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### Far-infrared, Raman, and Mössbauer Spectra of Trihalogenostannate(II) Complexes, [SnX<sub>3</sub>]<sup>-</sup>, [SnX<sub>2</sub>Y]<sup>-</sup>, and [SnXYZ]<sup>-</sup>, with Different Cations

By M. Goldstein \* and G. C. Tok, Department of Chemistry, Northern Polytechnic, Holloway Road, London N7 8DB

All ten of the binary and mixed trihalogeno-complexes of tin(II), [SnXYZ]- (X, Y, or Z = CI, Br, or I), have been prepared as salts of one or more of the cations  $[Et_4N]^+$ ,  $[Bun_4N]^+$ , and  $[Ph_4As]^+$ . Their far-i.r. (to 80 cm<sup>-1</sup>) and Raman spectra show that discrete pyramidal trihalogeno-anions are present in solution. This structure is retained in the solid state for the  $[Bun_4N]^+$  salts, but with  $[Ph_4As]^+$  and  $[Et_4N]^+$  cations there is increasing solid-state interaction resulting in a lowering of symmetry. This is shown also by the <sup>119</sup>Sn Mössbauer data. For salts of a given cation, the isomer shifts show a regular variation with the sums of the electronegativities of the halide ligands. Quadrupole splitting was observed in each case, and showed an inverse relationship to the isomer shifts in each series; this is most readily interpreted as a consequence of a quadrupole splitting-electronegativity correlation. The species absorbed by an anion-exchange resin in the halide (X- or Y-) form from SnX<sub>0</sub>-HX solutions (X or

Y = CI, Br, or I) are shown to be  $[SnX_3]^-$  or  $[SnX_2Y]^-$ , and not  $[SnX_4]^{2-}$  as previously reported for X = CI.

PREVIOUS studies on trifluorostannates(II) have indicated that with some cations, anion-association takes place in the solid state.<sup>1,2</sup> With tribromo- and tri-iodostannates(II) the vibrational spectra show that with such large cations as [Ph<sub>4</sub>As]<sup>+</sup> the anion is three-coordinate but has lower symmetry than  $C_{3n}$ , unlike the chloro-analogues.<sup>3</sup> The few data available at the commencement of this work 4-6 suggested that the Mössbauer parameters of halogeno-anions of tin(II) are also dependent upon the cation. It was therefore of interest to investigate in more detail the influence of cations on the vibrational and Mössbauer spectra of solid trihalogenostannate(II) salts.

The cations chosen for this study were such that

satisfactory Mössbauer and solution-phase vibrational spectra could be obtained. At the same time, extension of the Mössbauer isomer shift-electronegativity correlation found in hexahalogenostannate(IV) anions 7-9 to stannate(II) species could be investigated. During the preparation of this paper, some vibrational and Mössbauer spectral results were reported for tetraethylammonium salts of [SnX<sub>3</sub>]<sup>-</sup> and [SnX<sub>2</sub>Y]<sup>-</sup> anions; <sup>10</sup> relevant aspects of this are referred to in the Discussion section.

### EXPERIMENTAL

All manipulations were carried out under rigorously anhydrous and oxygen-free conditions, with de-aerated

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 <sup>8</sup> C. A. Clausen and M. L. Good, *Inorg. Chem.*, 1970, 9, 817.
 <sup>9</sup> A. G. Davies, L. Smith, and P. J. Smith, *J. Organometallic*

Chem., 1970, 23, 135. <sup>10</sup> R. J. H. Clark, L. Maresca, and P. J. Smith, J. Chem. Soc.

<sup>&</sup>lt;sup>1</sup> J. D. Donaldson, J. F. Knifton, J. O'Donoghue, and S. D. Ross, *Spectrochim. Acta*, 1966, **22**, 1173. <sup>2</sup> J. D. Donaldson and B. J. Senior, J. Chem. Soc. (A), 1967,

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<sup>&</sup>lt;sup>3</sup> I. Wharf and D. F. Shriver, Inorg. Chem., 1969, 8, 914. <sup>4</sup> J. D. Donaldson and B. J. Senior, J. Chem. Soc. (A), 1966, 1798.

