

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
THE UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, BRITISH COLUMBIA, CANADA

## Tin-119 Mössbauer Spectra of Tin (IV) Chloride Complexes with Oxygen-Donor Ligands<sup>1a</sup>

BY PHILIP A. YEATS, JOHN R. SAMS, AND FRIEDHELM AUBKE<sup>1b</sup>

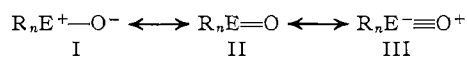
Received July 14, 1969

Tin-119 Mössbauer parameters have been collected for 30 stannic chloride complexes of the types  $\text{SnCl}_4 \cdot 2\text{L}^{\text{I}}$  and  $\text{SnCl}_4 \cdot \text{L}^{\text{II}}$ . The ligands  $\text{L}^{\text{I}}$  and  $\text{L}^{\text{II}}$  are mono- and bidentate oxygen-donor molecules, primarily with  $>\text{SO}$ ,  $>\text{SO}_2$ ,  $>\text{PO}$ , and  $>\text{CO}$  as functional groups. In contrast to similar complexes formed by nitrogen-donor molecules, all adducts with few exceptions show quadrupole splittings of the order of 0.5–1.6 mm/sec. Two principal reasons for the occurrence of quadrupole splitting are seen in the weak Lewis acid–Lewis base interaction in some adducts and molecular distortion due to steric hindrance by bulky ligand groups in others. Infrared and structural data are included in the discussion. The use of Mössbauer spectroscopy to distinguish between *cis* and *trans* isomers and to detect molecular association for  $\text{SnCl}_4 \cdot \text{L}^{\text{II}}$  complexes is demonstrated on a few selected examples.

### Introduction

Mössbauer spectroscopy has been applied previously to the study of molecular complexes formed by the Lewis acid–base interaction of tin(IV) halides with primarily nitrogen- and to a lesser extent with oxygen-, phosphorus-, and sulfur-donor ligands.<sup>2–5</sup> The resulting complexes of the type  $\text{SnX}_4 \cdot 2\text{L}^{\text{I}}$  show hexacoordination around tin with a more or less distorted octahedral environment for the central atom depending on the strength of the interaction, with the possibility of *cis* and *trans* isomerism.

O-Donor ligands of the general type  $\text{R}_n\text{EO}_m$ , where E = C, N, P, S, As, or Se,  $n = 2$  or 3, and  $m = 1$  or 2, were selected because element–oxygen multiple bonding exists in all these molecules, as expressed by the resonance structures



The degree of multiple bonding will increase with an increase in the electronegativity of R and the base character will consequently decrease. These ideas are reflected in the observed E–O bond distances and in the vibrational spectra.<sup>6,7</sup> It should therefore be possible to vary the interaction strength with stannic chloride over a fairly large range and observe the effect on the Mössbauer spectra. The negative shift of the element–oxygen stretching frequency upon complex formation could be used, as reported previously,<sup>8,9</sup> as an approximate measure of the strength of such an interaction.

(1) (a) Presented at the 25th Northwest Regional Meeting of the American Chemical Society, Salt Lake City, Utah. (b) To whom inquiries should be addressed.

(2) V. I. Gol'danskii, E. F. Makarov, R. A. Stukan, T. N. Sumarokova, V. A. Trukhtanov, and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, **156**, 400 (1964).

(3) N. N. Greenwood and J. N. Ruddick, *J. Chem. Soc., A*, 1679 (1967).

(4) (a) D. Hristov, T. Bonchev, and K. Bourin, *Compt. Rend. Acad. Bulgare Sci.*, **19**, 293 (1966); (b) S. Ichiba, M. Mishima, H. Sakai, and H. Negita, *Bull. Chem. Soc. Jap.*, **41**, 49 (1968); (c) S. Ichiba, M. Mishima, and H. Negita, *ibid.*, **42**, 1486 (1969).

(5) J. Philip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, **7**, 1895 (1968).

(6) D. W. Cruikshank, *J. Chem. Soc.*, 5486 (1961).

(7) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).

(8) D. M. I. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **82**, 5774 (1960).

(9) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

In addition, some structural studies on  $\text{SnCl}_4$ -O-donor complexes have been reported for the complexes  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ ,<sup>10</sup>  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ ,<sup>11</sup> and  $\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{SO}$ <sup>12</sup> and should help in interpreting the Mössbauer spectra.

Many  $\text{SnCl}_4$  complexes have been studied over the years<sup>13,14</sup> and a variety of methods have been employed in their investigation.

A systematic Mössbauer study should also afford information on the molecular geometry and, in case of bidentate ligands, on the intermolecular association.

### Experimental Section

**Materials.**—Anhydrous stannic chloride was supplied by Fisher Scientific Co. and purified by repeated vacuum distillation. Methyl maleate, methyl fumarate, methyl cinnamate, and diethyl sulfoxide were student preparations; the purities were checked by ir and <sup>1</sup>H nmr spectra and the melting points or the refractive indices. The remaining organic bases were supplied by Eastman Organic Chemicals or the Aldrich Chemical Co. and were of the highest purity available. All compounds were allowed to react without further purification. Solvents used were of reagent grade quality and were dried over Linde molecular sieves.

