Reactions of the Pentachlorostannate(IV) Anion with Lewis Bases, and Mössbauer Data for some Adducts of the Type Pentachlorostannate(IV)–Base (1/1)

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Reactions of tetraethylammonium pentachlorostannate(IV) with a variety of Lewis bases have been investigated. Those with acetonitrile, pyridine, tetrahydrofuran, and salicylaldehyde as base (L) result in the formation of adducts $[NEt_4][SnCl_5{\cdot}L]$, while with trimethylamine, 2,2′-bipyridyl (bipy), phosphines, arsines, phosphine oxides, and arsine oxides the products are $[NEt_4]_2[SnCl_6]$ and 1 : 2 adducts of tin(IV) tetrachloride (a 1 : 1 adduct in the case of bipy). Reactions with quinolin-8-ol (Hquin), pentane-2,4-dione (Hpd), and tropolone (Htrop) result in the elimination of HCl and the formation of $[NEt_4][SnCl_4L']$ (L′ = quin, pd, or trop). Mössbauer quadrupole-splitting data for the adducts $[NEt_4][SnCl_5{\cdot}L]$ are in agreement with those predicted from the point-charge model.

THE acceptor properties of tin(IV) tetrahalides have been thoroughly investigated and a very extensive range of both 1 : 1 and 1 : 2 adducts have been isolated. However, a study of the acceptor properties of the pentachlorostannate(IV) species has not hitherto been made, although the ease with which it complexes with chloride ion suggests that it might also complex with neutral donor molecules. Thus the present study was undertaken with the aim of investigating reactions of the $[SnCl_5]^-$ ion with Lewis bases. Furthermore, it was hoped to obtain Mössbauer quadrupole-splitting data for adducts of the type $[SnCl_5{\cdot}L]^-$ as such data taken in conjunction with quadrupole-splitting data for appropriate adducts $SnCl_4{\cdot}2L$ should enable one to make a simple and precise check on the applicability of the point-charge model to tin(IV) halide adduct systems (see Discussion).

RESULTS AND DISCUSSION

Tetraethylammonium pentachlorostannate(IV) was treated with a fairly extensive range of donor molecules in dichloromethane at room temperature. The nitrogen-donor molecules were trimethylamine, pyridine (py), 2,2′-bipyridyl (bipy), and acetonitrile. Other Group 5 donor molecules included both triphenyl- and trialkyl-phosphines and the corresponding arsines. The oxygen-donor molecules were salicylaldehyde (Hsal) pentane-2,4-dione (Hpd), tropolone (2-hydroxycyclohepta-2,4,6-trien-1-one, Htrop), tetrahydrofuran (thf), $POCl_3$, both phosphine and arsine oxides, and quinolin-8-ol (Hquin) which contains both nitrogen- and oxygen-donor atoms.

Several types of behaviour were observed in these reactions and only in a limited number of cases were adducts of the type $[SnCl_5{\cdot}L]^-$ isolated. These were formed with Hsal, thf, MeCN, and py. Clear evidence for adduct formation was obtained from elemental analyses and both i.r. and Mössbauer spectroscopy. In fact, while this paper was in the course of preparation, the crystal structure of $[Mo(CO)_4(dppe)(SnCl_3)][SnCl_5{\cdot}H_2O]$ [dppe = 1,2-bis(diphenylphosphino)ethane] was published,[1,2] thus unequivocally demonstrating the ability of $[SnCl_5]^-$ to form an adduct with a neutral Lewis base.

The shifts in the positions of some of the bands in the i.r. spectra of Hsal and MeCN on complex formation with $[SnCl_5]^-$ are typical of those previously observed on adduct formation with other Lewis acids. For example, the band at 1 660 cm^{-1} [ν(C=O)] in the spectrum of salicylaldehyde is shifted to 1 632 cm^{-1} in that[3] of $SnCl_4{\cdot}2Hsal$ and to 1 628 cm^{-1} in that of $[NEt_4][SnCl_5{\cdot}Hsal]$. Bands which occur at 2 296 and 2 319 cm^{-1} in the spectrum of acetonitrile occur at 2 283 and 2 300 cm^{-1} in the spectrum[4] of $SnCl_4{\cdot}2MeCN$ and at 2 296 and 2 319 cm^{-1} in the spectrum of $[NEt_4][SnCl_5{\cdot}MeCN]$.