<sup>&</sup>lt;sup>5</sup> J. D. Donaldson, D. G. Nicholson, and B. J. Senior, J. Chem. Soc. (A), 1968, 2928.

<sup>(</sup>A), 1970, 2687.

solvents. The trihalogenostannate(11) compounds are extremely sensitive to oxidation, the appearance of a very intense tin(IV) Mössbauer shift of  $0-0.5 \text{ mm s}^{-1}$  (relative to SnO<sub>2</sub>) being a convenient criterion for the presence of impurity. For those species containing bromo- or iodoligands, the oxidation process can also be noted by a darkening in colour.

Preparation of Complexes.---[Et<sub>4</sub>N][SnCl<sub>3</sub>]<sup>11</sup> and [Ph<sub>4</sub>As]-[SnCl<sub>a</sub>]<sup>3</sup> were obtained by published procedures, but these were unsatisfactory for the other compounds owing to more could be prepared entirely in a glove-box and then rapidly transferred to the evacuated sample chamber of the interferometer with the minimum of oxidation since the sample was dispersed in a Polythene matrix; if necessary the transfer may be effected in a sealed Polythene bag. Sampling of the anion-exchange resins was carried out similarly. Spectra of saturated solutions of the complexes, at 0.1 or 0.2 mm path-lengths, were obtained with a vacuumtight cell described previously.13

Raman spectra of the samples, sealed in glass ampoules

TABLE 1
Analytical data for trihalogenostannates(II)

			Found (%)			Required (%)					
Compound	Colour	c	н	N	Sn	Hal	c	н	N	Sn	Hal •
Et <sub>4</sub> N][SnCl <sub>3</sub> ]	White	$27 \cdot 1$	5.6	3.8	33.10	28.9	27.0	5.7	3.9	33.4	29.9
Bun <sub>4</sub> N][SnCl <sub>3</sub> ]	White	42.4	$8 \cdot 2$	3.1		22.4	41.1	7.8	3.0		22.8
Ph, As][SnCl,]	White	<b>46·6</b>	3.4		19.4 •		47.4	3.3		19.5	
Bu <sup>n</sup> <sub>4</sub> N][SnBr <sub>3</sub> ]	Lemon	$32 \cdot 1$	$6 \cdot 2$	$2 \cdot 3$	19.0*		32.0	6.0	$2 \cdot 3$	19.8	
Bu <sup>n</sup> <sub>4</sub> N <sup>†</sup> [SnI <sub>4</sub> ]	Yellow	26.0	5.0	1.9		50.3	25.9	4.9	1.9		51.3
Bu <sup>n</sup> N][SnCl,Br]	White	38.1	7.3	$2 \cdot 8$	22.90		37.5	7.1	2.7	$23 \cdot 2$	
Et,N][SnClBr.]	White	$21 \cdot 1$	4.5	$3 \cdot 2$	25.93		21.6	4.5	3.2	26.7	
Bun,N][SnClBr,]	White	<b>34</b> ·0	6.6	2.5	21.00		34.5	6.5	2.5	21.3	
Ph, Asj [SnClBr, ]	White	41.1	2.8		17.2 •		41.3	2.9		17.0	
Bun, N][SnCl.I]	Yellow	33.9	6.5	2.7	21.10	36.1	34.4	6.5	2.5	21.2	35.6
Et.NISnCIL.	Yellow	18.2	3.8	$2 \cdot 6$		53.6	17.9	3.8	2.6		54.5
Bu <sup>n</sup> ,N][SnClI.]	Yellow	29.6	5.8	1.9	18.60	45.5	29.6	5.6	$\overline{2 \cdot 2}$	18.3	44.5
Ph.Asi SnCll.	Yellow	36.2	2.5		15.2 .	35.4	36.4	2.6		15.0	36.6
Bun, NIISnBr.II	Yellow	30.4	5.9	$2 \cdot 1$	18.5 0	44.4	29.7	5.6	$2 \cdot 2$	18.3	44.2
Bu <sup>n</sup> ,NİlSnBrİ,İ	Orange	28.1	5.3	1.9		47.7	27.7	5.2	2.0		48.0
Bun <sub>4</sub> N][SnClBrI]	Yellow	31.4	6.0	$2 \cdot 2$	19·6 ¢		31.9	6·0	$\overline{2}\cdot \overline{3}$	19.7	20 0