**Preparations.**—Two principal methods were used. (a) The 1:2 adducts of  $\text{SnCl}_4$  with dimethyl sulfoxide, dimethyl sulfite, diethyl sulfoxide, di-*n*-propyl sulfoxide, tetramethylene sulfoxide, phosphorus oxychloride, dichlorophenylphosphine oxide, phenyl dichlorophosphinate, diphenyl chlorophosphinate, and selenium oxychloride, and the 1:1 adducts with tetramethylene sulfone, 1,4-dioxane, methyl maleate, diethyl carboethoxymethylphosphonate, and diethyl cyanomethylphosphonate were all prepared by adding an excess of  $\text{SnCl}_4$  to the donor compound in a two-part reactor consisting of a 50- or 100-ml flask with a B-19 inner joint and a top part with vacuum line adaptor, a B-19 outer joint, and Teflon stem greaseless stopcock. Conventional vacuum-line techniques were used for the transfer of materials. The reaction mixtures were stirred magnetically until a precipitate formed, and the excess tin(IV) chloride was removed by pumping. All complexes were prepared on a 3–5-g scale and the reactions were followed by weight.

(b) The 1:2 adducts of  $\text{SnCl}_4$  with di-*n*-butyl sulfoxide, tri-

(10) C. I. Branden, *Acta Chem. Scand.*, **17**, 759 (1963).

(11) Y. Hermodsson, *Acta Cryst.*, **13**, 656 (1960).

(12) A. Hansson and O. Brunge, private communication quoted by I. Lindquist, "Inorganic Adduct Molecules of Oxo-compounds," Academic Press, New York, N. Y., 1963.

(13) I. R. Beattie, *Quart. Rev. (London)*, **17**, 383 (1963).

(14) I. Lindquist, "Inorganic Adduct Molecules of Oxo-compounds," Academic Press, New York, N. Y., 1963.

TABLE I

Ligand	Compn	Mp, <sup>a</sup> °C	Mössbauer data, mm/sec				Ir data, cm <sup>-1</sup>		
			δ	Δ	Γ <sub>1</sub>	Γ <sub>2</sub>	ν <sub>E-O1</sub>	ν <sub>E-Oc</sub>	Δν <sub>E-O</sub>
Donor type S-O									
(CH <sub>3</sub> ) <sub>2</sub> SO	2:1	284 (280)	0.38	...	1.11		1047	920, 905 d	127, 142
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO	2:1	231-233	0.36	...	1.27		1021	909	112
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> SO	2:1	205-208	0.38	0.59	0.82	0.77	1018	915, 899 d	103, 119
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO	2:1	165-167	0.37	0.67	0.91	0.84	1028	915, 909	113, 119
(CH <sub>3</sub> ) <sub>4</sub> SO	2:1	176-180	0.35	...	1.01		1020	918, 896	102, 134
(CH <sub>3</sub> O) <sub>2</sub> SO	2:1	122-124	0.34	...	1.40		1241	1168	73
Donor type SO <sub>2</sub>									
(CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>	1:1	82	0.38	0.916	0.72	1.02	1221	1185	36
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	1:1	62-65	0.406	0.863	0.85	0.88	1204	1175	29
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> SO <sub>2</sub>	1:1		0.403	0.859	0.90	1.15			
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> SO <sub>2</sub>	1:1	63-64	0.433	1.571	0.84	0.86	1219	1206	13
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO <sub>2</sub>	1:1	64-70	0.393	0.830	0.74	0.80	1224	1199	25
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	1:1	70-71	0.426	1.072	0.85	0.80	1229	1229	0
(CH <sub>3</sub> ) <sub>4</sub> SO <sub>2</sub>	1:1	58-60	0.508	1.150	0.85	0.70	1223	1215	8
Donor type P-O									
Cl <sub>3</sub> PO	2:1	55 (55)	0.51	1.12	0.88	0.99	1296	1262, 1197 d	34, 99
Cl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> )PO	2:1	149	0.39	1.61	0.79	0.80	1257	1180	77
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PO	2:1	323 (323-327)	0.27	0.51	0.82	0.74	1189	1120	69
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> PO	1:1	147	0.53	...	1.05		1189	1132	57
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> PO	2:1	117-118	0.24	...	1.15		1150	1085	65
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> PO	1:1	79-83	0.41	0.52	0.83	0.77	1150	1071	79
(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub> PO	2:1	109	0.34	0.71	0.74	0.79	1296	1212	84
Cl(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> PO	2:1	...	0.38	0.75	0.89	0.83	1301	1214	87
Cl <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> O)PO	2:1	66-70	0.42	1.13	0.84	0.83	1308	1218	90
Miscellaneous donors									
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsO	2:1	148	0.437	0.70	0.80	0.72	880	854	26
C <sub>6</sub> H <sub>5</sub> NO	2:1	232 (235)	0.42	...	1.53		1244	1195	49
Cl <sub>2</sub> SeO	2:1	51 (52)	0.37	...	1.09		944	916, 812 d	28, 132
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	1:1	93-94	0.37	0.69	0.79	0.81	1733 (CO)	1701, 1615 d	32, 118
							1265 (PO)	1233, 1158 d	32, 107
(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)CH <sub>2</sub> C=N	1:1	93-95	0.36	0.86	0.77	0.81	2255 (CN)	2305	-50
							1268 (PO)	1170	98
<i>cis</i> -CH <sub>3</sub> OC(=O)CH=CHCO(=O)CH <sub>3</sub>	1:1	124-127	0.38	0.91	0.84	0.91	1726	1651, 1612	75, 114
<i>trans</i> -CH <sub>3</sub> OC(=O)CH=CHCO(=O)CH <sub>3</sub>	1:1	98	0.41	1.04	0.84	0.83	1731	1647, 1608	84, 123
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	1:1	187	0.49	1.48	0.96	0.96			
C <sub>6</sub> H <sub>5</sub> CH=CHCO(=O)CH <sub>3</sub>	2:1	121-124	0.38	1.09	0.88	1.06	1720	1579	141

