

## Mössbauer Spectra of Six-co-ordinate Organotin(IV) Compounds with Oxygen Donors: Structure, Bonding, and Correlation with Antimony(V) $e^2qQ$ Values

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Mössbauer spectra are reported for twenty-six six-co-ordinate  $\text{Sn}^{\text{IV}}$  compounds of the type  $[\text{R}_2\text{SnL}_4][\text{X}]_2$ , (I),  $\text{R}_2\text{SnL}_2\text{Cl}_2$ , (II), and  $\text{R}_3\text{SnL}_2\text{Cl}$ , (III) ( $\text{R} = \text{Me}$  or  $\text{Ph}$ ;  $\text{L} = \text{oxygen donor}$ ;  $\text{X} = \text{Ph}_4\text{B}^-$ ,  $\text{ClO}_4^-$ , or  $\text{PF}_6^-$ ). The quadrupole splittings show that compounds (I) and (III) have *trans* R groups, while (II) are *trans*-isomers. From the derived partial quadrupole splittings, the donor properties of the ligands L increase in the order  $\text{Ph}_3\text{PO} < (\text{Me}_2\text{N})_3\text{PO} < \text{Me}_2\text{SO} < \frac{1}{2}\text{Ph}_2(\text{O})\text{PCH}_2\text{P}(\text{O})\text{Ph}_2 < \frac{1}{2}\text{Ph}_2(\text{O})\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2 < \text{HCO}\cdot\text{NMe}_2 < \text{Ph}_2(\text{O})\text{AsCH}_2\text{As}(\text{O})\text{Ph}_2 < \text{Ph}_3\text{AsO} < \frac{1}{2}\text{bipydo}$  (bipydo = 2,2'-bipyridyl *NN'*-dioxide). Extension of a previous correlation between  $\text{Sb}^{\text{V}}$  and  $\text{Sn}^{\text{IV}}$   $e^2qQ$  values for  $\text{SbCl}_5\text{L}$  and corresponding *cis*- $\text{Cl}_2\text{SnL}_2$  compounds again indicates that an excellent correlation is obtained with a correlation coefficient  $r$  of 0.995 for ten compounds. This correlation further supports assumptions made in the ratio method for obtaining accurate quadrupole parameters.

ALTHOUGH  $^{119}\text{Sn}$  Mössbauer spectra of a large number of six-co-ordinate  $\text{Sn}^{\text{IV}}$  compounds containing neutral ligands,  $\text{R}_2\text{SnX}_2\text{L}_2$  and  $\text{X}_4\text{SnL}_2$  ( $\text{R} = \text{Ph}$ ,  $\text{Me}$ , etc.;  $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ;  $\text{L} = \text{neutral ligand}$ ) have been recorded,<sup>1-3</sup> the quadrupole splittings (q.s.) have not been particularly useful for elucidating bonding variations of the neutral donors or for predicting other six-co-ordinate structures. Quadrupole splitting values of  $\text{X}_4\text{SnL}_2$  species are often too small to be easily measured, and variations in q.s. for  $\text{R}_2\text{SnX}_2\text{L}_2$  compounds are small. Thus partial quadrupole splitting values (p.q.s.) for oxygen-donor ligands ( $\text{L} = \text{Me}_2\text{SO}$ ,  $\text{C}_5\text{H}_5\text{NO}$ ,  $\text{Bu}_3\text{PO}$ ,  $\text{Ph}_3\text{PO}$ , or  $\text{Ph}_3\text{AsO}$ ) derived from the latter compounds (ref. 1, Table 26) have a total range of only 0.06 mm s<sup>-1</sup>. In this study, we have recorded spectra for a large number of newly prepared compounds<sup>4-6</sup> of the types  $[\text{R}_2\text{SnL}_4]^{2+}$  (I:  $\text{R} = \text{Ph}$  or  $\text{Me}$ ;  $\text{L} = \text{Ph}_3\text{PO}$ ,  $\text{Ph}_3\text{AsO}$ ,  $\text{Me}_2\text{SO}$ , etc.) and  $\text{R}_2\text{SnCl}_2\text{L}_2$ , (II). The q.s. of compounds (I) have about twice the sensitivity to L as those of (II), and the significant differences in q.s. can be readily interpreted in terms of the bonding properties of the ligands. P.q.s. derived from the *trans*-(I) compounds are useful in assigning other six-co-ordinate structures.