Total halide. b Experimental values for tin(II).
 Total tin content.

rapid oxidation. These compounds were obtained from melts. Stoicheiometric quantities of [R]X and SnX<sub>2</sub> or  $SnY_2$  (R = cation) were mixed in ampoules under oxygenfree nitrogen and heated in vacuo until clear liquids were formed. On cooling to room temperature, the trihalogenostannates(II) crystallized (but [Bun<sub>4</sub>N][SnCl<sub>2</sub>I] remained as an oil from several preparations); evidence for their formulation is found from their Mössbauer and vibrational spectra. The compound [Bun<sub>4</sub>N][SnClBrI] was obtained similarly by use of  $SnCl_2 + SnBr_2 + [Bun_4N]I$ in 1:1:2 mol equivalent proportions.

Analyses are in Table 1. In order to confirm lack of oxidation of the complexes, tin was determined 12 as tin(II), or as total tin  $(SnO_2)$  where this was not practicable (e.g., iodides); total halide was estimated either by the Volhard or fluorescein methods, after oxidation of the samples to tin(IV).

The studies with the anion-exchange resin were made by converting the washed resin (Permutit Co. Ltd., 'De-Acidite ' FF-IP) into the appropriate halide form, eluting with an aqueous solution (X = Cl) of  $SnX_2$  (3 or 1.5 mol  $dm^{-3}$ ) in aqueous HX (6 or 3 mol  $dm^{-3}$ ), or with MeCOBu<sup>i</sup> extracts thereof (X = Br or I), washing with de-aerated water (X = Cl) or MeCOBu<sup>i</sup> (X = Br or I), and drying in a stream of oxygen-free nitrogen at 20 °C.

Vibrational Spectra.—Far-i.r. spectra (450—80 cm<sup>-1</sup>) were obtained on a Beckman-RIIC FS-520 interferometer to a resolution of 5 cm<sup>-1</sup>. The samples were studied in pressed discs in Polythene (B.D.H. Chemicals Ltd.) made by use of a Beckman-RIIC 'mini-die'. The latter had the advantage over conventional dies in that the discs J. S. Morrison and J. Haendler, J. Inorg. Nuclear Chem., 1967, 29, 393.
 J. D. Donaldson and W. Moser, Analyst, 1959, 84, 8.

or capillaries, were recorded on a Cary 81 spectrometer with He-Ne 632.8 nm laser excitation.

Mössbauer Spectra .--- These were obtained by courtesy of the P.C.M.U. (Harwell). The samples were studied in sealed containers at 77 K. The presence of small amounts of oxidation products did not affect the spectra of the tin(II) species. In each case, the resonance in the tin(II)region <sup>14</sup> of the spectrum appeared with distinct splitting, and was curve-fitted by computer to a quadrupole-split doublet. The spectra of the species adsorbed on the ionexchange resin were asymmetric; in these cases the midpoint of the signal was taken.

### **RESULTS AND DISCUSSION**

Vibrational Spectra.-In all cases the spectra show that the compounds isolated are individual species and not mixtures  $SnX_2 + X^-$ ,  $2[SnX_3]^- + [SnY_3]^-$ , etc. Neither is there dissociation or disproportionation into these on dissolution.

Deformation modes were not generally located, but the number of Raman and i.r. bands attributable to v(SnX) vibrations, and their Raman polarizations, shows that the species in solution are of pyramidal symmetry  $C_{3v}$  ([SnX<sub>3</sub>]<sup>-</sup>) or  $C_s$  ([SnX<sub>2</sub>Y]<sup>-</sup>). The solution-phase frequencies for the  $[SnX_3]^-$  salts are close to those of organic extracts of  $SnX_2$ -aq. HX solutions (Table 3 15).

 <sup>13</sup> M. Goldstein and H. A. Willis, Lab. Practice, 1970, 19, 808.
 <sup>14</sup> D. E. Fenton and J. J. Zuckerman, Inorg. Chem., 1969, 8. 1771.

