^{2-}$	614.5[b]	613.6	1179.8[b]	1186.2
			1245.4	
trans-$Sn(N_3)_2X_4^{2-}$	622.6	616.4	1346.3[b]	1383.7
cis-$Sn(N_3)_2X_4^{2-}$	635.1[b]	634.8	1532.5[b]	1433.7
			1552.8	
	643.1		1574.5	
			1681.9	
$Sn(N_3)X_5^{2-}$	673.0[b]	674.3	1818.1[b]	1731.3
SnX_6^{2-}	732.1[b]	-	2079.0[b]	-

(a) ±2 ppm for observed values; (b) major peaks; (c) ClCl = -61.008, ClN_3 = -46.550, N_3N_3 = -49.850 ppm; (d) BrBr = -173.250, BrN_3 = -86.334, N_3N_3 = -49.475 ppm.

for the bromo-system. In the latter system there was less of an assignment problem since the other species resonate at appreciably higher field.

On assigning the shift of -673.0 ppm to $Sn(N_3)Cl_5^{2-}$ for the chloro-azido system, it was possible to calculate the rest of the shifts expected for the $SnCl_{6-n}(N_3)_n^{2-}$ series. This gave a rough guide to the assignment of the observed signals and predicted that two of the most distinct peaks present, at -635.1 and -614.5 ppm, would correspond to cis-$Sn(N_3)_2Cl_4^{2-}$ and fac-$Sn(N_3)_3Cl_3^{2-}$. This assignment seemed reasonable on the grounds that the cis and fac isomers were found to be favoured in the $PCl_{6-n}(N_3)_n^-$ series.[157] Thus the ClN_3 terms were calculated from these three assigned ions, a weighted average (as for the cyanides in the previous section) was taken, and this was used for the final calculations shown in Table 6.12. The assignments shown in the table were based on these calculations, apart from $Sn(N_3)_5Cl^{2-}$ which was assumed to give the resonance at -598.2 ppm on the grounds that this was the only peak visible apart from that for $Sn(N_3)_6^{2-}$ when n approached zero for the stoichiometry $Sn(N_3)_{6-n}Cl_n^{2-}$ of the solution prepared. The assignment of the peak at -622.6 ppm may be in error, since this was the most prominent signal in the 1:1 $SnCl_4/N_3^-$ mixture and could well represent the shift of a dimeric azide-bridged ion (for reasons mentioned earlier). Indeed it would not be surprising if the isomer trans-$Sn(N_3)_2Cl_4^{2-}$ was not seen, since there was no evidence of its analogue in the phosphorous series[157] and ^{31}P n.m.r. is a more sensitive probe than ^{119}Sn n.m.r. The peaks at -578.0 and -590.6 ppm were rather weak, and bearing in mind the difference of $Sn(N_3)_5Cl^{2-}$ from its calculated value, the assignments of these signals must remain tentative. There appeared to be a glut of peaks in a small 20 ppm band between about -595 and -615 ppm in some spectra, so there may be some unresolved resonances in this region and the peaks at -578.0 and -590.6 ppm could be due to other species.

Pairwise interactions proved of limited use in assigning the observed peaks to $SnBr_{6-n}(N_3)_n^{2-}$ ions. The values shown in Table 6.12. represent the best fit of any reasonable combination of assignments and use a BrN_3 term calculated as the weighted average of the individual terms from $Sn(N_3)_5Br^{2-}$, trans- and cis-$Sn(N_3)_4Br_2^{2-}$ and fac-$Sn(N_3)_3Br_3^{2-}$. A comparison of the calculated and experimentally determined figures quickly shows a poor correlation. The assignments of cis-$Sn(N_3)_2Br_4^{2-}$ and $Sn(N_3)Br_5^{2-}$ were therefore made on the grounds that these peaks were important features in the spectra obtained from samples with a high $Br:N_3$ ratio and cannot reasonably be assigned to any other species. On chemical grounds these species are both expected to be present, since in the tin and phosphorus azidochloro-ions the introduction of the first N_3 group seems to favour cis-substitution by a second N_3. Statistically cis substitution is favoured 4:1 compared with trans, but the trans isomer was not detected in the phosphorus series,[157] implying that electronic effects also favour cis substitution. It was similarly found that gem-substitution of Cl or Br by N_3 occurred exclusively in cyclic halophosphazenes, and that the presence of an azide group activated the gem halide group to such an extent that the mono-substituted species could not be detected.[157] The designation of the signal at -1075.5 ppm to mer-$Sn(N_3)_3Br_3^{2-}$ may also be erroneous since this peak was predominant in $SnBr_4/N_3^-$ mixtures of 1:1 stoichiometry, and it may well arise from an azide bridged dimer.

The method of pairwise interactions may not work well for this series because of geometrical effects. The disparity of size between azide and bromide, and the difference in their electronic effects, may lead to a distortion of the regular octahedral geometry necessary for consistent pairwise terms to be obtained for all the ions. Since the Sn-N bonds of

the azides should normally be considerably shorter than the Sn-Br bonds, the close approach of the more electronegative azides would make them more electron repelling than the bromide ligands. These effects may be particularly marked when the first and second (cis)N_3^- groups are introduced, accounting for the large deviation between experimental and calculated values for these ions. The trans isomer $Sn(N_3)_2Br_4^{2-}$ (and also trans-$Sn(N_3)_4Br_2^{2-}$) are expected to have a more regular geometry. Pairwise interactions gave good agreement for at least part of the $SnCl_{6-n}(N_3)_n^{2-}$ series and worked reasonably for the $PCl_{6-n}(N_3)_n^-$ series,[157] but Cl is both smaller and more electronegative than Br, which could well reduce these effects considerably.

Another way of assigning the peaks in the $SnBr_{6-n}(N_3)_n^{2-}$ series would be to assume a statistical distribution of the ligands throughout the complexes. This would predict that the cis:trans and fac:mer ratios for those isomers should be in the intensity ratios of 4:1 and 2:3 respectively. Furthermore if it is assumed that the same substitution pattern prevails for tin as for phosphorous[120,157,158] the cis and fac isomers will be favoured, and in such a widely separated series (∿ 1500 ppm between $Sn(N_3)_6^{2-}$ and $SnBr_6^{2-}$) the ions of different stoichiometry are most unlikely to have overlapping shifts; cis (or fac) isomers also tend to give signals at higher field than the corresponding trans (or mer) isomers. Table 6.12. reveals there were ten major peaks observed for the azidobromostannates (IV) and this is the number expected if each isomer in the $Sn(N_3)_{6-n}Br_n^{2-}$ series is present. On this basis the assignments would be:

n = 0	-593.7	n = 4	-1346.3 (trans)
n = 1	-642.4		-1532.5 (cis)

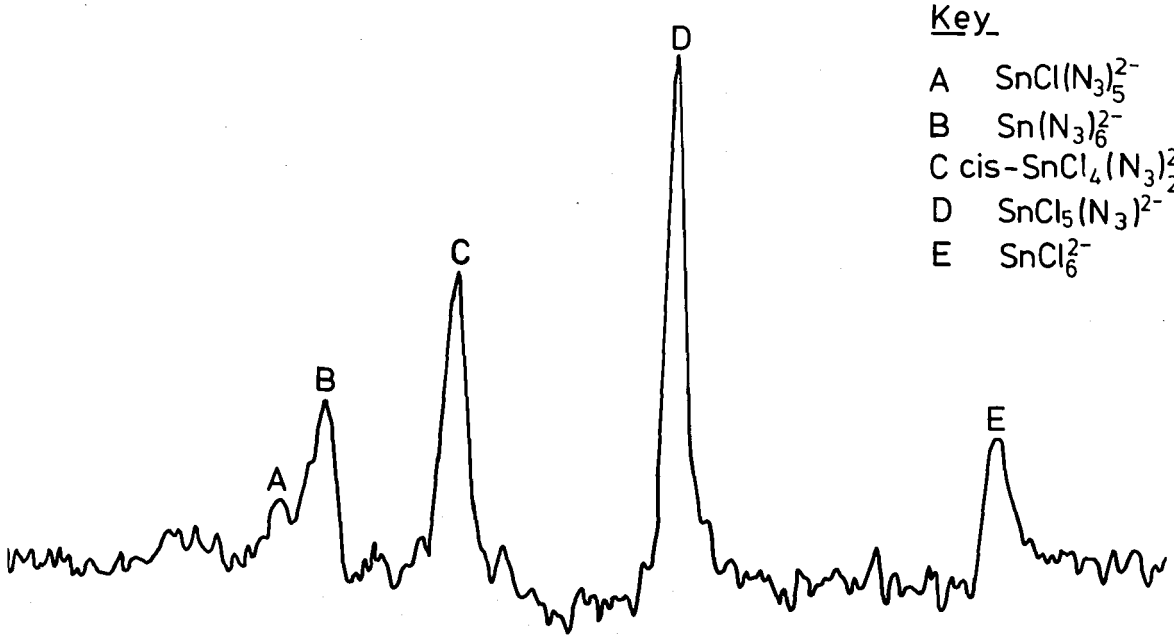
Figure 6.10

Sample ^{119}Sn n.m.r. Spectra from the Azidohalostannates (IV)

