Tin-119 Nuclear Magnetic Resonance Studies of some Pseudohalogeno-derivatives of $[SnX_6]^{2-}$ (X = Cl or Br)

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Several thiocyanato- and cyano-derivatives $[SnX_{6-n}Y_n]^{2-}$ (X = Cl or Br, Y = NCS or CN) of the hexahalogenostannate(IV) ions $[SnX_6]^{2-}$ have been identified in solution by ^{119}Sn n.m.r. spectroscopy. Some isomeric configurations have been deduced by the method of pairwise interactions. The ligands in $[Sn(NCS)_6]^{2-}$ were deduced to be N-bonded on the basis of i.r. spectroscopy.

Although pseudohalogeno-derivatives of $[SnX_6]^{2-}$ ions are well known, very few n.m.r. data are available for these species. $^{117,119}Sn$–^{14}N Coupling has recently been observed for the $[Sn(NCS)_6]^{2-}$ ion in methanol solution, and its ^{119}Sn chemical shift was measured as −842.0 p.p.m.[1] No shifts have been reported for cyano-derivatives, however, or for mixed species $[SnX_{6-n}Y_n]^{2-}$ (X = Cl or Br; Y = NCS or CN). We report the results of studies by ^{119}Sn n.m.r. spectroscopy on thiocyanato- and cyano-derivatives of $[SnX_6]^{2-}$ (X = Cl or Br). Some isomeric configurations have been assigned by the method of pairwise interactions,[2] which has been applied previously to six-co-ordinate mixed halogenostannates(IV),[3] as well as to thiocyanato- and cyano-derivatives of the PCl_6^- ion.[4]

Experimental

All manipulations including n.m.r. sample preparation were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, in general without further purification except for tetra-alkylammonium chlorides which were dried as described previously.[4]

Tetra-n-butylammonium cyanide was prepared according to the method of Platt.[5] Aqueous NBu_4OH (20 cm^3, 41%) and MeOH (40 cm^3) were placed in a flask connected to a vacuum line, frozen to 77 K, and evacuated. Hydrogen cyanide (1.4 cm^3) was then condensed into a graduated cold-finger, and transferred to the flask. After the mixture had been allowed to warm to room temperature, the solvent was pumped off on a water-bath. The solid which remained was redissolved in toluene, and the solvent was again pumped off. The compound was then dried on the line for 3 h to leave the anhydrous product (Found: C, 74.9; H, 16.7; N, 9.3. $C_{17}H_{36}N_2$ requires C, 76.1; H, 13.5; N, 10.4%).

Tetra-n-butylammonium hexathiocyanatostannate(IV) was obtained by stirring a solution of $[NBu_4]_2[SnBr_6]$ with 10 equivalents of NH_4NCS in acetone for 24 h. The volume of the solvent was then reduced, and a precipitate was formed on the addition of low-boiling (303—313 K) light petroleum. This was filtered off, washed with Et_2O, redissolved in CH_2Cl_2, filtered to remove any remaining NH_4NCS, and pumped to dryness *in vacuo* (Found: C, 46.9; H, 8.1; N, 12.1; S, 18.7; Sn, 11.3. $C_{38}H_{72}N_8S_6Sn$ requires C, 47.9; H, 7.6; N, 11.8; S, 20.2; Sn, 12.5%).

Attempts to prepare hexacyanostannates(IV), either by reaction of a hexaiodostannate[3] with AgCN in Me_2CO or CH_2Cl_2, or by reaction of $[NEt_4]_2[SnI_6]$ with $Zn(CN)_2$ in CH_2Cl_2 or $EtNO_2$, were unsuccessful. The cyano-complexes were therefore prepared *in situ*, as indicated in the Results and Discussion section. ^{119}Sn N.m.r. spectra were recorded as described previously;[3] chemical shifts (±2 p.p.m.) are expressed relative to external $SnMe_4$, with the downfield (high-frequency) direction taken as positive. Elemental analyses and i.r. spectra were obtained as indicated in earlier papers.[6,7]