The Mössbauer chemical shifts (δ) of the new adducts (see Table 1) were always significantly smaller than those of the parent $[SnCl_5]^-$ and this is consistent with an increase in the co-ordination of tin as a result of adduct formation.[5] The Hsal, thf, and MeCN adducts showed resolved quadrupole splittings in their Mössbauer spectra and the magnitude of these splittings are related to those observed for analogous tin(IV) tetrahalide 1 : 2

TABLE 1

Mössbauer parameters of adducts [a]

	δ [b] ± 0.03 mm s^{-1}	Δ ± 0.03 mm s^{-1}
$[NEt_4][SnCl_5]$ [c]	0.59	0.77
$[NEt_4][SnCl_5{\cdot}MeCN]$	0.46	0.81
$SnCl_4{\cdot}2MeCN$ [d]	0.38	0.91
$[NEt_4][SnCl_5{\cdot}py]$	0.49	0.0
$SnCl_4{\cdot}2py$	0.51 [d]	0.0
	0.47 [e]	0.0
$[NEt_4][SnCl_5{\cdot}Hsal]$	0.50	0.56
$SnCl_4{\cdot}2Hsal$ [f]	0.43	1.10
$[NEt_4][SnCl_5{\cdot}thf]$	0.46	0.65
$SnCl_4{\cdot}2thf$ [g]	0.43	1.29

[a] Recorded at 80 K. Parameters of new complexes are accurate to ±0.03 mm s^{-1}. [b] Mössbauer chemical shifts (δ) are relative to $BaSnO_3$. [c] R. V. Parish and R. H. Platt, *J. Chem. Soc.* (*A*), 1969, 2145. [d] Ref. 7. [e] Ref. 11. [f] Ref. 8. [g] A quadrupole splitting of 1.14 mm s^{-1} has previously been measured for this adduct using an $^{119}SnO_2$ source (S. Ichiba, M. Mishima, H. Sakai, and H. Negita, *Bull. Chem. Soc. Japan*, 1968, **41**, 49).

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[3] M. J. Frazer and I. Douek, unpublished work.

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adducts in a manner predicted by point-charge calculations. [Parameters of the relevant tin(IV) tetrahalide adducts are also included in Table 1.] Assuming regular octahedral bond angles, point-charge calculations predict [6] equation (1) where $\Delta(\mathrm{SnCl_5{\cdot}L})$ indicates

$$\Delta(\mathrm{SnCl_5{\cdot}L}) = \Delta(cis\text{-}\mathrm{SnCl_4{\cdot}2L}) = \tfrac{1}{2}\Delta(trans\text{-}\mathrm{SnCl_4{\cdot}2L}) \qquad (1)$$

the quadrupole splitting of $[\mathrm{SnCl_5{\cdot}L}]$, *etc.* Thus $\mathrm{SnCl_4{\cdot}2MeCN}$ with *cis*-acetonitrile groups [4] has a quadrupole splitting [7] of 0.91 mm $\mathrm{s^{-1}}$ compared to a value of 0.81 mm $\mathrm{s^{-1}}$ for $[\mathrm{SnCl_5{\cdot}MeCN}]^-$. On the other hand, $[\mathrm{SnCl_5{\cdot}thf}]^-$ and $[\mathrm{SnCl_5{\cdot}Hsal}]^-$ have quadrupole splittings which are almost half the values observed [8] for $\mathrm{SnCl_4{\cdot}2thf}$ and $\mathrm{SnCl_4{\cdot}2Hsal}$ respectively, both of which have been postulated as having donor groups in *trans* positions.[8,9] The compound [10] *trans*-$\mathrm{SnCl_4{\cdot}2py}$ does not give rise to resolved quadrupole splitting [7,11] and consequently $[\mathrm{SnCl_5{\cdot}py}]^-$ also gives a single-line spectrum. Thus the quadrupole-splitting data almost definitely establish the adduct structures of $[\mathrm{NEt_4}][\mathrm{SnCl_5{\cdot}L}]$ (L = MeCN, thf, or Hsal) and are consistent with an adduct structure for $[\mathrm{NEt_4}][\mathrm{SnCl_5{\cdot}py}]$.

The quadrupole-splitting data in Table 1 are significant in another respect insofar as they are the first available data which give a precise indication of the applicability of the point-charge model to tin(IV) halide adduct systems. This has not previously been possible as *cis–trans* pairs of adducts $\mathrm{SnCl_4{\cdot}2L}$ have not been isolated and quadrupole-splitting data have not hitherto been available for adducts $[\mathrm{SnCl_5{\cdot}L}]^-$. In Table 2 a comparison is made between the experimental and calculated ratios $\Delta(\mathrm{SnCl_4{\cdot}2L}) : \Delta(\mathrm{SnCl_5{\cdot}L})$. The agreement is remarkably good, being less good for the adducts of MeCN than for those of Hsal and thf. However, a crystallographic study [4] has revealed a very distorted *cis* structure for $\mathrm{SnCl_4{\cdot}2MeCN}$ and, if on the basis of the crystallographic data the point-charge quadrupole-splitting expression for a regular *cis*-octahedral adduct is modified to allow for this distortion, it is found that the experimental ratio $\Delta(cis\text{-}\mathrm{SnCl_4{\cdot}2MeCN}) : \Delta(\mathrm{SnCl_5{\cdot}MeCN})^-$ is now in much better agreement with point-charge predictions. In view of this excellent agreement between the predictions of the point-charge model and experiment it would seem that the geometries of many adducts $\mathrm{SnX_4{\cdot}2L}$ (X = halogen) could be confidently assigned from their Mössbauer quadrupole-splitting data if reliable values of partial quadrupole splittings for donor molecules could be found from other series of complexes.