<sup>15</sup> L. A. Woodward and M. J. Taylor, J. Chem. Soc., 1962, 407.

		TAB	BLE 2		
	Vibrati	ional spectra (cm <sup>-1</sup> ) o	f trihalogenostannates(	(I) $a, b$	
Compound	Method	ν(SnCl)	$\nu(SnBr)$	$\nu(SnI)$	Bending modes •
[Et <sub>4</sub> N][SnCl <sub>3</sub> ]	I.r., solid Raman, solid I.r., MeCN Raman, MeCN	280m, 240s, 217s 263s, 236m, 220sh 295m, 259s 298s.p. 260m.dp			134sh, 110m
$[\operatorname{Bun}_4N][\operatorname{SnCl}_3]^d$	I.r., solid I.r., MeCN	297m, 264sbr 295m, 259s			131w, 113w
[Ph4As][SnCl3]	I.r., solid Raman, solid I.r., MeCN Raman, MeCN	289m, 254s 288s, 260sh 295m, 258s 298s,p, 264m,dp			110w 104sh
[Res][SnCl <sub>3</sub> ]•	I.r., solid	292m, 250s			129sbr, 95w
[Bu <sup>a</sup> <sub>4</sub> N][SnBr <sub>3</sub> ]	I.r., solid Raman, solid I.r., Me <sub>2</sub> CO Raman, Me <sub>2</sub> CO		197m, 178s 205s, 180s 206m, 185s 207s,p, 185s,dp		70sh
[Res][SnBr <sub>8</sub> ] *	I.r., solid		204m, 178sbr		96sh, 86s
[Bu <sup>n</sup> <sub>4</sub> N][SnI <sub>3</sub> ]	I.r., solid Raman, solid I.r., CHCl <sub>3</sub> Raman, CHCl <sub>3</sub>			162sh, 146s 164s, 148m 162m, 147s 164s,p, 150sh,dp	
[Res][Snl <sub>3</sub> ] <sup>e</sup>	I.r., solid	000m 062a	190	166msn, 152s	
[Bu <sup>u</sup> 4N][SIICI2BI]	Raman, solid I.r., Me <sub>2</sub> CO Raman, Me <sub>2</sub> CO	292m, 263s 294m, 264m 292m, 263s 292s,p, 264ms,dp	1895 190m 187m 190ms,p		
[Et <sub>4</sub> N][SnClBr <sub>2</sub> ]	I.r., solid Raman, solid I.r., MeCN Raman, MeCN Raman, Me2CO	242sbr 247m 273mbr 280m,p 280m,p	167s, 149ms 173s, 156sh 203sh, 182s 205m,p, 180brsh,dp? 204ms,p, 184w,dp?		
$[\operatorname{Bun}_4N][\operatorname{SnClBr}_2]^d$	I.r., solid I.r., MeCN	268sbr 270sbr	200sh, 180s 198sh, 179m		
$[Ph_4As][SnClBr_2]^{d,f}$	I.r., solid Raman, solid	275m, 253s 255m	177s 207m, 216m		
$[\text{Res}][\text{SnClBr}_2]$ *	I.r., solid	273mbr	204mw, 177s		105brsh, 86w
$[\mathrm{Bu}^{n}_{4}\mathrm{N}][\mathrm{SnCl}_{2}\mathrm{I}]$	I.r., liquid Raman, liquid I.r., Me <sub>2</sub> CO Raman, Me <sub>2</sub> CO	292m, 261s 300s,p, 272sh,dp 292m, 263s 296m,p, 266m,dp		150s 155s,p 153m 155s,p	90w,dp
[Et <sub>4</sub> N][SnClI <sub>2</sub> ] <sup>f</sup>	I.r., solid Raman, solid	256sh, 234br 244mbr		130svbr 126m, 116sh	
$[\operatorname{Bun}_4N][\operatorname{SnClI}_2]$	I.r., solid Raman, solid I.r., Me <sub>2</sub> CO I.r., CHCl <sub>3</sub> Raman, Me <sub>2</sub> CO	264sbr 268mbr 275sbr 262sbr 264vw,p?		158sh, 145s 165s, 150m 161sh, 150s 161sh, 148s 162s,p, 150sh,dp	
[Ph <sub>4</sub> As][SnClI <sub>2</sub> ] <sup>f</sup>	I.r., solid Raman, solid Raman, Me <sub>2</sub> CO	261sbr 249mbr <i>h</i>		151m, 143m, 151mw, 135s 160w,p, 158w,dp?	121s 130sh
$[\operatorname{Bun}_4 N][\operatorname{SnBr}_2 I]$	I.r., solid Raman, solid I.r., Me <sub>2</sub> CO Raman, Me <sub>2</sub> CO		195msh, 180s 200m, 180m 203m, 185s 202s,p, 186sh,dp	148s 148mbr 152ms 153s,p	
$[\operatorname{Bu}_4^n][\operatorname{SnBrI}_2]$	I.r., solid Raman, solid I.r., CHCl <sub>3</sub> Raman, CHCl <sub>3</sub>		189s 183w 183mbr 190w,p	160sh, 149s 160sh, 140s 153sh, 147s 150s,p, 143sh,dp	60w
[Bu <sup>n</sup> <sub>4</sub> N][SnClBrI]	I.r., solid Raman, solid I.r., Me <sub>2</sub> CO Raman. Me <sub>2</sub> CO	270sbr 275mbr 276s 278mbr.p	187s 193s 189s 196m.p	148s 155m 152m 155s,p	