Results and Discussion

(*a*) *Thiocyanato-complexes.*—Freely exchanging systems were produced either by mixing $[NBu_4]_2[Sn(NCS)_6]$ with salts containing $[SnBr_6]^{2-}$ or $[SnCl_6]^{2-}$ ions in solution, or by adding NH_4NCS to the hexahalogenostannates(IV). The relative intensities of the peaks in the ^{119}Sn n.m.r. spectra could then be controlled to some extent by varying the proportions of the reagents. Several spectra were obtained for each of the systems, and average values of the chemical shifts corresponding to the different species detected were calculated. The results are shown in Table 1, together with assignments based on the pairwise additivity model.[2–4] The shift of −842.5 p.p.m. for the $[Sn(NCS)_6]^{2-}$ ion was obtained by dissolving $[NBu_4]_2[Sn(NCS)_6]$ in CH_2Cl_2, and is in excellent agreement with the value reported recently for the potassium salt in MeOH.[1] Hence the NCS:NCS term was obtained directly from this measurement as −70.208 p.p.m. The Cl:Cl and Br:Br terms were similarly derived as −60.992 and −172.208 p.p.m. from the shifts for $[SnCl_6]^{2-}$ and $[SnBr_6]^{2-}$ respectively. In the $[SnCl_{6-n}(NCS)_n]^{2-}$ system the resonance at −809.8 p.p.m. was initially assigned to $[SnCl(NCS)_5]^{2-}$, enabling the NCS:Cl term to be determined as −62.034 p.p.m. and the shifts of all the other possible ions to be evaluated. Individual values for the Cl:NCS terms from the assigned resonances of the species with n = 1—4 were then determined, and the weighted average of these values (−62.172 p.p.m.) was used for calculating the data shown in Table 1. A similar procedure was adopted for the $[SnBr_{6-n}(NCS)_n]^{2-}$ series; the signal at −1 786.0 p.p.m. was assigned to $[SnBr_5(NCS)]^{2-}$, and the Br:NCS term was derived as −102.084 p.p.m. The weighted average for this term (−101.072 p.p.m.) was evaluated as above from the results for the species with n = 1—5, and the resultant calculated shifts are included in Table 1.

The data show that the pairwise interaction method gives a reasonable fit to the experimental results, although some species show bigger deviations than others. In the chlorothiocyanato-stannates a more intense signal was found for *trans*-$[SnCl_4(NCS)_2]^{2-}$ than for the *cis* isomer, but no signal corresponding to *trans*-$[SnCl_2(NCS)_4]^{2-}$ was observed. It is noteworthy that the compound $[NMe_4]_2[SnCl_4(NCS)_2]$ has been isolated from reaction between NMe_4NCS and $SnCl_4$ in liquid SO_2, and that it was assigned a *trans* structure on the basis of vibrational and Mössbauer spectroscopy.[8] For $[SnCl_3(NCS)_3]^{2-}$ there was no clear-cut preference between the isomers; the signal-to-noise ratio was poor even after a large number of pulses. The sequence in the chlorostannates is similar

Table 1. δ(^{119}Sn)/p.p.m. for halogenothiocyanatostannates(IV) in CH_2Cl_2

	X = Cl		X = Br	
Ion	Observed	Calculated	Observed[a]	Calculated
$[SnX_6]^{2-}$	−731.9	—	−2 066.5	—
$[SnX_5(NCS)]^{2-}$	−734.2[b]	−736.6	−1 786.0	−1 782.0
trans-$[SnX_4(NCS)_2]^{2-}$	−740.0	−741.3	−1 515.2	−1 497.4
cis-$[SnX_4(NCS)_2]^{2-}$	−749.3	−748.2	−1 547.5	−1 537.7
mer-$[SnX_3(NCS)_3]^{2-}$	−764.6	−759.8	−1 295.2	−1 293.4
fac-$[SnX_3(NCS)_3]^{2-}$	−766.8	−766.6	−1 310.8	−1 333.7
trans-$[SnX_2(NCS)_4]^{2-}$		−778.2	−1 098.4	−1 089.4
cis-$[SnX_2(NCS)_4]^{2-}$	−783.3	−785.1		−1 129.7
$[SnX(NCS)_5]^{2-}$	−809.8	−810.4	−946.4	−966.0
$[Sn(NCS)_6]^{2-}$	−842.5	—	−842.5	—

[a] An additional peak was found at −1 274.7 p.p.m. (see text). [b] Weak resonance.

Table 2. δ(^{119}Sn)/p.p.m. for cyanohalogenostannates(IV) in CH_2Cl_2

	X = Cl		X = Br	
Ion	Observed	Calculated	Observed	Calculated
$[SnX_6]^{2-}$	−734.2	—	−2 075.7	—
$[SnX_5(CN)]^{2-}$	−728.1	−729.8	−1 690.7	−1 767.2
trans-$[SnX_4(CN)_2]^{2-}$	—	−725.3	−1 453.1	−1 458.7
cis-$[SnX_4(CN)_2]^{2-}$	—	−742.7	−1 482.0	−1 516.6
mer-$[SnX_3(CN)_3]^{2-}$	−760.3	−755.7	−1 285.1	−1 266.0
fac-$[SnX_3(CN)_3]^{2-}$	−773.4	−773.1	−1 308.3	−1 324.0
trans-$[SnX_2(CN)_4]^{2-}$	—	−786.0	−1 093.7	−1 073.4
cis-$[SnX_2(CN)_4]^{2-}$	−800.1	−803.4	−1 168.3	−1 131.3
$[SnX(CN)_5]^{2-}$	—	−851.1	−1 052.5	−996.5
$[Sn(CN)_6]^{2-}$	−916.2	—	−919.7	—