TABLE 2

Calculated and experimental ratios of $\Delta(\mathrm{SnCl_4{\cdot}2L}) : \Delta(\mathrm{SnCl_5{\cdot}L})$

	Ratio	
Donor group (L)	Expt.	Calc.
Hsal	1.96	2.0
thf	1.98	2.0
MeCN	1.12	1.0

In those reactions between $[\mathrm{NEt_4}][\mathrm{SnCl_5}]$ and donor molecules containing only one donor atom which did not result in the formation of adducts of the type $[\mathrm{NEt_4}][\mathrm{SnCl_5{\cdot}L}]$, precipitates were always formed which contained $[\mathrm{NEt_4}]_2[\mathrm{SnCl_6}]$ (confirmed by *X*-ray diffraction patterns) and the only other products found in these reactions were adducts $\mathrm{SnCl_4{\cdot}2L}$. The reaction occurring is thus as in (2). A similar type of reaction took place

$$2[\mathrm{SnCl_5}]^- + 2\mathrm{L} \longrightarrow [\mathrm{SnCl_6}]^{2-} + \mathrm{SnCl_4{\cdot}2L} \qquad (2)$$

with bipy except that in this case the 1 : 1 adduct $\mathrm{SnCl_4{\cdot}bipy}$ rather than a 1 : 2 adduct was formed. The alternative approach of treating the insolable adduct $\mathrm{SnCl_4{\cdot}PPh_3}$ with tetraethylammonium chloride was investigated in a further effort to obtain a phosphine adduct $[\mathrm{SnCl_5}]^-$, but the products were as in reaction (2), *i.e.* (3) occurs, and the reaction followed the same course

$$2\mathrm{SnCl_4{\cdot}PPh_3} + 2\mathrm{Cl^-} \longrightarrow [\mathrm{SnCl_6}]^{2-} + \mathrm{SnCl_4{\cdot}2PPh_3} \qquad (3)$$

when tetra-n-butylammonium chloride was used in place of $[\mathrm{NEt_4}]\mathrm{Cl}$. However, subsequent work [12] has revealed that $\mathrm{SnCl_4{\cdot}PPh_3}$ can react with other donor molecules (*e.g.* thf) as with chloride ion, *i.e.* as in (4), so that the

$$2\mathrm{SnCl_4{\cdot}PPh_3} + 2\mathrm{L} \longrightarrow \mathrm{SnCl_4{\cdot}2L} + \mathrm{SnCl_4{\cdot}2PPh_3} \qquad (4)$$

occurrence of reaction (3) rather than the formation of $[\mathrm{NEt_4}][\mathrm{SnCl_5{\cdot}PPh_3}]$ or $[\mathrm{NBu^n_4}][\mathrm{SnCl_5{\cdot}PPh_3}]$ is probably not a consequence of the unfavourable anion to cation size ratio which might result in the solid adducts. We were able to isolate adducts $[\mathrm{NEt_4}][\mathrm{SnCl_5{\cdot}L}]$ and $[\mathrm{NEt_4}]_2[\mathrm{SnCl_5}]_2{\cdot}\mathrm{L}$ (L = a bulky salicylaldiminato- or pentane-2,4-dionato-metal complex [13]) so that the anion to cation size ratio probably does not play a dominant role (if at all important) in determining the course of any of the reactions which we investigated between $[\mathrm{NEt_4}][\mathrm{SnCl_5}]$ and donor molecules. In fact the tendency for $[\mathrm{SnCl_5}]^-$ to react with Lewis bases in accordance with reaction (2) seems to parallel the tendency of $\mathrm{SbCl_5}$ (which is isoelectronic with $[\mathrm{SnCl_5}]^-$) to form species $[\mathrm{SbCl_4{\cdot}2L}][\mathrm{SbCl_6}]$.[14]

Reactions of Htrop, Hpd, and Hquin with $[\mathrm{NEt_4}][\mathrm{SnCl_5}]$ at room temperature and at −4 °C resulted in the immediate loss of HCl and the formation of compounds $[\mathrm{NEt_4}][\mathrm{SnCl_4L'}]$ (L′ = trop, quin, and pd). The pentane-2,4-dionato-compound has previously been prepared as the triethylammonium salt by treating [15]

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[12] D. Cunningham and K. McLoughlin, unpublished work.