The recent report of several  $^{121}\text{Sb}$  q.s. for  $\text{SbCl}_5\text{L}$  compounds<sup>7</sup> makes it again possible to correlate values for  $\text{Sn}^{\text{IV}}$  and  $\text{Sb}^{\text{IV}}$  using methods previously discussed.<sup>8,9</sup> The good correlation thus obtained further supports the assumption made earlier<sup>9</sup> that bonding in  $\text{Sb}^{\text{V}}$  and  $\text{Sn}^{\text{IV}}$  compounds is very similar, and that the  $Q(^{119}\text{Sn})$  value derived earlier is reasonable.

### EXPERIMENTAL

The compounds were prepared as reported previously.<sup>4-6</sup> Mössbauer spectra were obtained at 80 K using a 5 mCi  $\text{BaSnO}_3$  source at room temperature, and an Austin Science

Associates spectrometer. Absorptions were generally ca. 5%, and the linewidths (Tables 1 and 2) were very similar. Calibration was carried out using the  $^{57}\text{Fe}$  spectrum of a 99.99% Fe foil, and centre shifts are quoted with respect to the centre of a room-temperature  $\text{BaSnO}_3$ - $\text{BaSnO}_3$  spectrum using the scan-centre method.<sup>10</sup> The spectra were computed using methods described previously.<sup>10,11</sup> The reproducibility of the results is within  $\pm 0.03$  mm s<sup>-1</sup> for both the centre shift and quadrupole splitting.

### RESULTS AND DISCUSSION

**Structure and Bonding.**—The q.s. in Tables 1 and 2 are all characteristic of six-co-ordinate  $\text{Sn}^{\text{IV}}$  compounds with *trans* R groups,<sup>1</sup> as was suggested by i.r. and n.m.r. evidence.<sup>4-6</sup> The q.s. cannot distinguish between the two possible *trans* R isomers for compounds (II). These two isomers differ in expected quadrupole splitting only by a small  $\eta$  term<sup>1</sup> which makes a difference in quadrupole splitting of no more than 0.05 mm s<sup>-1</sup> (footnote to Table 4).

The q.s. for  $[\text{Me}_2\text{Sn}(\text{bipydo})_2][\text{X}]_2$  (bipydo = 2,2'-bipyridyl *NN'*-dioxide;  $\text{X} = \text{Ph}_4\text{B}$ ,  $\text{PF}_6$ , or  $\text{ClO}_4$ ) showed a slight variation (0.22 mm s<sup>-1</sup>). Two additional pieces of evidence showed that the q.s. for the  $\text{Ph}_4\text{B}$  compounds are not significantly affected by the counter ion. First, a plot of quadrupole splitting for  $[\text{R}_3\text{SnL}_2]^+$  compounds against those for (I)<sup>12</sup> gave a good correlation. Second, predicted and observed q.s. (Table 4) were generally in satisfactory agreement using partial quadrupole splitting values (Table 3) derived from compounds (I;  $\text{R} = \text{Me}$ ). We used the following partial quadrupole splitting values<sup>13</sup> to obtain the values in Table 3: -1.03 (Me), -0.95 (Ph), 0.00 (Cl), and +0.07 mm s<sup>-1</sup> (NCS); the usual assumption of 90° bond angles was also made. It is noticeable that the predicted quadrupole splitting values for the Ph compounds are

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<sup>10</sup> G. M. Bancroft, 'Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists,' McGraw-Hill, Maidenhead, 1973.

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<sup>1</sup> G. M. Bancroft and R. H. Platt, *Adv. Inorg. Radiochem.*, 1972, **15**, 59.

<sup>2</sup> P. G. Harrison, B. C. Lane, and J. J. Zuckerman, *Inorg. Chem.*, 1972, **11**, 1537.

<sup>3</sup> D. Cunningham, M. J. Fraser, and J. D. Donaldson, *J.C.S. Dalton*, 1972, 1647.

<sup>4</sup> V. G. Kumar Das and W. Kitching, *J. Organometallic Chem.*, 1967, **10**, 59.

<sup>5</sup> V. G. Kumar Das, W. Kitching, and C. J. Moore, *J. Organometallic Chem.*, 1970, **22**, 399.