in some respects to that in the $[PCl_{6-n}(NCS)_n]^-$ series, where a *trans*, *mer*, *cis* preference was deduced for $n = 2$, 3, and 4 respectively, although in the phosphorus complexes only one isomer was seen for each value of n.[4] The series $[NbCl_{6-n}(NCS)_n]^-$, on the other hand, is reported to show a *cis*, *fac*, *cis* preference.[9] In the $[SnBr_{6-n}(NCS)_n]^{2-}$ series a stronger preference for the *trans*, *mer*, and *trans* isomers for $n = 2$, 3, and 4 respectively was evident, possibly implying a particular stability for *trans* NCS groups. This may be indicative of a *trans* influence of the –NCS ligand, as observed previously in octahedral platinum(IV) complexes.[10]

The i.r. spectrum of $[NBu_4]_2[Sn(NCS)_6]$ (Nujol mull) showed a strong band at 2 050 cm^{-1}, which indicates bonding through nitrogen rather than sulphur.[11] This conclusion is entirely in accord with deductions from ^{14}N n.m.r. measurements on the $[Sn(NCS)_6]^{2-}$ ion.[1] Indeed it is probable that this mode of co-ordination occurs in all the mixed species, unlike the niobium(V) complexes where both types of bonding were found.[9] There was one unassigned resonance at −1 274.7 p.p.m. from the bromothiocyanatostannate system, and this could possibly arise from the presence of an isomer bonded through sulphur.

(*b*) *Cyano-complexes.*—Attempted preparations of hexacyanostannates(IV) proved unsuccessful (Experimental section), so the six-co-ordinate mixed complexes were prepared *in situ*. Two main methods were used, reactions (1) and (2) (X = Cl or Br). Some AgCN was also added to selected samples to try to obtain complexes containing more CN than halide.

$$SnX_4 + xNBu_4CN + yN(C_5H_{11})_4X \longrightarrow [SnX_{4+y}(CN)_x]^{2-} + \text{cations} \quad (1)$$
$$(x + y = 2)$$

$$SnX_2 + CNX + 2NBu_4CN \longrightarrow [NBu_4]_2[SnX_3(CN)_3] \quad (2)$$

The ^{119}Sn n.m.r. spectra of the cyanohalogenostannate(IV) systems showed several peaks (Table 2), and interpretation was again attempted *via* the method of pairwise interactions.[2–4] Although $[Sn(CN)_6]^{2-}$ could not be isolated in a solid compound, a resonance at *ca.* −917 p.p.m. appeared in both the chloro- and bromo-cyanide spectra, and was therefore assigned to this moiety. Hence the CN:CN interaction term was readily derived as −76.350 p.p.m. while the Cl:Cl and Br:Br terms were obtained as −61.183 and 172.975 p.p.m. from the shifts of the hexahalogenostannates. Correct assignment of one resonance to a specific cyanohalogenostannate from each system should thus enable the Cl:CN and Br:CN terms to be evaluated, and allow prediction of the shifts of the other possible species in each case. This was accomplished by preparing solutions containing mainly halide in the total of six ligands, allowing resonances to be ascribed to $[SnX_5(CN)]^{2-}$, and the X:CN term to be derived as −59.659 and −76.725 p.p.m. for X = Cl and Br respectively. Pairwise calculations were then made from these values, enabling further peaks to be assigned. This method worked quite well in the chlorocyanostannates, but poorly for the bromo-complexes. The spectra from the bromo-species were therefore re-examined, on the basis that *trans* isomers usually occur at higher frequency than *cis* isomers (and similarly *mer* isomers at higher frequency than *fac*), and that the shift separation between isomeric pairs is usually smaller than the separation between ions of different stoicheiometries. Signals could then be attributed to the ions $[SnBr_{6-n}(CN)_n]^{2-}$ for $n = 1$—3, and from these assignments a value for the Br:CN term was calculated in each case. The weighted average was then evaluated, enabling preliminary assignments for other species to be made. The X:CN parameters used for the calculated values in Table 2 were finally

Table 3. Calculated Br:CN pairwise interaction terms

Ion	Br:CN term p.p.m.
$[SnBr_5(CN)]^{2-}$	−76.725
$[SnBr_4(CN)_2]^{2-}$	−90.081 (*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*)
$[SnBr(CN)_5]^{2-}$	−109.841

obtained from the weighted averages (−60.077 and −95.850 p.p.m. for X = Cl and Br) of these terms from all the assigned resonances in each system.