[13] D. Cunningham and J. Finnegan, unpublished work.

[14] See, for example, M. Webster, *Chem. Rev.*, 1966, **66**, 87.

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TABLE 3

Analytical data (%) for new complexes

	Found				Calc.			
Compound	C	H	N	Halide	C	H	N	Halide
$[NEt_4][SnCl_5\cdot MeCN]$	25.5	4.9	5.8	38.4	25.7	5.0	6.0	38.0
$[NEt_4][SnCl_5\cdot py]$	31.3	5.1	5.7	35.3	30.9	5.0	5.5	35.1
$[NEt_4][SnCl_5\cdot Hsal]$	33.4	4.7	2.6	32.3	32.9	4.8	2.6	32.3
$[NEt_4][SnCl_5\cdot thf]$	28.4	5.5	3.0	35.5	28.9	5.7	2.8	35.6
$[NEt_4][SnCl_4(pd)]$	31.8	5.5	3.0	29.0	31.9	5.6	2.9	29.0
$[NEt_4][SnCl_4(trop)]$	35.0	4.9	2.8	27.9	35.2	4.9	2.7	27.7
$[NEt_4][SnCl_4(quin)]$	38.1	5.0	5.1	26.6	38.1	4.9	5.2	26.5

NEt_3 with the adduct $SnCl_4\cdot Hpd$, but the quinolin-8-olato- and tropolonato-compounds seem to be new species. Our i.r., Mössbauer, and n.m.r. data for the pd complex anion are in excellent agreement with those previously reported. We were also able to form the above compounds by the reaction of $[NEt_4]_2[SnCl_6]$ with the sodium salts of Htrop and Hpd and with Hquin directly when the ligand to $[SnCl_6]^{2-}$ ratio was 1 : 1. However, when the ligand to $[SnCl_6]^{2-}$ ratio was 2 : 1 further elimination of $[NEt_4]Cl$ took place and the compounds $SnCl_2L_2$ were obtained.

EXPERIMENTAL

Reactions of Tetraethylammonium Pentachlorostannate(IV) *with Lewis Bases.*—Tetraethylammonium pentachlorostannate(IV) was treated with the following bases: trimethylamine, acetonitrile, pyridine, 2,2′-bipyridyl, triphenyl- and triethyl-phosphine, triphenyl- and triethyl-arsine, triphenyl- and triethyl-phosphine oxide, triphenyl- and triethyl-arsine oxide, phosphoryl chloride, tetrahydrofuran, salicylaldehyde, quinolin-8-ol, tropolone, and pentane-2,4-dione. In each reaction (excluding that with NMe_3) a dry dichloromethane solution of the base (1 mol) was added dropwise to a dry dichloromethane solution of $[NEt_4][SnCl_5]$ (1 mol) which was prepared by literature methods.[16] In the reaction with NMe_3 the base was bubbled through a dichloromethane solution of $[NEt_4]$-$[SnCl_5]$. Reactions were carried out at room temperature and those with Hpd, Htrop, and Hquin were also carried out at −4 °C. In each case, a white precipitate was obtained immediately and was separated by filtration under dry nitrogen, washed with a small quantity of dry solvent, and dried *in vacuo*.

The moisture-sensitive solids obtained from the reactions with MeCN, py, Hsal, and thf gave elemental analyses which are consistent with their formulation as adducts $[NEt_4][SnCl_5\cdot L]$ (see Table 3). Moisture-stable solids were obtained from the reactions with Hpd, Htrop, and Hquin and elemental analyses of these are consistent with their formulation as $[NEt_4][SnCl_4L']$ (L' = pd, trop, and quin) (see Table 3). The same products were obtained when these latter reactions were carried out at −4 °C. *X*-Ray powder-diffraction patterns of the solids obtained from all the other reactions showed that they contained predominantly $[NEt_4]_2[SnCl_6]$. When dry hexane was added to the filtrates from these reactions further white solids were obtained. Halide analyses, i.r. spectra, and *X*-ray powder-diffraction patterns of these latter solids indicated that they were adducts $SnCl_4\cdot 2L$ contaminated with a very small quantity of $[NEt_4]_2[SnCl_6]$.

Mössbauer Measurements.—Samples for Mössbauer measurements were mounted in Perspex holders in a dry-box and immediately cooled to 80 K. Barium stannate was used as source and the spectra were calibrated with a cobalt–stainless-steel source and iron absorber at room temperature. The percentage resonance dips were *ca.* 10% when *ca.* 200 000 counts per channel had accumulated. The Mössbauer equipment has previously been described.[17]

[6/1161 *Received*, 11*th June*, 1976]

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