$SnCl_4 + 2But_4NN_3$ in CH_2Cl_2

Spectral width 223ppm

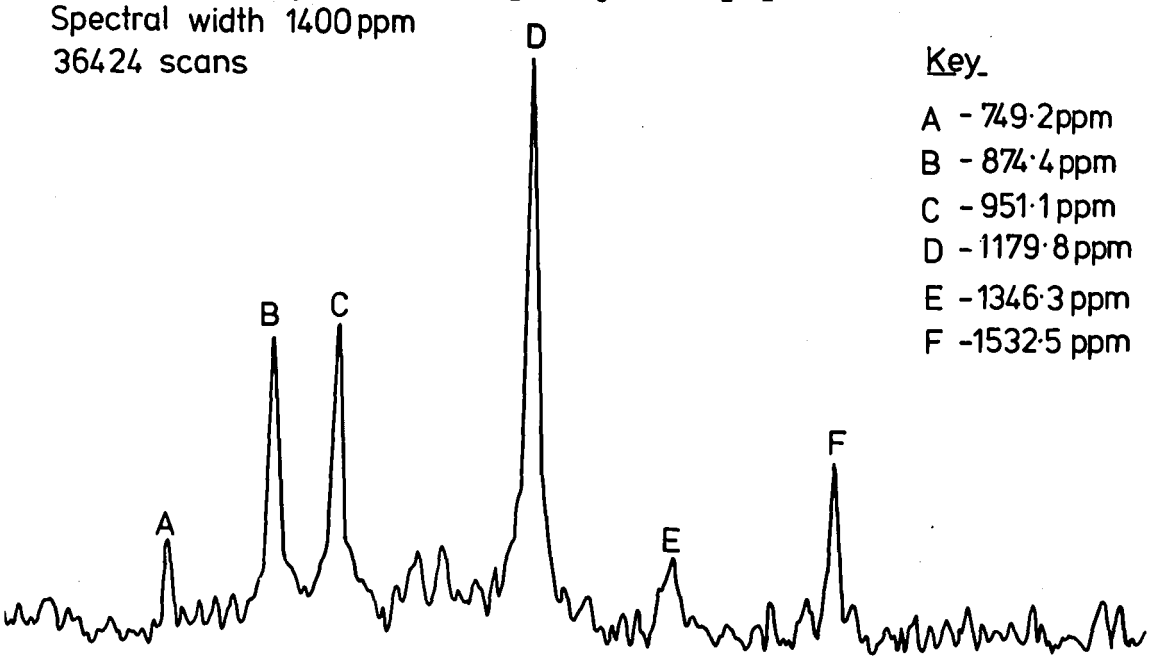
35187 scans



$3{\cdot}5(But_4P)_2Sn(N_3)_6 + 2{\cdot}5(But_4P)_2SnBr_6$ in CH_2Cl_2

Spectral width 1400ppm

36424 scans



n = 2	-749.2 (trans)	n = 5	-1818.1
	-874.4 (cis)	n = 6	-2079.0 ppm
n = 3	-951.1 (mer)		
	-1179.8 (fac)		

It can be seen from Figure 6.10. that such assignments put the cis and fac isomers as the dominant ones, although this was not always the case in all the spectra. Additionally this method allows the assignment of the major peak at -642.4 ppm (Table 6.12.) which pairwise interactions did not, but this peak could correspond to an azide-bridged dimer containing only one or two Br ligands (since it is quite close to the shift of $Sn(N_3)_6^{2-}$).

The assignments from this method were applied in a pairwise treatment and all of the BrN_3 terms calculated. These are shown in Table 6.13. and clearly exhibit a tendency for increasing numbers of bromine substituents to increase the pairwise terms, in an analogous fashion to the cyanide system. This observation perhaps gives some credence to these assignments although the overall conclusion must be that pairwise interactions are insufficient to account for the overall variation in shifts.

Table 6.13.

Pairwise Interaction Parameters from the $SnBr_{6-n}(N_3)_n^{2-}$ series

Ion	BrN_3 term/- ppm*	Ion	BrN_3 term
$SnBr(N_3)_5^{2-}$	61.65	fac $SnBr_3(N_3)_3^{2-}$	85.27
trans $SnBr_2(N_3)_4^{2-}$	68.91	trans $SnBr_4(N_3)_2^{2-}$	81.66
cis $SnBr_2(N_3)_4^{2-}$	75.63	cis $SnBr_4(N_3)_2^{2-}$	102.80
mer $SnBr_3(N_3)_3^{2-}$	63.22	$SnBr_5(N_3)^{2-}$	108.03

Calculated from N_3N_3 = -49.475, BrBr = -173.250 ppm.

(iii) Thiocyanate Complexes

Tetrabutylammoniumhexathiocyanatostannate was prepared and its exchange reactions with hexachloro- and hexabromostannate ions were studied in dichloromethane. It was found that freely exchanging systems were produced on mixing the thiocyanato- and halostannates, or by adding NH_4NCS to halostannates, and that the relative intensities of the exchange peaks in the ^{119}Sn n.m.r. spectra could be controlled by varying the proportions of the thiocyanate and halide ions. Several spectra for each system were thus obtained and average values of the chemical shifts corresponding to each species were evaluated. These results together with assignments based on pairwise interactions are shown in Table 6.14.

The shift of -842.5 ppm is that of $(But_4N)_2Sn(NCS)_6$ in CH_2Cl_2 and does not come from the spectra of samples also containing halogens, since it has a relatively broad linewidth and was only properly identified on its own. The NCSNCS pairwise term was thus obtained from this measurement. The ClCl and BrBr terms were also simply obtained from the known positions of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ (a peak at -734.2 ppm was checked to confirm that it did not correspond to $SnCl_6^{2-}$ by preparation of a sample containing mostly Cl and little NCS and noting the position of the largest peak).

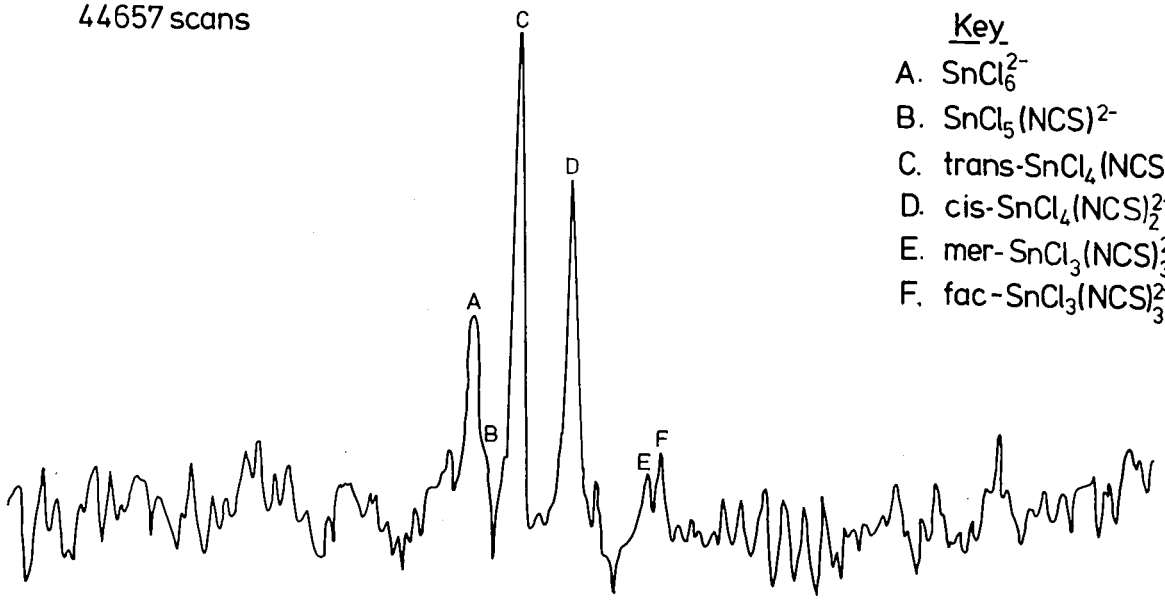
In the $SnCl_{6-n}(NCS)_n^{2-}$ system the peak at -809.8 ppm was initially assigned to n = 5 and the shifts of the other ions were calculated approximately. From these calculations it was then possible to assign peaks to all the species with n = 1, 2, 3 and 4 and individual values of the ClNCS term for each one could be calculated. The weighted average of these terms was then taken as for the cyanides and azides and this figure was the one used for the calculations in Table 6.14. A similar procedure was adopted for the $SnBr_{6-n}(NCS)_n^{2-}$ system: by first picking out δ = -1786.0 ppm

Figure 6.11.