<sup>6</sup> V. G. Kumar Das, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 155.

<sup>7</sup> J. M. Friedt, G. K. Shenoy, and M. Burgard, *J. Chem. Phys.*, 1973, **59**, 4468.

TABLE 1  
 Mössbauer parameters (mm s<sup>-1</sup>) at 80 K for the compounds [R<sub>3</sub>SnL<sub>4</sub>][X]<sub>2</sub>, (I)

R	L	X	Centre shift $\pm 0.03$	Quadrupole splitting $\pm 0.03$	$\Gamma_1 \pm 0.05$	$\Gamma_2 \pm 0.05$
Me	$\frac{1}{2}$ bipydo	Ph <sub>4</sub> B	1.26	4.00	1.07	1.07
Me	$\frac{1}{2}$ bipydo	PF <sub>6</sub>	1.17	3.78	1.11	1.05
Me	$\frac{1}{2}$ bipydo	ClO <sub>4</sub>	1.23	3.97	1.08	1.14
Me	Ph <sub>3</sub> AsO	Ph <sub>4</sub> B	1.27	4.03	0.99	0.99
Me	$\frac{1}{2}$ Ph <sub>2</sub> (O)AsCH <sub>2</sub> As(O)Ph <sub>2</sub>	Ph <sub>4</sub> B	1.19	4.08	1.20	1.21
Me	HCO·NMe <sub>2</sub>	Ph <sub>4</sub> B	1.27	4.26	1.02	1.14
Me	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> CH <sub>2</sub> P(O)Ph <sub>2</sub>	Ph <sub>4</sub> B	1.29	4.38	1.16	1.05
Me	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	Ph <sub>4</sub> B	1.27	4.50	1.00	1.02
Me	Me <sub>2</sub> SO	Ph <sub>4</sub> B	1.39	4.52	0.98	1.04
Me	(Me <sub>2</sub> N) <sub>3</sub> PO	Ph <sub>4</sub> B	1.27	4.58	1.14	1.20
Me	Ph <sub>3</sub> PO	Ph <sub>4</sub> B	1.35	4.75	1.10	1.10
Ph	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	Ph <sub>4</sub> B	1.30	3.78	1.08	1.11
Ph	Me <sub>2</sub> SO	Ph <sub>4</sub> B	1.24	4.30	1.09	1.08

bipydo = 2,2'-Bipyridyl NN'-dioxide.

 TABLE 2  
 Mössbauer parameters (mm s<sup>-1</sup>) at 80 K for the compounds R<sub>2</sub>SnCl<sub>2</sub>L<sub>2</sub>, (II), and R<sub>3</sub>SnCIL, (III)

R	L	Centre shift $\pm 0.03$	Quadrupole splitting $\pm 0.03$	$\Gamma_1 \pm 0.05$	$\Gamma_2 \pm 0.05$
(a) (II)					
Me	C <sub>5</sub> H <sub>5</sub> NO	1.42 <sup>a</sup>	$\pm 3.96$ <sup>a</sup>		
Me	$\frac{1}{2}$ bipydo	1.39	4.08	1.09	1.13
Me	NCS, $\frac{1}{2}$ bipydo	1.32	4.07	1.11	1.10
Me	Ph <sub>3</sub> AsO	1.31	4.14	1.31	1.13
Bu	Ph <sub>3</sub> AsO	1.49 <sup>b</sup>	4.04 <sup>b</sup>		
Me	$\frac{1}{2}$ Ph <sub>2</sub> (O)AsCH <sub>2</sub> As(O)Ph <sub>2</sub>	1.30	4.06	1.21	1.20
Me	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> CH <sub>2</sub> P(O)Ph <sub>2</sub>	1.27	4.19	1.05	1.05
Me	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	1.44	4.32	1.28	1.30
Me	Me <sub>2</sub> SO	1.40 <sup>a,c</sup>	4.13 <sup>a,c</sup>		
Me	(Me <sub>2</sub> N) <sub>3</sub> PO	1.32	4.28	1.27	1.16
Me	Ph <sub>3</sub> PO	1.37	4.30	1.15	1.02
Bu	Ph <sub>3</sub> PO	1.62 <sup>b</sup>	4.11 <sup>b</sup>		
Ph	$\frac{1}{2}$ bipydo	1.28	3.49	1.29	1.23
Ph	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> CH <sub>2</sub> P(O)Ph <sub>2</sub>	1.26	3.65	1.05	1.01
Ph	$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	1.27	3.78	1.17	1.18
Ph	Me <sub>2</sub> SO	1.23 <sup>c</sup>	3.54 <sup>c</sup>		
(b) (III)					
Me	Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	1.35	3.58	0.99	1.05
Ph	Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	1.29	3.25	1.19	1.09