Kaman, Me<sub>2</sub>CO 278mbr,p 196m,p 1958,p \* v = Very, s = strong, m = medium, w = weak, br = broad, sh = shoulder, p = polarized, dp = depolarized. A question mark indicates that the depolarization ratio obtained is only probable. <sup>b</sup> Internal modes of cations were eliminated by comparison with spectra of simple halides of these. The halide form of the anion-exchange resin used showed no i.r. bands in the region studied (see Figure 1). <sup>c</sup> Raman spectral data of the bending modes for the solutions could not generally be obtained because of solvent scattering and limited solubilities. No suitable solvent was found which had useful i.r. transmission properties below 150 cm<sup>-1</sup>. I.r. measurements restricted to above 80 cm<sup>-1</sup>. Bending modes observed are in good agreement with the ranges expected from Table 3. <sup>d</sup> Satisfactory Raman spectral data could not be obtained because of fluorescence problems. <sup>e</sup> [Res]<sup>+</sup> = cation of anion-exchange resin. <sup>f</sup> Solubility considerations prevented i.r. and/or Raman spectral measurements on solutions. <sup>g</sup> Obtained decomposition.

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The data for the  $[Et_4N]^+$  salts agree with those obtained concurrently.<sup>10</sup> The spectra of solid  $[Et_4N]$ - $[SnCl_3]$  are quite different from those of its solutions (Figure 1); more bands are found, and at lower wavenumbers, and there is lack of coincidence between Raman and i.r. bands. Likely origins of this are lower symmetry, association, and correlation splitting.  $[Et_4N][SnI_2Cl]$  was too insoluble for study, but the solid has two v(SnCl) i.r. bands. The anion modes of  $[Et_4N][SnBr_2Cl]$  show large shifts to lower frequencies on passing from solution to the solid state. These effects are attributed to solid-state association, probably with lowering of symmetry.

In contrast, with the larger cation  $[Bun_4N]^+$  the spectra of the solids and their solutions are not significantly different (Table 2). In these cases the regular structure of the anions is retained in the solid state.

from  $SnCl_2$ -aq. HCl solutions (1:2 mol equiv.) showed an i.r. spectrum similar to *solutions* of  $[SnCl_3]^-$  salts (Figure 1). There was no evidence of bands attributable to ' $[SnCl_4]^{2-}$ '. The latter ion has previously been stated to be absorbed under such conditions,<sup>16</sup> but despite many studies on various systems we have not obtained evidence for its existence.

Spectra of  $[SnBr_3]^-$ ,  $[SnI_3]^-$ , and  $[SnClBr_2]^-$  anions absorbed on the resin have also been obtained (Table 2). Their v(SnX) frequencies are close to those of *solutions* of corresponding isolated salts. This observation has important relevance to the variation with cation of modes of anions,<sup>17</sup> and is currently being investigated further.