Sample ^{119}Sn n.m.r. Spectra of the Halothiocyanatostannates(IV)

$3{\cdot}5\ SnCl_6^{2-} + 2{\cdot}5\ Sn(NCS)_6^{2-}$ in CH_2Cl_2

Spectral width 223 ppm
44657 scans

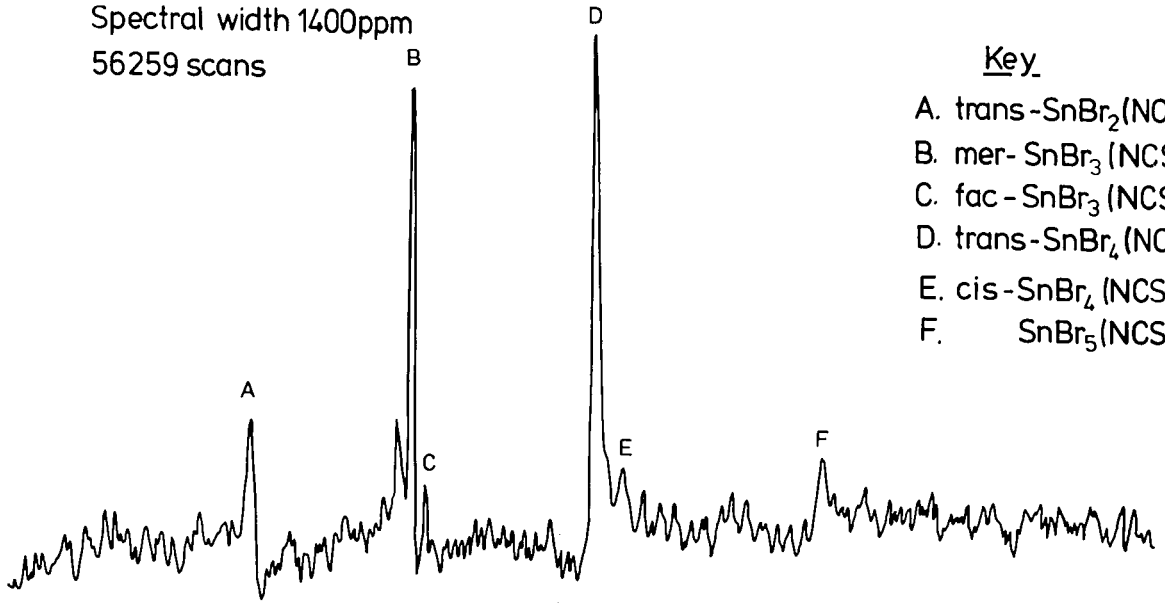


Key

A. $SnCl_6^{2-}$
B. $SnCl_5(NCS)^{2-}$
C. trans-$SnCl_4(NCS)_2^{2-}$
D. cis-$SnCl_4(NCS)_2^{2-}$
E. mer-$SnCl_3(NCS)_3^{2-}$
F. fac-$SnCl_3(NCS)_3^{2-}$

$SnBr_6^{2-} + 3NH_4SCN$ in CH_2Cl_2

Spectral width 1400 ppm
56259 scans



Key

A. trans-$SnBr_2(NCS)_4^{2-}$
B. mer-$SnBr_3(NCS)_3^{2-}$
C. fac-$SnBr_3(NCS)_3^{2-}$
D. trans-$SnBr_4(NCS)_2^{2-}$
E. cis-$SnBr_4(NCS)_2^{2-}$
F. $SnBr_5(NCS)^{2-}$

Table 6.14.

Chemical Shifts of Halothiocyanoatostannates (IV) in CH_2Cl_2

Ion	-δ/ppm[a]			
	X=Cl		X=Br	
	Observed	Calculated[c]	Observed	Calculated[d]
SnX_6^{2-}	731.9	-	2065.5	-
$SnX_5(NCS)^{2-}$	734.2[b]	736.3	1786.0	1784.4
trans-$SnX_4(NCS)_2^{2-}$	740.0	740.7	1515.2	1502.2
cis-$SnX_4(NCS)_2^{2-}$	749.3	747.7	1547.5	1541.3
mer-$SnX_3(NCS)_3^{2-}$	764.6	759.1	1295.2	1298.2
fac-$SnX_3(NCS)_3^{2-}$	766.8	766.2	1310.8	1337.3
			1274.7	
trans-$SnX_2(NCS)_4^{2-}$		775.6	1098.4	1094.2
cis-$SnX_2(NCS)_4^{2-}$	783.3	784.6		1133.3
$SnX(NCS)_5^{2-}$	809.8	810.0	946.4	968.4
$Sn(NCS)_6^{2-}$	842.5	-	842.5	-

(a) ±2 ppm for observed values; (b) weak peak; (c) ClCl = -60.992, ClNCS = -62.092, NCSNCS = -20.208 ppm; (d) BrBr = -172.208, BrNCS = - 101.674, NCSNCS = -70.208 ppm.

corresponding to $SnBr_5(NCS)^{2-}$, most of the other species could be identified and the weighted average of all the BrNCS terms thus found was computed. Table 6.14. shows that pairwise interactions gives a reasonable fit to the experimental data for the thiocyanates.

The chlorothiocyanatostannate spectra show the absence of trans-$SnCl_2(NCS)_4^{2-}$, and that fac-$SnCl_3(NCS)_3^{2-}$ and trans-$SnCl_4(NCS)_2^{2-}$ are the favoured

isomers over their respective counterparts. A cis-, mer-, trans-sequence (for increasing Cl) was observed for the $PCl_{6-n}(NCS)_n^-$ series,[160] but $NbCl_{6-n}(NCS)_n^-$ on the other hand shows a cis-, fac-, cis-preference.[150] The $SnBr_{6-n}(NCS)_n^{2-}$ series, however, shows preference for the trans-, mer- and trans-isomers for n = 2, 3, and 4 respectively. This sequence implies that a particular stability exists for trans-NCS groups and may be indicative of the type of trans-effect noted previously for square planar complexes[161] i.e. the NCS ligand labilises the substitute in a trans-position to itself. No such simple rationale seems possible for the chloro-system, however, though the higher electronegativity of chloride than bromide may have an effect.

The i.r. spectrum of $(But_4N)_2Sn(NCS)_6$ shows a strong absorption at 2050 $cm.^{-1}$ which is indicative of N-bonded NCS.[162] It is therefore assumed that this is the mode of bonding existing throughout the mixed halo-thiocyanato-complexes. There are sufficient peaks in each series to account for all N-bonded NCS and little evidence of S-bonded ligands (unlike $NbCl_{6-n}(NCS)_n^-$ where both types of bonding were found to occur[150]). The only strong peak unassigned is one at -1274.7 ppm from the bromothiocyanato-stannate system and the presence of an S-bonded NCS tin species might account for this.

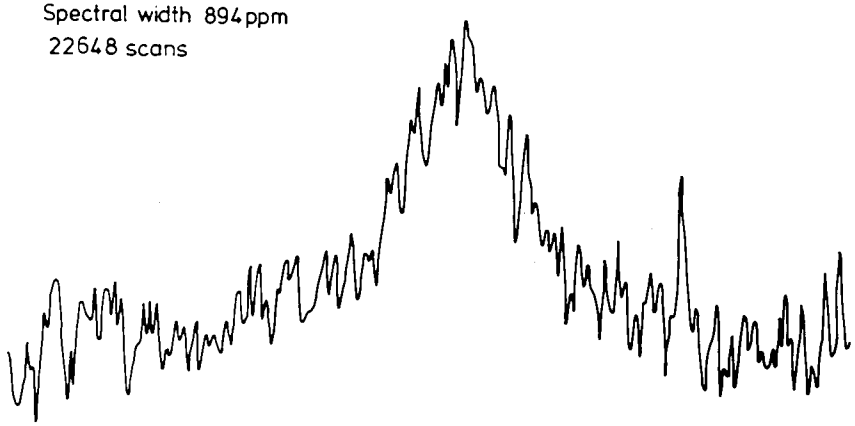
(f) Solid State N.m.r. Spectra of Tin (IV) Compounds

The ^{119}Sn n.m.r. spectra of solid $(Me_3S)_2SnCl_6$, $(Me_3S)_2SnBr_6$ and K_2SnF_6 showed broad resonances at -710, -2140 (estimated) and -810 ppm respectively, and are shown in Figure 6.12. No signal was detected for $(Me_3S)_2SnI_6$. Unlike the stannous halides in the previous chapter, these compounds give resonances of similar magnitude to their solution shifts (i.e. $SnCl_6^{2-}$:-734 ppm; SnF_6^{2-}:-810 ppm; $SnBr_6^{2-}$:-2080 ppm). This is not

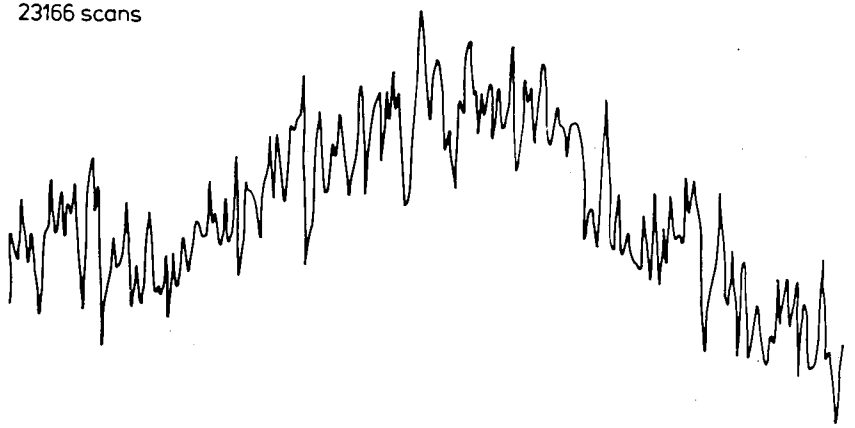
Figure 6.12.