<sup>a</sup> A. G. Davies, L. Smith, and P. J. Smith, *J. Organometallic Chem.*, 1970, **23**, 135. <sup>b</sup> F. P. Mullins, *Canad. J. Chem.*, 1971, **49**, 2719. <sup>c</sup> R. C. Poller, J. N. R. Ruddick, B. Taylor, and D. L. B. Toley, *J. Organometallic Chem.*, 1970, **24**, 341.

appreciably larger than the observed values. In addition, it is interesting that the quadrupole splitting for compounds (II; R = Me) plotted against those for (I)

 TABLE 3  
 Partial quadrupole splitting values (mm s<sup>-1</sup>) for oxygen-donor ligands

Ligand	P.q.s.
Ph <sub>3</sub> PO	+0.16
(Me <sub>2</sub> N) <sub>3</sub> PO	+0.12
Me <sub>2</sub> SO	+0.10
$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> P(O)Ph <sub>2</sub>	+0.10
$\frac{1}{2}$ Ph <sub>2</sub> (O)PCH <sub>2</sub> CH <sub>2</sub> P(O)Ph <sub>2</sub>	+0.07
HCO·NMe <sub>2</sub>	+0.04
$\frac{1}{2}$ Ph <sub>2</sub> (O)AsCH <sub>2</sub> As(O)Ph <sub>2</sub>	-0.01
Ph <sub>3</sub> AsO	-0.02
$\frac{1}{2}$ bipydo	-0.03

[L = Ph<sub>3</sub>PO, (Me<sub>2</sub>N)<sub>3</sub>PO, Ph<sub>2</sub>(O)PCH<sub>2</sub>P(O)Ph<sub>2</sub>, Ph<sub>2</sub>(O)PCH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>, Cl, Ph<sub>3</sub>AsO, Ph<sub>2</sub>(O)AsCH<sub>2</sub>As(O)Ph<sub>2</sub>, or bipydo] gave a reasonable linear correlation with gradient 0.33 ( $r = 0.83$ ). Considering the very small range of q.s. (0.22 mm s<sup>-1</sup> for the Me<sub>2</sub>SnCl<sub>2</sub>L<sub>2</sub> species), this is in reasonable agreement with the expected gradient of 0.5.

The p.q.s. for the neutral ligands are now useful for predicting signs and magnitudes of q.s., assigning structures and predicting bonding properties of ligands.<sup>1</sup> The predicted q.s. for the *cis*-Cl<sub>4</sub>SnL<sub>2</sub> compounds (Table 4, L = Me<sub>2</sub>SO and Ph<sub>3</sub>PO) are positive, as has been found experimentally for Cl<sub>4</sub>Sn(NCMe)<sub>2</sub>,<sup>3,14</sup> and confirm that the L groups are generally poorer donors than Cl (ref. 1, p. 146). For compounds such as Me<sub>3</sub>SnCIL and Ph<sub>3</sub>SnCIL [Table 4, L = Ph<sub>2</sub>(O)PCH<sub>2</sub>P(O)Ph<sub>2</sub>], it is now possible to make structural predictions using the partial quadrupole splitting values. Although the low  $J(^{119}\text{Sn}-\text{CH}_3)$  in solution<sup>6</sup> indicates that the Me compound contains five-co-ordinate tin in solution, the multiple  $\nu(\text{Sn}-\text{C})$  stretching bands in the i.r. spectrum strongly suggests six-co-ordination in the solid state.<sup>6</sup> The predicted q.s. for the *trans*-isomers are in good agreement with the observed values, while the predicted *cis* quadrupole splitting is close to zero. This evidence strongly indicates that these two compounds have the *trans*-structure. For compounds such