It was noted that the Br:CN term appeared to increase systematically with the number of cyano-groups in the complex (Table 3). A similar, though smaller, effect was observed previously for the chlorofluorostannates(IV).[3] This variation is responsible for the poor agreement in Table 2 between the observed and calculated values for some species, and may arise either from distortions from a regular octahedral configuration of the ligands, or from π-bonding interactions. It has been found previously that cyanide gives bigger differences between observed and calculated shifts in six-co-ordinate phosphorus(V) complexes than other halide or pseudo-halide ligands.[4,12–15] In contrast with the $[PCl_{6-n}(CN)_n]^-$ series,[4] however, no particular stability was found for $[SnCl_3(CN)_3]^{2-}$, which may argue against a major π-bonding contribution in the cyanostannates.

The results show that several ions in the $[SnCl_{6-n}(CN)_n]^{2-}$ series were not detected, including both isomers of $[SnCl_4(CN)_2]^{2-}$. This could be due to increased reactivity of these species compared with their precursors, such that they readily undergo either further substitution or disproportionation. The failure to observe $[SnCl(CN)_5]^{2-}$, in contrast, was probably because solutions could not be prepared with a high enough CN:Cl ratio. Silver cyanide appeared not to react with $[SnCl_6]^{2-}$, and 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 the intermediate exchange products. The relative amounts of $[SnCl_6]^{2-}$ and $[Sn(CN)_6]^{2-}$ varied according to the quantities of Cl^- and CN^- added. When CNCl was in excess, however, $[SnCl_6]^{2-}$ became the exclusive product, probably because of reactions of the type (3). These samples were typically dark brown in colour, suggesting that the cyanogen polymerises, thus removing it from the system and pulling the above equilibrium to the right. The n.m.r. data showed that *mer*-$[SnCl_3(CN)_3]^{2-}$ and *cis*-$[SnCl_2(CN)_4]^{2-}$ are the favoured isomers, in accordance with statistical expectations for random exchange, although the failure to detect *trans*-$[SnCl_2(CN)_4]^{2-}$ indicates that the *cis* isomer may have extra stability in this case.

$$[SnCl_5(CN)]^{2-} + CNCl \rightleftharpoons [SnCl_6]^{2-} + (CN)_2 \quad (3)$$

The $[SnBr_{6-n}(CN)_n]^{2-}$ series showed all ten possible species in its n.m.r. spectra; the preferred isomers for n = 2—4 had *trans*, *mer*, and *cis* configurations respectively. The presence of *trans*-$[SnBr_4(CN)_2]^{2-}$ in this sequence is contrary to the statistical prediction of its *cis* analogue as the preferred isomer, possibly implying a particular stability for two *trans* cyano-groups. This could arise from a type of *trans* effect in the octahedral complex, similar to that seen in octahedral platinum(IV) complexes[10] and in the thiocyanatostannates, such that the CN group in $[SnBr_5(CN)]^{2-}$ labilises the bromine *trans* to it, and facilitates substitution at this position. If this is the case, however, it is not clear why *cis*-$[SnBr_2(CN)_4]^{2-}$ should be favoured over the *trans* isomer, although the *cis* isomer is predicted statistically to be more abundant. Preparation of the bromocyano-complexes by oxidation of $SnBr_2$ initially yielded spectra in which only the preferred isomers were detected. After the solutions had been left to stand for several weeks, however, signals were also observed from the less favoured isomers. Hence thermodynamic equilibrium is attained only slowly in the systems prepared by oxidation of tin(II) starting materials, in contrast with the behaviour of the complexes obtained directly from tin(IV) precursors.

The results thus indicate that several thiocyanato- and cyano-derivatives of hexahalogenostannates(IV), $[SnX_6]^{2-}$ (X = Cl or Br), may be identified by ^{119}Sn n.m.r. solution spectroscopy, and that some isomeric configurations may be assigned by the method of pairwise interactions, although this procedure gives better numerical agreement for the thiocyanato- than for the cyano-complexes. The substituents appear to exert directing effects on further substitution in some systems, since the observed isomeric patterns frequently differ from that predicted statistically for a randomly exchanging system.

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