Solid State ^{119}Sn n.m.r. Spectra of some Tin(IV) Compounds

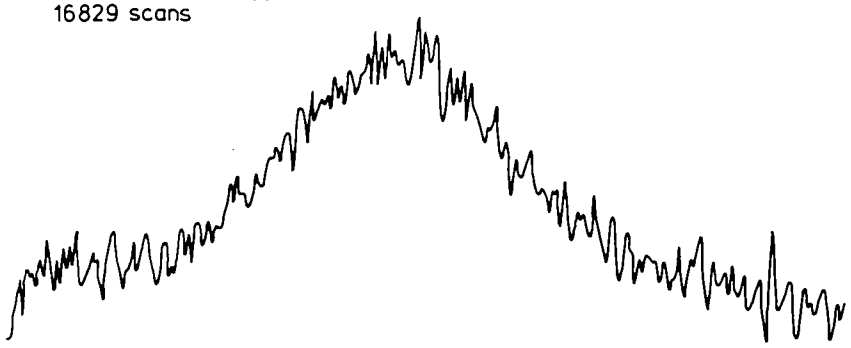
$(Me_3S)_2SnCl_6$
Spectral width 894 ppm
22648 scans



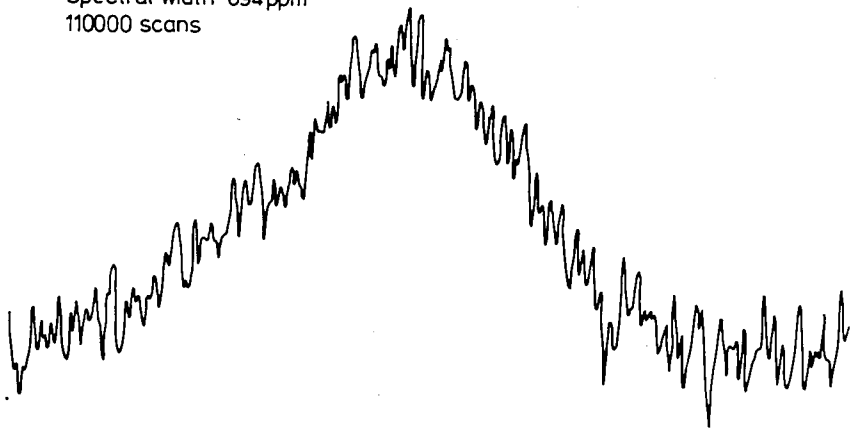
$(Me_3S)_2SnBr_6$
Spectral width 894 ppm
23166 scans



K_2SnF_6
Spectral width 894 ppm
16829 scans



SnF_4
Spectral width 894 ppm
110000 scans



surprising since the hexahalostannate ions exist as such in the solid state[122] while the stannous halides often have tin with various co-ordination numbers (from 4 to 8) in the solid state[122] but probably are no more than three- or four-fold co-ordinated in solution. Similarly solid SnF_4 (δ = -720 ppm) and solid SnI_4 (δ = -1800 ppm) gave shifts in approximately the same positions as they gave in solution: SnF_4 in H_2O (δ = -761.8 ppm) and SnI_4 in CS_2 (δ = -1700 ppm). The exact environments of the tin in these cases are not expected to be the same in solution and in the solid state, although the similarity of the shifts indicates that magnetic environments in each are similar. A "solid state" spectrum of neat $SnBr_4$ yielded a shift of -654.6 ppm, but this was really the shift of the liquid since the sample melted in the n.m.r. probe. This value compares well with a figure of -636.7 ppm for $SnBr_4$ in CS_2.

All of the tin (IV) solid state n.m.r. spectra produced extremely broad resonances and a line-narrowing technique would be necessary to obtain more useful results from these compounds.

(g) Experimental

(i) General

The quantities of all reactants in the n.m.r. experiments were determined by weighing except for ClCN which was measured by a graduated cold finger on the vacuum line. The tetrapentylammonium halides and anhydrous stannic halides were handled in the glove box to avoid moisture, but this was found to be largely unnecessary for the stannate salts of the tetrapentylammonium and other bulky cations. But_4NF was supplied by Dr. C.J. Ludman of this department in the form of a water clathrate containing between 27 and 33 moles of H_2O. The exact fluoride content was determined by elemental analysis. This compound was used to obtain the

$SnCl_{6-n}F_n^{2-}$ salts, by addition of the fluoride to appropriate quantities of $SnCl_4$, SnF_4 and $Pent_4NCl$ in CH_2Cl_2. Once the fluoride dissolved in CH_2Cl_2, the water separated out and was pipetted off. Little evidence of hydrolysis was noted in using this procedure.

(ii) Preparation of Compounds

$(But_4P)_2SnCl_6$. But_4PCl and $SnCl_4$ were stirred in cHCl in a 2:1 ratio for $\sim$ 1 hr. The resulting solid was filtered off, dried under vacuum and recrystallised from acetone to give white needles of product.

Analysis:

$(But_4P)_2SnCl_6$ requires C 45.19% H 8.47%

found C 45.32% H 8.90%

^{119}Sn n.m.r. spectrum: single peak at -734.2 ppm (in CH_2Cl_2).

$(But_4P)_2SnBr_6$. But_4PCl and $SnBr_4$ in a 2:1 ratio were stirred in a large excess of cHBr for several hours. The resulting solid was then filtered off, dried under vacuum and recrystallised from acetone to give yellow needles of product.

Analysis:

$(But_4P)_2SnBr_6$ requires C 34.41% H 6.45% P 5.56% Sn 10.64% Br 42.97%

found C 34.57% H 7.32% P 4.6% Sn 12.05% Br 40.4%

The ^{119}Sn n.m.r. of the product in CH_2Cl_2 showed a small peak corresponding to $SnBr_5Cl^{2-}$ (δ = -1815 ppm), though the Cl impurity was judged to be of the order of only 1% from the relative intensities of the $SnBr_6^{2-}$ (δ = -2075 ppm) and $SnBr_5Cl^{2-}$ peaks.

$(Me_3S)_2SnI_6$. SnI_4 was recrystallised from $CHCl_3$ and then redissolved in a fresh quantity of the same solvent. The stoichiometric quantity of Me_3SI in acetone was then added and the mixture stirred for 30 mins. The

product obtained showed evidence of incomplete reaction so it was stirred in a 50/50 mixture of cHI and acetone for 2 hrs. before filtering off and washing with EtOH and Et_2O. The product was then dried in a desiccator.

Analysis:

$(Me_3S)_2SnI_6$ requires C 6.96% H 1.74% S 6.19% Sn 11.48% I 73.63%

found C 7.15% H 1.73% S 6.3% Sn 11.9% I 70.1%

$(Prop_4N)_2SnI_6$. 5.59 mmoles of SnI_4 (freshly recrystallised from $CHCl_3$) and 11.19 mmoles $Prop_4NI$ were each dissolved in 50 mls. of $CHCl_3$ and added together. An instant black precipitate was formed which was filtered off and washed with Et_2O.

Analysis:

$(Prop_4N)_2SnI_6$ requires C 23.00% H 4.48% N 2.24% Sn 9.48% I 60.81%

found C 22.3% H 4.69% N 2.6% Sn 7.45% I 60.55%

$(Et_4N)_2Sn(N_3)_6$ was prepared according to the literature. $(Et_4N)_2SnCl_6$ was stirred overnight in acetone with an excess of NaN_3. Precipitation of a white solid resulted on addition of Et_2O, and further purification was obtained by redissolving this solid and again precipitating out the product with ether. This was then filtered off and washed with Et_2O.

Analysis:

$(Et_4N)_2Sn(N_3)_6$ requires C 30.44% H 6.34% N 44.40% Sn 18.82%

found C 29.06% H 7.39% N 39.93% Sn 19.4%

i.r. spectrum: lit.[93]: 2115(m), 2080(vs), 1348(m), 1288(s), 659(s), 601(m), 390(s,br), 330(w,sh), 220(s)

found: 2115(m), 2070(vs), 1345(m), 1290(s), 660(m), 601(w), 390(s), 330(vw) $cm.^{-1}$.