<sup>14</sup> D. Cunningham, M. J. Frazer, and J. D. Donaldson, *J. Chem. Soc. (A)*, 1971, 2049.

as  $\text{RSnCl}_3\text{L}$  reported earlier [ref. 1, Table 27; Table 4,  $\text{PhSnCl}_3(\text{OPPh}_3)_2$ ], the predicted q.s. for the three isomers are still too similar to assign the structure with any confidence. Thus, for  $\text{PhSnCl}_3(\text{OPPh}_3)_2$ , the predicted q.s. vary from  $+1.77$  to  $+2.29 \text{ mm s}^{-1}$ , while the observed value is in between these values at  $2.01 \text{ mm s}^{-1}$ .

TABLE 4

Predicted and observed quadrupole splitting values ( $\text{mm s}^{-1}$ ) for organotin(IV) compounds with oxygen donors

Compound	Quadrupole splitting	
	Observed	Predicted <sup>a</sup>
$[\text{Ph}_2\text{Sn}\{\text{Ph}_2(\text{O})\text{PCH}_2\text{P}(\text{O})\text{Ph}_2\}_2[\text{Ph}_4\text{B}]_2$	3.78	+4.20
$[\text{Ph}_2\text{Sn}(\text{OSMe}_2)_4][\text{Ph}_4\text{B}]_2$	4.30	+4.20
$\text{Me}_2\text{SnCl}_2\{\text{Ph}_2(\text{O})\text{AsCH}_2\text{As}(\text{O})\text{Ph}_2\}$	4.06	+4.10
$\text{Me}_2\text{SnCl}_2(\text{bipydo})$	4.08	+4.06
$\text{Me}_2\text{Sn}(\text{NCS})_2(\text{bipydo})$	4.07	+4.20
$\text{Me}_2\text{SnCl}_2(\text{OAsPh}_3)_2$	4.14	+4.08
$\text{Bu}_2\text{SnCl}_2(\text{OAsPh}_3)_2$	4.04	+4.08
$\text{Me}_2\text{SnCl}_2(\text{OSMe}_2)_2$	4.16	+4.32
$\text{Me}_2\text{SnCl}_2\{\text{Ph}_3(\text{O})\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}$	4.19	+4.26
$\text{Me}_2\text{SnCl}_2\{\text{OP}(\text{NMe}_2)_3\}_2$	4.28	+4.36
$\text{Me}_2\text{SnCl}_2(\text{OPPh}_3)_2$	4.30	+4.44
$\text{Me}_2\text{SnCl}_2\{\text{Ph}_2(\text{O})\text{PCH}_2\text{P}(\text{O})\text{Ph}_2\}$	4.32	+4.32
$\text{Ph}_2\text{SnCl}_2(\text{bipydo})$	3.49	+3.74
$\text{Ph}_2\text{SnCl}_2(\text{OSMe}_2)_2$	3.54	+4.00
$\text{Ph}_2\text{SnCl}_2\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}$	3.65	+3.94
$\text{Ph}_2\text{SnCl}_2\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}$	3.78	+4.00
$\text{Me}_3\text{SnCl}\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}$	3.58	<i>trans</i> +3.71 ( $\eta$ 0.90)
		<i>cis</i> -0.20 ( $\eta$ 0)
$\text{Ph}_3\text{SnCl}\{\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}$	3.25	<i>trans</i> +3.45 ( $\eta$ 0.93)
		<i>cis</i> -0.20 ( $\eta$ 0)
<i>cis</i> - $\text{SnCl}_4(\text{OSMe}_2)_2$	<0.5 <sup>b</sup>	+0.20
<i>cis</i> - $\text{SnCl}_4(\text{OPPh}_3)_2$	0.56 <sup>c</sup>	+0.32
$\text{PhSnCl}_3(\text{OPPh}_3)_2$	2.01 <sup>d</sup>	+1.77 ( $\eta$ 0.28) <sup>d</sup> +2.22 ( $\eta$ 0) +2.29 ( $\eta$ 0.43)