*Mössbauer Spectra.*—All the compounds, as well as the ion-exchange resins containing absorbed halogenocomplexes, show doublet resonances with isomer shifts

TABLE 3

Vibrational	spectra	(cm <sup>-1</sup> ) of	f organic	extracts con	taining $[SnX_3]^-$	species

Aqueous solution <sup>a</sup>	Extractant	Method	$v_1(a_1)$	$\nu_{2}(a_{1})$	$v_{3}(e)$	$\nu_4(e)$	Species	Ref.
$SnCl_2(2M)$ in $HCl(6M)$	Et,O	Raman	297s,p	128w,p	$256 \mathrm{mbr,dp}$	103mbr,dp	[SnCl <sub>3</sub> ]-	15
$SnBr_2(1.5M)$ in $HBr(4M)$	Et <sub>2</sub> O	Raman	211s,p	83m,p	181mbr,dp	65m,dp ¯	$[SnBr_3]^-$	15
$\operatorname{SnBr}_2(2M)$ in $\operatorname{HBr}(6M)$	Et <sub>2</sub> O	Raman	210s, p	82sh,p?	184m,dp	67s,dp?	[SnBr <sub>3</sub> ]-	b
$\operatorname{SnBr}_2(1.5M)$ in $\operatorname{HBr}(3M)$	MeCOPr <sup>n</sup>	{ Raman I.r.	210s,p 207m	82sh,p?	182m,dp 183s	68s,dp?	$\left[ SnBr_{3}\right] $	b
$SnBr_{2}(1.5M)$ in HBr(3M)	MeCOBui	Raman	208s,p		186m,dp	64s,dp	$[SnBr_{3}]^{-}$	b
$SnI_2(2M)$ in $HI(4M)$	$Et_{2}O$	Raman	162s,p		140m,dp		[SnI <sub>3</sub> ] <sup></sup>	b

The  $[Ph_4As]^+$  compounds are intermediate in behaviour; there are small differences between solid- and solutionphase frequencies, but the number of bands and their

at 77 K  $\delta/(\text{mm s}^{-1})$ Compound  $\Delta E/(\text{mm s}^{-1})$  $\Sigma \chi b$  $\begin{array}{c} [\mathrm{Et_4N}][\mathrm{SnCl_3}]\\ [\mathrm{Bun_4N}][\mathrm{SnCl_3}]\\ [\mathrm{Ph_4As}][\mathrm{SnCl_3}]\end{array}$ 3.43 1.13 3.121.379.00 3.281.26[Res][SnCl<sub>8</sub>] 3.371.34 $\begin{bmatrix} \text{Ices}[\text{SnCl}_{s}]^{\circ} \\ [\text{Bu}^{a}_{4}\text{N}][\text{SnBr}_{s}] \\ [\text{Res}[\text{SnBr}_{s}]^{\circ} \\ [\text{Bu}^{a}_{4}\text{N}][\text{SnCl}_{s}] \\ [\text{Bu}^{a}_{4}\text{N}][\text{SnCl}_{s}\text{Pr}_{s}] \\ [\text{Et}_{4}\text{N}][\text{SnClBr}_{s}] \\ [\text{Bu}^{a}_{4}\text{N}][\text{SnClBr}_{s}] \\ [\text{Ph}_{4}\text{As}][\text{SnClBr}_{s}] \\ [\text{Ph}_{s}\text{SnClBr}_{s}] \\ \end{bmatrix}$ 3.251.028.28 3.48 1.02 3.39 0.79 7.688.76 3.151.263.540.943.19 1.128.523.321.10  $[Res][SnClBr_2]$ 3.451.07 $\begin{bmatrix} \operatorname{Res}[\operatorname{SnClBr}_2]^{\circ} \\ [\operatorname{Bu}^{a}_{4}N][\operatorname{SnCl}_2] \\ [\operatorname{Et}_4N][\operatorname{SnCl}_2] \\ [\operatorname{Bu}^{a}_{4}N][\operatorname{SnCl}_2] \\ [\operatorname{Bu}^{a}_{4}N][\operatorname{SnBr}_2] \\ [\operatorname{Bu}^{a}_{4}N][\operatorname{SnBr}_2] \\ [\operatorname{Bu}^{a}_{4}N][\operatorname{SnBr}_2] \end{bmatrix}$ 3.21 8·56 1.13 3.67 0.358.12  $3 \cdot 29$ 0.920.803.45 8.08 3.340.873.350.837.88[Bun<sub>4</sub>N][SnClBrI] 3.251.038.32