$(But_4P)_2Sn(N_3)_6$. $(But_4P)_2SnBr_6$ was stirred for 48 hrs. with 8 equivalents of NaN_3 in CH_2Cl_2. The resulting solid was then filtered off and most of the

CH_2Cl_2 removed on the vacuum line at ∿ 310K. The remainder of the solvent was then removed by stirring the residue with 30 - 40° petroleum ether for 12 hrs. to give a pinkish precipitate of the product. This was filtered off and dried in vacuo.

Analysis:

$(But_4P)_2Sn(N_3)_6$ requires C 43.21% H 8.10% N 28.36% Sn 13.36% P 6.98%

found C 49.68% H 8.23% N 26.85% Sn 14.8% P 2.6%*

i.r. spectrum: azide vibrations: 2060(vs,br), 600(m), 388(s), 335(w), 220(s) $cm.^{-1}$

$(But_4N)_2Sn(NCS)_6$. $(But_4N)_2SnBr_6$ was stirred with 10 equivalents of NH_4SCN for 24 hrs. in acetone. The volume of the solvent was then reduced. A precipitate was formed on the addition of 30 - 40° petroleum ether which was filtered off and washed with Et_2O. This was then redissolved in CH_2Cl_2, filtered to remove any remaining NH_4SCN, and pumped to dryness on the vacuum line.

Analysis:

$(But_4N)_2Sn(NCS)_6$ requires C 47.96% H 7.57% N 11.78% Sn 12.49% S 20.20%

found C 46.90% H 8.14% N 12.10% Sn 11.34% S 18.73%

i.r. spectrum; NCS vibrations: 2050(vbr,vs), 380(s), 310(br,vs), 230(w) $cm.^{-1}$.

(iii) Attempts to Prepare Hexacyanostannate Complexes

0.88 mmoles $(Prop_4N)_2SnI_6$ and 5.56 mmoles of AgCN were stirred in 35 mls. acetone for about ½ hr. The initial dark red solution turned colourless and 1.3 g. of a yellow precipitate were formed (1.29 g. of AgI were expected for complete reaction). The solid was removed by filtration and attempts to precipitate the product by addition of Et_2O initially failed. The volume of the solution was therefore reduced, by blowing N_2 gas over it, until only

* Analytical difficulties were experienced with the phosphorous analysis.

10 mls. remained. Et_2O was again added and a pinkish precipitate formed which was filtered off and washed with Et_2O.

Analysis:

$(Prop_4N)_2Sn(CN)_6$ requires C 55.67% H 8.66% N 17.32% Sn 18.35%

found C 46.82% H 6.96% N 10.78% Sn 8.4% Ag 25.4% I 3.1%

The analyses clearly indicate that the preparation failed and that a mixture of products was probably obtained. A repeated attempt, using $(Pent_4N)_2SnI_6$ (prepared "in situ" from SnI_4 and $2Pent_4NI$) with 8 equivalents of AgCN also gave analyses indicating the presence of silver (41.2%) with little tin (12.32%), though no iodine was found this time.

Further attempts proceeded under dry, oxygen-free conditions (i.e. under a nitrogen atmosphere). 6.4 mmoles $(Et_4N)_2SnI_6$ (prepared "in situ" from SnI_4 with 2 equivalents of Et_4NI) were stirred with 43.8 mmoles AgCN in CH_2Cl_2 for 48 hrs. The solids were then filtered off and washed several times with CH_2Cl_2. (The washings were pumped on the vacuum line to yield only 0.5 g. of a yellow, waxy solid which gave no ^{119}Sn n.m.r. signals in CH_2Cl_2.) The solids were then stirred in $\sim$ 80 mls. EtOH and the solution was filtered. The EtOH washings were then allowed to evaporate slowly under N_2 for 48 hrs. to leave a white product.

Analyses:

Solid residues from EtOH washings: C 5.49% H 1.30% N 1.13% Ag 31.9% I 59.2%

White product : C 40.77% H 7.98% N 13.98% Ag 34.9%

I 0.81% Sn 0%

$(Et_4N)Ag(CN)_2$ requires : C 41.4% H 6.90% N 14.49% Ag 37.20%

The analyses indicate that the product formed was $(Et_4N)Ag(CN)_2$ with a small amount of Et_4NI. It is not understood where the tin went in this reaction.

Reactions were also attempted between $(Et_4N)_2SnI_6$ and $Zn(CN)_2$, both in

CH_2Cl_2 and $EtNO_2$ solution by stirring for 24 hrs. Unfortunately, however, only the starting materials were isolated and it is concluded that no reaction occurred.

CHAPTER 7

Suggestions for Future Work

Instrumentally, the development of nuclear quadrupole resonance spectrometers lags some way behind that of their nuclear magnetic resonance counterparts, despite the evolution of the two techniques at a similar time (c. 1950). The n.m.r. spectrometers used in modern day chemistry are most commonly Fourier transform pulsed instruments and have a high sensitivity, while most n.q.r. measurements in the literature are derived from super-regenerative oscillator type spectrometers which give single scan spectra. These n.q.r. machines are analogous to the outmoded continuous wave n.m.r. instruments formerly used. Rapid advances in n.q.r. spectroscopy could be made once the electronic difficulties of building general purpose pulsed n.q.r. spectrometers are overcome. In routine work, spectra should be able to be accumulated in far less time and the sensitivity of the technique would be improved. Furthermore the complex lineshapes obtained from the superregenerative oscillators would be replaced by simple absorption (perhaps Gaussian) curves, thus facilitating the resolution of closely spaced lines. It is not anticipated that much could be done to narrow the linewidths of the signals because of the inherent quadrupolar broadening of the nuclei, although special pulse sequences may possibly be devised when the necessary spectrometers become available, and these may effect some line narrowing as seen in solid state n.m.r. spectroscopy. Several n.q.r. measurements from pulsed spectrometers have been reported, particularly in the Russian literature, but no instruments are commercially available at present.

When more sensitive n.q.r. equipment is operational it would probably prove worthwhile to repeat the measurements in this work on those compounds which gave no signals on the current machine. These should undoubtedly give signals when in a sufficiently pure state, since it is most unlikely that the quadrupolar nuclei present in any of them are situated in spherically symmetrical electric field gradients. Thus further data could be accumulated to check the validity of the bond length/frequency relationships already established. In this context it would also be desirable to have x-ray diffraction data on previously undetermined structures of the halostannates for which n.q.r. results have been obtained. The structures of $MeNH_3SnCl_3$, $Me_2NH_2SnCl_3$ and $Me_3NHSnCl_3$ would be particularly useful. The investigation of bond length/frequency correlations might also be extended into the tribromostannates and the use of a higher frequency instrument allowing ^{127}I resonances to be detected, would also enable the work to be extended to iodostannates.

The spectra from the variable temperature n.q.r. experiments often gave signals which were closely spaced and poorly resolved. This made it difficult to measure them and to judge their relative intensities. Clearly, should better instruments become available, some of the results would be worth checking, and perhaps fine structure in the lines might be observed, as for the low temperature phase of $(pyH)_2SnCl_6$. This may in turn lead to a better understanding of the structural phase changes which occur. Low temperature crystal structure determinations would of course give valuable information as well. More sensitive spectrometers would also remove the possibility of missing resonances, as was the case in the study of $(Me_4N)_2SnCl_6$.

It is expected that many of the distorted hexachloro- and hexabromo-stannate ions should attain regular octahedral geometries once high enough

temperatures are reached. Hence measurements at higher temperatures on compounds which exhibit more than one n.q.r. line at 300K should show the presence of further phase changes. Once the complete range and nature of these transitions are established, a full insight into the processes involved might be attained.

The tin (II) halide solutions studied by ^{119}Sn n.m.r. spectroscopy showed a marked dependence on concentration and temperature, but although various equilibria were proposed to account for this behaviour, further research would be necessary to establish conclusively the species present. This might take the form of n.m.r. experiments at varying temperatures. Such results should lead to obtaining some thermodynamic data, e.g. ΔH values for the equilibria. At low temperatures it might also be possible to slow down the chemical exchange to a point where the different tin-containing species in solution give separate signals instead of single average exchange peaks. Low temperature experiments might also lead to line narrowing for $SnCl_4$ and $SnBr_4$ and their exchange products in ethanol and methanol. This would be necessary before the species present in these solutions could be adequately identified. Low temperatures might also help to narrow the (presumed) very broad resonances of SnI_6^{2-} which were not detected.

An alternate method for resolving overlapping signals in n.m.r. is to rerun the spectra on an instrument with a more powerful magnet. Apart from the $SnCl_4/SnBr_4$ system mentioned above, the $SnCl_{6-n}(N_3)_n^{2-}$ system where several peaks around -600 ppm were noted, would benefit from this method of investigation. Further research is also necessary into the six-co-ordinate pseudohalide complexes of tin (IV) to confirm the predicted assignments of the peaks in the n.m.r. spectra for those compounds where poor agreement

was obtained between observed and calculated shifts. This may take the form of further n.m.r. measurements though an adaption of, or a replacement for, the pairwise interaction theory needs to be evolved to improve the accuracy of the predictions. Perhaps taking into account the relative electronegativities or π-bonding capabilities of ligands, together with their effects on the geometries of the complex ions, might help, although it is difficult to see how this could be done in any simple way. Many of the species in solution have never been isolated individually, so there is a lack of structural information, and probable structures would have to be calculated from ligand dimensions and data for other systems. There is also room for further work to be carried out to identify and isolate the azide-bridged dimers presumed to exist, or cyano-derivatives of tin (II) or tin (IV).