<sup>a</sup> For the  $\text{R}_2\text{SnCl}_2\text{L}_2$  compounds, the predicted values refer to the *cis*-*cis*-*L* isomer for which  $\eta = 0$ . For all-*trans*-isomer, the predicted quadrupole splitting is very slightly larger. For  $\text{Me}_2\text{SnCl}_2(\text{OPPh}_3)_2$ , the predicted quadrupole splitting for the all-*trans*-isomer is  $+4.48 \text{ mm s}^{-1}$ ,  $\eta = 0.22$ . <sup>b</sup> Ref. 2; J. Philip, M. A. Mullen, and C. Curran, *Inorg. Chem.*, 1968, **7**, 1895; P. A. Yeats, J. R. Sams, and F. Aubke, *ibid.*, 1970, **9**, 740. <sup>c</sup> Average of values from last two references in <sup>b</sup>. <sup>d</sup> Table 27, ref. 1; the predicted values correspond to isomers b, c, and d respectively in this Table.

Since the partial quadrupole splitting value for a ligand becomes more negative as the donor strength of the ligand increases,<sup>1,13</sup> the donor strength of these ligands increases in the order  $\text{Ph}_3\text{PO} < (\text{Me}_2\text{N})_3\text{PO} < \text{Me}_2\text{SO} \sim \frac{1}{2}\text{Ph}_2(\text{O})\text{PCH}_2\text{P}(\text{O})\text{Ph}_2 < \frac{1}{2}\text{Ph}_2(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2 < \text{HCO}\cdot\text{NMe}_2 < \text{Ph}_2(\text{O})\text{AsCH}_2\text{As}(\text{O})\text{Ph}_2 < \text{Ph}_3\text{AsO} < \frac{1}{3}\text{bipydo}$ . This order of donor strengths correlates well with the order deduced from  $J(^{119}\text{Sn}-\text{Me})$  values derived from the compounds (I;  $\text{R} = \text{Me}$ ),<sup>6</sup>

\*  $1\text{b} = 10^{-28} \text{ m}^2$ .

<sup>15</sup> C. I. Branden and I. Lindqvist, *Acta Chem. Scand.*, 1963, **17**, 759.

except for  $\text{Me}_2\text{SO}$ . The order is also consistent with the ideas suggested earlier<sup>4-6</sup> for formation of  $\text{Me}_2\text{SnPh}_2$  in solution from the compounds (I;  $\text{R} = \text{Me}$ ,  $\text{X} = \text{Ph}_4\text{B}$ ) by reaction of the  $\text{Ph}_4\text{B}$  phenyl groups with the  $[\text{Me}_2\text{SnL}_4]^{2+}$  cation. Thus, only for strong donors such as  $\text{L} = \text{Ph}_3\text{AsO}$  could the six-co-ordinate  $[\text{Me}_2\text{SnL}_4]^{2+}$  species be detected in solution. In other cases, the  $\text{Ph}$  from  $\text{Ph}_4\text{B}$  effectively competed with poorer donors for co-ordination to the  $\text{Sn}$ .

**$\text{Sn}^{\text{IV}}-\text{Sb}^{\text{V}}$  Correlations.**—The recent publication of  $\text{Sb}^{\text{V}}$  Mössbauer parameters for  $\text{SbCl}_5\text{L}$  ( $\text{L} = \text{MeCN}$ ,  $\text{Me}_2\text{PO}$ ,  $\text{Ph}_3\text{PO}$ ,  $\text{Cl}_3\text{PO}$ , etc.) compounds<sup>7</sup> makes it possible to extend the  $\text{Sn}^{\text{IV}}-\text{Sb}^{\text{V}}$  correlations published previously using the ratio method.<sup>9</sup> As shown previously, for iso-electronic, isostructural,  $\text{Sn}^{\text{IV}}$  and  $\text{Sb}^{\text{V}}$  compounds, equation (1) can be written. A plot of  $(e^2qQ)_{\text{Sb}}$  against

$$(e^2qQ)_{\text{Sb}} = [Q_{\text{Sb}}q_{5p(\text{Sb})}/Q_{\text{Sn}}q_{5p(\text{Sn})}](e^2qQ)_{\text{Sn}} \quad (1)$$

$(e^2qQ)_{\text{Sn}}$  gave a straight line of gradient  $+3.40$ .<sup>9</sup> From literature values of  $Q_{\text{Sb}}$ ,  $q_{5p(\text{Sb})}$ , and  $q_{5p(\text{Sn})}$ ,  $Q_{\text{Sn}}$  was found to be  $-0.062 \text{ b}$ ,\* in good agreement with other recent values.