 TABLE 4

 Mössbauer parameters <sup>a</sup> for trihalogenostannates(II)

<sup>a</sup> Relative to  $SnO_2$ . <sup>b</sup> Mulliken values. <sup>c</sup> [Res]<sup>+</sup> = cation of an ion-exchange resin.

Raman polarizations are consistent with regular pyramidal structures in both phases. Any association in the solid  $[Ph_4As]^+$  compounds must be weak.

The species absorbed by an anion-exchange resin <sup>16</sup> V. I. Baranovskii, G. M. Gorodinskii, L. M. Krizhanskii, B. I. Rogozev, and S. B. Tomilov, *Radiokhimiya*, 1966, **8**, 365. in the 'tin(II) region '.<sup>14</sup> Previous studies have found a relationship between isomer shifts ( $\delta$ ) of hexahalogenostannate(IV) ions and the sums of the electronegativity coefficients of the ligands ( $\Sigma \chi$ ).<sup>7-9</sup> Such relationships



will only be valid within structurally analogous series. The correlation shown here by the  $[Bun_4N]^+$  salts <sup>17</sup> D. M. Adams, 'Metal-Ligand and Related Vibrations,' Arnold, London, 1967, p. 42.



(Figure 2) extends this relationship to tin(II) systems, and shows that the anions have regular structures as deduced above. The  $[Et_4N]^+$  salts have markedly different  $\delta$  values from their  $[Bun_4N]^+$  analogues, as expected from the structural differences. The less regular  $\delta - \Sigma \chi$  correlation in the  $[Et_4N]^+$  series (*cf.* also ref. 10) shows that the extent of association is variable. The  $[Ph_4As]^+$  compounds have isomer shifts between the other two series, indicating that these are only weakly associated, as concluded from the vibrational spectral study. The isomer shifts are influenced more by the cation than by changing the halide ligands (Table 4 and Figure 2).



FIGURE 2 Correlation between <sup>119</sup>Sn Mössbauer isomer shifts and sums of Mulliken electronegativity coefficients of the halide ligands. Cations:  $\bigcirc$ ,  $[Bu^n_4N]^+$ ;  $\triangle$ ,  $[Ph_4As]^+$ ;  $\square$ ,  $[Et_4N]^+$ ;  $\diamondsuit$ ,  $[Res]^+$ , the cation of anion-exchange resin

Inverse relationships between quadrupole splitting parameters ( $\Delta E$ ) and isomer shifts of tin(II) compounds have been reported,<sup>18-20</sup> and are found also in this work (Table 4). The various series show different relation-

<sup>18</sup> V. I. Goldanskii, V. V. Khrapov, V. Y. Rochev, T. N. Sumarokova, and D. E. Surpina, *Doklady Akad. Nauk S.S.S.R.*, 1968, **183**, 364.

<sup>19</sup> J. K. Lees and P. A. Flinn, J. Chem. Phys., 1968, 48, 882.

ships, as expected from the structural variations, which are seen as dependence of  $\Delta E$  on  $\Sigma \chi$  in Figure 3. This now clearly shows, as suggested,<sup>20</sup> that the electric field



FIGURE 3 Correlation between quadrupole splitting parameters and sums of Mulliken electronegativity coefficients of the halide ligands; symbols as in Figure 2

gradient around the tin(II) nucleus is influenced by polarity of the tin-ligand bonds. The effect is as important as in five- and six-co-ordinate tin(IV) compounds.<sup>21</sup>

For a given anion, when the  $[Bu^n_4N]^+$  cation is replaced by  $[Ph_4As]^+$  or  $[Et_4N]^+$ ,  $\delta$  increases while  $\Delta E$ decreases. This is consistent with increased association in the last two series, by  $Sn-X \cdots Sn$  or  $Sn-X \cdots$  cation interactions.

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