The ^{119}Sn n.m.r. solid state spectra invariably consisted of very broad lines. Dipolar interactions present in the crystals cause a certain amount of this broadening and these could be largely removed by the application of special pulse sequences or magic angle spinning (or both).[163] Should accurate enough data be obtained it would then be interesting to compare the solid state n.m.r. results with the corresponding n.q.r. data. This might enable accurate calculations of the field gradient and chemical shielding tensors to be made. Accurate solid state measurements could also confirm whether mixed halostannates of the type $SnX_4Y_2^{2-}$ can be formed purely in the cis configuration as reported from vibrational spectroscopy,[50] since both cis and trans isomers are certainly present in solution.

APPENDIX

Lectures, Seminars, Conferences and Induction Courses

(a) Lectures and Seminars Organised by the Department of Chemistry from October 1979 to October 1982

(* denotes those attended by the author)

*21 November 1979

Dr. J. Muller (University of Bergen),

"Photochemical Reactions of Ammonia".

*28 November 1979

Dr. B. Cox (University of Stirling),

"Macrobicyclic Cryptate Complexes, Dynamics and Selectivity".

5 December 1979

Dr. G.C. Edmond (University of Liverpool),

"Synthesis and Properties of Some Multicomponent Polymers".

12 December 1979

Dr. C.I. Ratcliffe (University of London),

"Rotor Motions in Solids".

*19 December 1979

Dr. K.E. Newman (University of Lausanne),

"High Pressure Multinuclear N.m.r. in the Elucidation of the Mechanisms of Fast, Simple Reactions".

*30 January 1980

Dr. M.J. Barrow (University of Edinburgh),

"The Structures of Some Simple Inorganic Compounds of Silicon and Germanium-Pointers to Structural Trends in Group IV".

6 February 1980

Dr. J.M.E. Quirke (University of Durham),

"Degradation of Chlorophyll-a in Sediments".

23 April 1980

B. Grievson (University of Durham),

"Halogen Radiopharmaceuticals".

14 May 1980

Dr. R. Hutton (Waters Associates, U.S.A.),

"Recent Developments in Multi-milligram and Multi-gram Scale Preparative High Performance Liquid Chromatography".

21 May 1980

Dr. T.W. Bentley (University of Swansea),

"Medium and Structural Effects in Solvolytic Reactions".

10 July 1980

Professor P. Des Marteau (University of Heidelburg),

"New Developments in Organonitrogen Fluorine Chemistry".

*7 October 1980

Professor T. Felhner (Notre-Dame University, U.S.A.),

"Metalloboranes - Cages or Co-ordination Compounds"?

15 October 1980

Dr. R. Adler (University of Bristol),

"Doing Chemistry Inside Cages - Medium Ring Bicyclic Molecules".

*12 November

Dr. M. Gerloch (University of Cambridge),

"Magnetochemistry is about Chemistry".

19 November 1980

Dr. T. Gilchrist (University of Liverpool),

"Nitroso Olefins as Synthetic Intermediates".

*3 December 1980

Dr. J.A. Connor (University of Manchester),

"Thermochemistry of Transition Metal Complexes".

18 December 1980

Dr. R. Evans (University of Brisbane, Australia),

"Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry".

*18 February 1981

Professor S.F.A. Kettle (University of East Anglia),

"Variations in the Molecular Dance at the Crystal Ball".

*25 February 1981

Dr. K. Bowden (University of Sussex),

"The Transmission of Polar Effects of Substituents".

4 March 1981

Dr. S. Craddock (University of Edinburgh),

"Pseudo-linear Pseudohalides".

11 March 1981

Dr. J.F. Stoddard (I.C.I. Ltd./University of Sheffield),

"Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors".

17 March 1981

Professor W. Jencks (Brandsis University, Massachusetts),

"When is an Intermediate not an Intermediate"?

*18 March 1981

Dr. P.J. Smith (International Tin Research Institute),

"Organotin Compounds - A Versatile Class of Organometallic Compounds".

*9 April 1981

Dr. W.H. Meyer (R.C.A. Zurich),

"Properties of Aligned Polyacetylenes".

6 May 1981

Professor M. Syware, F.R.S.,

"Ions and Ion Pairs".

*10 June 1981

Dr. J. Rose (I.C.I. Plastics Division),

"New Engineering Plastics".

17 June 1981

Dr. P. Moreau (University of Montpellier),

"Some Recent Results in Perfluoroorganometallic Chemistry".

21 September 1981

Dr. P. Plimmer (Dupont),

"From Conception to Commercialisation of a Polymer".

*14 October 1981

Professor E. Kluk (University of Katowice),

"Some Aspects of the Study of Molecular Dynamics in Simple Molecular Liquids".

28 October 1981

Dr. R.J.H. Clark (University College London),

"Resonance Raman Spectroscopy - A New Technique for Chemical, Spectroscopic and Structural Studies".

6 November 1981

Dr. W. Moddeman (Monsanto Research Labs., St. Louis, Missouri),

"High Energy Materials".

*18 November 1981

Professor M.J. Perkins (Chelsea College),

"Spin Trapping and Nitroxide Radicals".

25 November 1981

Dr. M. Baird (University of Newcastle),

"Intramolecular Reactions of Carbenes and Carbenoids".

*9 December 1981

Dr. G. Beamson (University of Durham),

"Photoelectrons in a Strong Magnetic Field".

20 January 1982

Dr. M.R. Bryce (University of Durham),

"Organic Metals".

*27 January 1982

Dr. D.L.H. Williams (University of Durham),

"Nitrosation and Nitrosamines".

*3 February 1982

Dr. D. Parker (University of Durham),

"Modern Methods for the Determination of Enantiomeric Purity".

10 February 1982

Dr. D. Pethrick (Strathclyde),

"Conformational Dynamics of Small and Large Molecules".

*17 February 1982

Professor D.T. Clark (University of Durham),

"The Structure, Bonding, Reactivity and Synthesis of Polymer Surfaces".

*24 February 1982

Dr. L. Field (University of Oxford),

"The Application of N.m.r. Methods to the Study of Penicillin Biosynthesis".

3 March 1982

Dr. P. Bamfield (I.C.I. Organics Division),

"Computer Aided Synthesis Design: A View from Industry".

*17 March 1982

Professor R.J. Haines (University of Cambridge/University of Natal),

"Clustering around Ruthenium, Iron and Rhodium".

5 May 1982

Dr. G. Tennant (University of Edinburgh),

"Exploitation of the Aromatic Nitro-group in the Design of New Heterocyclisation Reactions".

*12 May 1982

Dr. C.D. Garner (University of Manchester),

"The Structure and Function of Molybdenum Centres in Enzymes".

*19 May 1982

Professor R.D. Chambers (University of Durham),

"Fluorocarbons - Some 'Alice in the Looking Glass' Chemistry".

*26 May 1982

Dr. A. Welch (University of Edinburgh),

"Conformation Patterns and Distortions in Carbamettaboranes".

14 June 1982

Professor C.M. Stirling (University College of Wales, Bangor),

"How Much Does Strain Affect Reactivity"?

28 June 1982

Professor D.J. Burton (University of Iowa),

"Some Aspects of the Chemistry of Fluorinated Phosphonium Salts and Phosphonates".

2 July 1982

Professor H.F. Koch (Ithaca College, U.S.A.),

"Proton Transfers to, and Elimination Reactions from, Localised and Delocalised Carbanions".

(b) Research Conference Attended

The 3rd Annual Congress of the Chemical Society, Durham, 9-11 April, 1980.