Although the  $[\text{SnCl}_5\text{L}]^-$  analogues of the  $\text{SbCl}_5\text{L}$  compounds are not known, the partial quadrupole splitting treatment predicts that the magnitudes of *cis*- $\text{SnCl}_4\text{L}_2$  and  $[\text{SnCl}_5\text{L}]^-$   $e^2qQ$  values should be the same, but of opposite sign. The opposite sign for such species has been confirmed:  $e^2qQ$  for  $\text{SbCl}_5(\text{NCMe})$  is negative,<sup>7</sup> while that for *cis*- $\text{SnCl}_4(\text{NCMe})_2$  is positive.<sup>3</sup> Thus it should be possible to use the ratio method to correlate the known  $\text{SbCl}_5\text{L}$  and *cis*- $\text{SnCl}_4\text{L}_2$  ( $\text{L} = \text{POCl}_3$ ,  $\text{MeCN}$ ,  $\text{POPh}_3$ , or  $\text{Me}_2\text{SO}$ ) q.s. (Table 5). Crystallographic

TABLE 5

Quadrupole splitting values ( $\text{mm s}^{-1}$ ) for *cis*- $\text{SnCl}_4\text{L}_2$  and  $\text{SbCl}_5\text{L}$  analogues

L	$e^2qQ(^{119}\text{Sn})$	Ref.	$e^2qQ(^{121}\text{Sb})$	Ref.
$\text{POCl}_3$	(+) 2.24	3,14	-6.84 ( $\eta$ 0.37)	7
$\text{MeCN}$	+1.82	3,14	-6.93 ( $\eta$ 0.03)	7
$\text{POPh}_3$	(+) 1.12	*	-5.51 ( $\eta$ 0.37)	7
$\text{Me}_2\text{SO}$	not resolved	*	-5.28 ( $\eta$ 0.0)	7

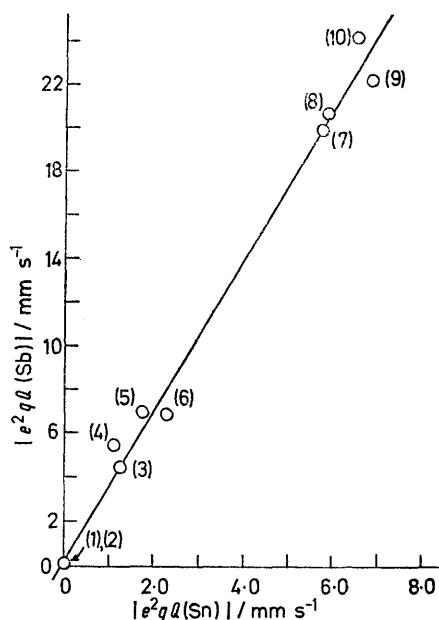
\* J. Philip, M. A. Mullen, and C. Curran, *Inorg. Chem.*, 1968, **7**, 1895; P. A. Yeats, J. R. Sams, and F. Aubke, *ibid.*, 1970, **9**, 740.

studies<sup>15-17</sup> confirm that the  $\text{POCl}_3$ ,  $\text{Me}_2\text{SO}$ , and  $\text{MeCN}$  compounds have the *cis*-structure. In addition, there is substantial crystallographic evidence to indicate that bonding in the  $\text{Sn}$  and  $\text{Sb}$  compounds is very similar. Thus, the  $\text{Sn}-\text{Cl}$  bond lengths in  $\text{SnCl}_4(\text{OPCl}_3)_2$ ,  $\text{SnCl}_4^-(\text{OSMe}_2)_2$ , and  $\text{SnCl}_4(\text{NCMe})_2$  range from 2.31 to 2.36,<sup>15</sup> 2.36 to 2.47,<sup>15</sup> and 2.339 to 2.356 Å<sup>17</sup> respectively, while the  $\text{SbCl}_5\text{L}$  analogues give very similar  $\text{Sb}-\text{Cl}$  bond lengths of 2.32–2.35 ( $\text{L} = \text{POCl}_3$ ),<sup>15</sup> 2.26–2.37 ( $\text{Me}_2\text{SO}$ ),<sup>16</sup> and 2.33–2.40 Å ( $\text{MeCN}$ ).<sup>18</sup> Thus the assumption of identical bonding which is inherent in the treatment is not unreasonable.

<sup>16</sup> A. Hansson and O. Brunge, personal communication quoted in I. Lindqvist, 'Inorganic Adduct Molecules of Oxo Compounds,' Academic Press, New York, 1963.

<sup>17</sup> M. Webster and H. E. Blayden, *J. Chem. Soc. (A)*, 1969, 2443.

<sup>18</sup> H. Binas, *Z. anorg. Chem.*, 1967, **352**, 271.



Plot of  $^{121}\text{Sb}$  and  $^{119}\text{Sn}$   $e^2qQ$  values for the following pairs of complexes: (1),  $[\text{SbCl}_6]^- - [\text{SnCl}_6]^{2-}$ ; (2),  $[\text{SbBr}_6]^- - [\text{SnBr}_6]^{2-}$ ; (3),  $\text{SbCl}_5 - [\text{SnCl}_6]^{2-}$ ; (4),  $(\text{Ph}_3\text{PO})\text{SbCl}_5 - \text{cis}-(\text{Ph}_3\text{PO})_2\text{SnCl}_4$ ; (5),  $(\text{MeCN})\text{SbCl}_5 - \text{cis}-(\text{MeCN})_2\text{SnCl}_4$ ; (6),  $(\text{Cl}_3\text{PO})\text{SbCl}_5 - \text{cis}-(\text{Cl}_3\text{PO})_2\text{SnCl}_4$ ; (7),  $\text{Ph}_3\text{SbBr}_2 - [\text{Ph}_3\text{SnBr}_2]^-$ ; (8),  $\text{Ph}_3\text{SbCl}_2 - [\text{Ph}_3\text{SnCl}_2]^-$ ; (9),  $\text{Me}_3\text{SbBr}_2 - [\text{Me}_3\text{SnBr}_2]^-$ ; and (10),  $\text{Me}_3\text{SbCl}_2 - [\text{Me}_3\text{SnCl}_2]^-$ .

The Sn and Sb  $|e^2qQ|$  \* values were plotted against each other in the same way as previously<sup>9</sup> for the pairs of compounds (3), (7), and (8)—(10) (Figure). The gradient and intercept of the line in the Figure were  $+3.38$  and  $+0.34 \text{ mm s}^{-1}$ , in excellent agreement with  $+3.40$  and  $+0.25 \text{ mm s}^{-1}$  respectively given previously for the five points. The correlation coefficient was  $0.995$ , strongly suggesting that the assumptions inherent in the ratio method are reasonable, and that the  $Q(^{119}\text{Sn})$  value derived earlier ( $-0.062 \text{ b}$ ) is accurate if  $Q(^{121}\text{Sb})$  and the  $q$  values used are accurate. A very recent report<sup>19</sup> of four-co-ordinate  $\text{Sb}^{\text{V}}$   $e^2qQ$  values for compounds of the type  $[\text{R}_{3-x}\text{SbM}_x]^+$  [ $\text{R} = \text{Bu, Me, Ph, Cl, Br, I, or CF}_3$ ;  $\text{M} = \text{Fe}(\text{CO})_2(\text{cp})$ ,  $\text{cp} = \eta\text{-cyclopentadienyl}$ ] makes it possible to correlate these  $e^2qQ$  values with the neutral  $\text{Sn}^{\text{IV}}$  analogues.<sup>20</sup> Although the gradient is close to our value, the intercept is close to  $+6 \text{ mm s}^{-1}$ . Although this may be due to differences in bonding between the Sn and Sb analogues, it is also possible that the very large Sb  $e^2qQ$  values are at least partially due to not using the transmission integral in the analyses of the  $^{121}\text{Sb}$  spectra.<sup>7</sup>

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\* The magnitudes have to be plotted because  $\text{SbCl}_5\text{L}$  and  $\text{cis-SnCl}_4\text{L}_2$  have  $e^2qQ$  values of opposite sign, as discussed earlier.

<sup>19</sup> W. R. Cullen, D. J. Patmore, J. R. Sams, and J. C. Scott, *Inorg. Chem.*, 1974, **13**, 649.

<sup>20</sup> J. R. Sams, personal communication.