(c) First Year Induction Course

As an introduction to the services available within the chemistry department at Durham the following were discussed in one hour presentations:

(i)	Departmental Organisation	Dr. E.J.F. Ross
(ii)	Safety Matters	Dr. M.R. Crampton
(iii)	Electrical Appliances and Infrared Spectroscopy	Mr. R.N. Brown
(iv)	Chromatography and Microanalysis	Mr. T.F. Holmes
(v)	Library Facilities	Mr. W.B. Woodward (Keeper of Science Books)
(vi)	Atomic Absorptiometry and Inorganic Analysis	Mr. R. Coult

(vii)	Mass Spectrometry	Dr. M. Jones
(viii)	N.m.r. Spectroscopy	Dr. R.S. Matthews
(ix)	Glassblowing Techniques	Mr. W.H. Fettis and Mr. R. Hart

BIBLIOGRAPHY

1. L. Ramakrishnan, S. Soundararajan, V.S.S. Sastry and J. Ramakrishna, Coord. Chem. Revs., 22, 123 (1977).

2. D. Nakamura, Bull. Chem. Soc. Japan, 36, 1662 (1963) and references therein.

3. M. Kubo and D. Nakamura, Advances in Inorganic Chemistry and Radiochemistry, 8, 257 (1966).

4. C.H. Townes and B.P. Dailey, J. Chem. Phys., 17, 782 (1949).

5. B.P. Dailey and C.H. Townes, ibid., 23, 118 (1955).

6. H. Bayer, Z. Phys., 130, 227 (1951).

7. T. Kushida, J. Sci. Hiroshima Univ., Ser A: Maths. Phys. Chem., 19, 327 (1955).

8. R.L. Armstrong and K.R. Jeffrey, Can. J. Phys., 47, 1095 (1969).

9. R.L. Armstrong and D.F. Cooke, ibid., 49, 2381 (1971).

10. T. Kushida, G.B. Benedek and N. Bloembergen, Phys. Rev., 104, 1364 (1956).

11. R.J.C. Brown, J. Chem. Phys., 32, 116 (1960).

12. R. Keat, A.L. Porte, R.A. Shaw and D.A. Tong, J.C.S. Dalton, 1648 (1972).

13. T.S. Cameron, C.Y. Cheng, T. Demir, K.D. Howlett, R. Keate, A.L. Porte, C.K. Prout and R.A. Shaw, Angew. Chemie. Int. Ed., 11, 510 (1972).

14. C.W. Fryer, Chem. Comm., 902 (1970).

15. K.B. Dillon and T.C. Waddington, Inorg. Nucl. Chem. Lett., 14, 415 (1978).

16. D.E. Scaife, Aust. J. Chem., 24, 1753 (1971).

17. P.G. Huggett, R.J. Lynch, T.C. Waddington and K. Wade, J.C.S. Dalton, 1164 (1980).

18. T.B. Brill and W.A. Welsh, J.C.S. Dalton, 357 (1973).

19. T.B. Brill, R.C. Gearhart and W.A. Welsh, J. Mag. Res., 13, 27 (1974).

20. I.D. Brown, Can. J. Chem., 42, 2758 (1964).

21. R.L. Armstrong and H.M. van Driel, Advances in Nuclear Quadrupole Resonance, 2, 179 (1975).

22. K. Roessler and J. Winter, Chem. Phys. Lett., 46, 566 (1977).

23. R.G.C. McElroy, R.L. Armstrong and M. Sutton, J. Mag. Res., 38, 253 (1980).

24. C. Dimitropolous, J.J. van der Klink, J. Pelzl, M. Regelsberger and K. Roessler, Faraday Symp. Chem. Soc., 13, 124 (1978).

25. J.J. van der Klink and C. Dimitropolous, J. Mol. Struct., 58, 359 (1980).

26. E.A.C. Lucken, ibid., 58, 121 (1980).

27. A. Sasane, D. Nakamura and M. Kubo, J. Mag. Res., 3, 76 (1970).

28. J.D. Graybeal, R.J. McKown and S.D. Ing, J. Phys. Chem., 74, 1814 (1970).

29. C. Dimitropolous and J. Pelzl, J. Mol. Struct., 58, 107 (1980).

30. T. Kitayume, M. Sekiyaki and M. Suhara, ibid., 58, 161 (1980).

31. Y. Kume, R. Ikeda and D. Nakamura, J. Mag. Res., 33, 331 (1979).

32. R.W. Berg, J. Chem. Phys., 69, 1325 (1978).

33. J.E. Fergusson and P.F. Heveldt, Aust. J. Chem., 27, 661 (1974).

34. H. Negita, N. Nakamura and H. Chihara, Koen Yoshishu-Bunshi Koyo Sogo Toronkai, 44 (1979).

35. H. Negita, N. Nakamura and H. Chihara, Solid State Comm., 34, 949 (1980).

36. B.I. Swanson, Phys. Status Solidi A, 47, K95 (1978).

37. T. Higashi, S. Syoyama and K. Osaki, Acta Cryst., B35, 144 (1979).

38. R.C. Gearhart, T.B. Brill, W.A. Welsh and R.H. Wood, J.C.S. Dalton, 359 (1973).

39. R.W.G. Wyckoff and R.B. Corey, Am. J. Sci., 18, 437 (1929).

40. R.B. Corey and R.W.G. Wyckoff, Z. Kristallogr. (A), 89, 469 (1934).

41. W. Schaffer, Acta Cryst., 7, 242 (1954).

42. Structure Reports (for the International Union of Crystallography) - various references.

43. A.C.A. Monograph No. 5. Crystal Data Determinative Tables (2nd ed.).

44. J.A. Lerbscher and J. Trotter, Acta Cryst., B32, 2671 (1976).

45. O. Knop, T.S. Cameron and M.A. Jones, Can. J. Chem., 59, 2550 (1981).

46. A.V. Uvarov, Y.Y. Kharitonov, A.I. Gusev, V.D. Sheludyakov and S.N. Gurkova, Koordinatsionnaya Khimiya, 2, 712 (1976).

47. R.G. Whitehead, Ph.D. thesis (Durham), 1979.

48. C. Kung-Du, L. Chao-Fa and T. You-Chi, Acta Chim. Sinica, 25, 65 (1959).

49. J.A.A. Ketelaar, A.A. Rietdijk and C.H. van Staveren, Rec. Trav. Chim. de Pays Bas, 56, 907 (1937).

50. R.J.H. Clark, L. Maresca and L. Puddephat, Inorg. Chem., 7, 1603 (1968).

51. M.L. Good and C.A. Clausen, Proc. Symp. Coord. Chem., 1, 445 (1970).

52. M.L. Good and C.A. Clausen, Inorg. Chem., 9, 817 (1970).

53. F. Cariati, G. Marcotrigiano, L. Menabue, F. Moraynoni, G.C. Pellacani and G.M. Nanderigli, Spectrochimica Acta, 34A, 801 (1978).

54. W.E. Schwarty, P.H. Watts, J.C. Watts, E.R. Lippincott and J.E. Huhey, Inorg. Chem., 11, 2632 (1972).

55. W.E. Schwarty, P.H. Watts, J.C. Watts, E.R. Lippincott, J.W. Brasch, Anal. Chem., 44, 2001 (1972).

56. T.N. Sumarkova, R.A. Slavinskaya, I.G. Lutvyak and Z.F. Orlova, Zh. Neorg. Khim., 13, 712 (1968).

57. K. Nielsen and R.W. Berg, Acta Chem. Scand., A34, 153 (1980).

58. S.R.A. Bird, J.D. Donaldson and J. Silver, J.C.S. Dalton, 1950 (1972).

59. J.D. Donaldson, D.G. Nicholson and G.J. Senior, J. Chem. Soc. (A), 2928 (1968).

60. G. Bergerhoff, L. Goost and E. Schultye-Rhonhof, Acta Cryst., B24, 803 (1968).

61. G. Bergerhoff and H. Namgung, ibid., B34, 699 (1978).

62. R.J.H. Clark, L. Maresca and P.J. Smith, J. Chem. Soc. (A), 2687 (1970).

63. M. Goldstein and G.C. Tok, ibid., 2303 (1971).

64. A. Tchakirian, Compt. Rend., 192, 233 (1931).

65. Gmelins Handbuch der Anorganische Chemie.

66. G.P. Haight and L. Johansson, Acta Chem. Scand., 22, 961 (1968).

67. J.S. Morrison and H.M. Haendler, J. Inorg. Nucl. Chem., 29, 393 (1967).

68. D. Weber, Z. Naturforsch. B: Anorg. Chem., Org. Chem., 33B, 862 (1978).

69. M.J. Tricker and J.D. Donaldson, Inorg. Chim. Acta, 31, L445 (1978).

70. W. Bues, M. Somer and W. Brockner, Z. Anorg. Allg. Chem., 435, 119 (1977).

71. S.L. Snib and P.F. Weller, J. Cryst. Growth, 48, 155 (1980).

72. R.R. McDonald, A.C. Larson and D.T. Cromer, Acta Cryst., 17, 1104 (1964).

73. G. Bergerhoff and L. Goost, ibid., B26, 19 (1970).

74. J. Andersson, Acta Chem. Scand., A30, 229 (1976).

75. B. Kamenar and D. Grdenic, J. Inorg. Nucl. Chem., 24, 1039 (1962).

76. J. Pirnat, Z. Luznik, Z. Trontelj and V. Kancic, J. Mol. Struct., 58, 547 (1980).

77. D.E. Scaife, P.F. Weller and W.G. Fischer, J. Solid State Chem., 9, 308 (1974).

78. G. Messin, Ann. Sci. Univ. Besancon Chim., 14, 3 (1977).

79. M.H. Ben Ghozlen, A. Daoud and J.W. Bats, Acta Cryst., B37, 1415 (1981).

80. H. Sowa, U. Drück and A. Kutoglu, Z. Krist., 154, 333 (1981).

81. P.J. Smith, and L. Smith, Inorg. Chim. Acta Revs., 7, 11 (1973).

82. A.G. Davies, P.G. Harrison, J.D. Kennedy, T.N. Mitchell, R.J. Puddephatt and W. McFarlane, J. Chem. Soc. C, 1136 (1969).

83. J.J. Burke and P.C. Lanterbur, J. Am. Chem. Soc., 83, 326 (1961).

84. A. Fratiello, S. Peak, R. Schuster and D. Davis, J. Phys. Chem., 74, 3730 (1970).

85. C.R. Lassigne and E.J. Wells, Can. J. Chem., 55, 927 (1977).

86. Ho-Mei Mimi Yeh and R.A. Geanangel, Inorg. Chim. Acta, 52, 113 (1981).

87. L.J. Farrugia and B.R. James, Inorg. Chim. Acta, 53, L261 (1981).

88. C.R. Lassigne, E.J. Wells, L.J. Farrugia and B.R. James, J. Mag. Res., 43, 488 (1981).

89. P.G. Harrison and S.R. Stobart, J.C.S. Dalton, 940 (1973).

90. P. Renand, Compt. Rend., 242, 1477 (1956).

91. W. Beck, E. Schuierer, P. Pöllman and W.P. Fehlhammer, Z. Naturforsch., 21b, 811 (1966).

92. E. Wiberg and H. Michaud, ibid., 9b, 500 (1954).

93. D. Foster and W. de W. Horrocks, Inorg. Chem., 5, 1510 (1966).

94. K. Dehnicke and P. Ruschke, Z. Anorg. Allg. Chem., 444, 54 (1978).

95. B. Busch, J. Pebler and K. Dehnicke, ibid., 416, 203 (1975).

96. P. Chevalier, J. Ritsma and J. Rouxel, J. Bull. Soc. Chim. Fr., 9/10, 1839 (1974).

97. O. Schmitz-DuMont and H.J. Goetze, Z. Anorg. Allg. Chem., 371, 38 (1969).

98. P. Ray and S.N. Ray, Quart. Ind. Chem. Soc., 3, 110 (1926).

99. D. Forster and D.M.L. Goodgame, J. Chem. Soc., 1286 (1965).

100. D. Potts, H.D. Sharma, A.J. Carty and A. Walker, Inorg. Chem., 13, 1205 (1974).

101. P.P. Singh and S.B. Sharma, J. Indian Chem. Soc., 52, 617 (1975).

102. K. Dehnicke, B. Busch and J. Pebler, Z. Anorg. Allg. Chem., 420, 219 (1976).

103. G. Brauer, Handbook of Preparative Inorganic Chemistry, Vol. 1, 2nd ed. (N.Y. Academic Press 1963-5).

104. R.A. Deans, Inorg. Chim. Acta, 30, 364 (1979).

105. J. Kendal and E. Crittenden, J. Am. Chem. Soc., 45, 963 (1923).

106. C.C. Hsu and R.A. Geanangel, Inorg. Chem., 16, 2529 (1977).

107. W.L. Jennings and W.B. Scott, J. Am. Chem. Soc., 41, 1241 (1919).

108. Decca Commercial Mid-range N.q.r. Spectrometer Handbook.

109. CRC Handbook of Chemistry and Physics, 60th ed.

110. K.B. Dillon, R.N. Reeve and T.C. Waddington, J. Chem. Soc. (A), 1410 (1977).

111. L.F. Audrieth and C.F. Gibbs, Inorg. Synthesis, 1, 77 (McGraw-Hill 1939).

112. W. Schaffer, Acta Cryst., 7, 242 (1954).

113. D.M. Adams and D.M. Morris, J. Chem. Soc. (A), 1669 (1967).

114. N.R.M. Smith, Ph.D. Thesis, Durham 1982.

115. T.B. Brill, Z.Z. Hugus and A.F. Schreiner, J. Phys. Chem., 74, 2999 (1970).

116. I.P. Birynkov, M.G. Voronkov and I.A. Safin, Tables of Nuclear Quadrupole Resonance Frequencies (Leningrad, 1968).

117. K.B. Dillon, A. Finch, P.N. Gates and T.H. Page, unpublished work.

118. R.M. Hart and M.A. Whitehead, Trans. Far. Soc., 67, 3451 (1971).

119. F.R. Poulsen and S.E. Rasmussen, Acta Chem. Scand., 24, 150 (1970).

120. A.W.G. Platt, Ph.D. Thesis, Durham University, 1980.

121. G.F. Hewittson, M.Sc. Thesis, Durham University, 1980.

122. P.A. Cusack and P.J. Smith, "A Bibliography of X-ray Crystal Structures of Tin Compounds", I.T.R.I. Publication No. 588.

123. H. Henke, Acta Cryst., B38, 920 (1982).

124. D. Nakamura, K. Ito and M. Kubo, Inorg. Chem., 1, 592 (1962).

125. J.A. Creighton and J.H.S. Green, J. Chem. Soc. (A), 808 (1968).

126. I. Wharf and D.F. Schriver, Inorg. Chem., 8, 914 (1969).

127. M. Debeau and J.P. Mathieu, Compt. Rend., 260, 5229 (1965).

128. N.S. Fortunatov and Z.A. Fokina, Ukr. Khim. Zh., 33, 640 (1967).

129. R.M. Silverstein, C.G. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, Wiley Int. Press, 3rd ed.

130. Z. Arnold, Chem. listy., 52, 468 (1958).

131. M. Grayson and E.J. Griffiths, Topics in Phosphorous Chemistry, Volume 6.

132. K.B. Dillon, R.J. Lynch, R.N. Reeve and T.C. Waddington, J.C.S. Dalton, 1243 (1976).

133. J. Stephenson, J. Chem. Soc., 127, 1874 (1925).

134. L.A. Woodward and J.A. Creighton, Spectrochim. Acta, 17, 596 (1961).

135. R.J.C. Brown and S.L. Segel, J. Mag. Res., 45, 284 (1981).

136. W. von der Ohe, J. Chem. Phys., 62, 3933 (1975) and 63, 2949 (1975).

137. M. Sutton and R.L. Armstrong, J. Mag. Res., 47, 68 (1982).

138. G. Wulfsberg and A. Weiss, Ber. Bunsenges Phys. Chem., 84, 474 (1980).

139. A. Finch, P.N. Gates, T.H. Page, K.B. Dillon and T.C. Waddington, J.C.S. Dalton, 2401 (1980) and references therein.

140. A. Finch, P.N. Gates, T.H. Page and K.B. Dillon, in press.

141. C.W. Fryer and J.A.S. Smith, J. Chem. Soc. (A), 1029 (1970).

142. A. Sasane, D. Nakamura and M. Kubo, J. Mag. Res., 8, 179 (1972).

143. J. Anderson, Acta Chem. Scand., 26, 1730/2543/3813 (1972).

144. S. Vilminot, W. Granier, Z. Al. Oraibi and L. Cot, Acta Cryst., B35, 2863 (1979).

145. F. Daniels and R.A. Alberty, Physical Chemistry, 3rd ed., Wiley Int.

146. P.A.W. Dean and D.F. Evans, J. Chem. Soc. (A), 1154 (1968).

147. T. Vladimiroff and E.R. Malinowski, J. Chem. Phys., 46, 1830 (1967).

148. R.G. Kidd and H.G. Spinney, Inorg. Chem., 12, 1967 (1973).

149. R.G. Kidd and H.G. Spinney, Can. J. Chem., 59, 2940 (1981).

150. R.G. Kidd and H.G. Spinney, J. Am. Chem. Soc., 103, 4759 (1981).

151. R. Colton, D. Dakternieks and C. Harvey, Inorg. Chim. Acta, 61, 1 (1982).

152. O.K. Poleshchuk, Y.K. Maksyutin and G.I. Orlov, Koord. Khim., 1, 666 (1975).

153. J.C. Barnes, H.A. Sampson and T.J.R. Weakley, J.C.S. Dalton, 949 (1980).

154. K.B. Dillon, M.G. Craveirinha Dillon and T.C. Waddington, J. Inorg. Nucl. Chem., 38, 1149 (1976).

155. R.S. Tobias, Acta Chem. Scand., 12, 198 (1958).

156. J.S. Hartmann and J.M. Miller, Inorg. Chem., 13, 1467 (1974).

157. K.B. Dillon, A.W.G. Platt and T.C. Waddington, Chem. Comm., 889 (1979).

158. K.B. Dillon, A.W.G. Platt and T.C. Waddington, J.C.S. Dalton, 1036 (1980).

159. K.B. Dillon, A.W.G. Platt and T.C. Waddington, ibid., 2292 (1981).

160. K.B. Dillon and A.W.G. Platt, ibid., 1199 (1982).

161. D.E. Clegg, J.R. Hall and G.A. Swile, J. Org. Chem., 38, 403 (1972).

162. S.M. Nelson and T.M. Shepherd, J. Inorg. Nucl. Chem., 27, 2123 (1965).

163. Progress in N.m.r. Spectroscopy, Vol. 8 (Editors: J.W. Emsley, J. Feeney, L.H. Sutcliffe).

164. Y. Furukawa, L.S. Prabhumirashi, R. Ikeda and D. Nakamura, Bull. Chem. Soc. Japan, 55, 995 (1982).