<sup>a</sup> Melting points in parentheses are literature values.

phenylarsine oxide, pyridine N-oxide, triphenyl phosphate, and methyl cinnamate as well as the 1:1 adducts with dimethyl sulfone, diethyl sulfone, di-*n*-butyl sulfone, diphenyl sulfone, triphenylphosphine oxide, tri-*n*-butylphosphine oxide, and methyl fumarate were formed by adding an excess of anhydrous tin tetrachloride to a solution of the ligand in dry chloroform.

The 2:1 adducts of tri-*n*-butylphosphine oxide and triphenylphosphine oxide were prepared from ethanol solution, following the method of Sheldon and Tyree.<sup>15</sup> The same reactor type was used and the reactions were followed by weight.

In general the complex formations were found to be very mildly exothermic. The majority of the adducts were found to be very hygroscopic. Samples for Mössbauer and infrared spectroscopy as well as for microanalysis were prepared in a glove box.

**Analyses.**—The compositions were checked by the weight ratio, carbon-hydrogen microanalysis, and the melting points when these were available in the literature.

**Infrared Spectra.**—Infrared spectra in the 3000-600-cm<sup>-1</sup> region were recorded on a Perkin-Elmer Model 21 double-beam spectrometer with a sodium chloride prism. The adducts and the solid donor compounds were measured as Nujol mulls between sodium chloride windows. Liquid ligands were run as thin films. No attempt was made to compensate for a stretching frequency

lowering due to hydrogen bridge bonding, which is certainly effective in a number of the compounds, by using solutions in inert solvents.

**Mössbauer Spectra.**—The Mössbauer spectrometer has been described.<sup>10</sup> Measurements were made with the absorber at 80 ± 1°K and the Ba<sup>119m</sup>SnO<sub>3</sub> source at room temperature. The doppler velocity scale was calibrated against the quadrupole splitting of an NBS standard nitroprusside absorber. All isomer shift values are reported relative to an SnO<sub>2</sub> absorber at 80°K. The estimated precision of the Mössbauer parameters is ±0.03 mm sec<sup>-1</sup>.

## Results

The Mössbauer data, isomer shift, δ, quadrupole splittings, Δ, and the line widths at half-peak-height, Γ<sub>1</sub> and Γ<sub>2</sub>, for the 30 compounds are listed in Table I. The uncorrected melting points of the adducts, together with the reported values, are also listed, as well as the element-oxygen stretching frequencies of the free ligand and the complex together with the negative shift Δν<sub>E-O</sub>. In the case of the

(16) W. R. Cullen, D. A. Harbourn, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 95 (1969).

(15) J. C. Sheldon and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).

sulfones, where the sulfur-oxygen vibration is split into an asymmetric and symmetric part, an average value has been calculated using Lehmann's rule.<sup>17</sup> Mössbauer data for two of the adducts  $\text{SnCl}_4 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$  and  $\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{SO}$  have been reported previously.<sup>5</sup> The agreement between both sets of values is satisfactory.

### Discussion

The isomer shifts are spread over a fairly wide range from 0.24 to 0.51 mm/sec indicating a varying degree of s character in the complexes formed. A decrease from the generally accepted value of 0.80 mm/sec for  $\text{SnCl}_4$ <sup>18</sup> is expected—in agreement with previous work. The lowest  $\delta$  values are found for strongly interacting ligands such as the sulfoxides, which show  $\delta$  values in the very narrow range of 0.34–0.38 mm/sec, and for P–O-donor complexes. In all cases very large shifts of the element-oxygen stretching frequency are observed. The sulfones, being far weaker bases as evidenced by the  $\nu_{\text{E-O}}$  in the 1204–1229- $\text{cm}^{-1}$  range as compared to the values for the sulfoxides ranging from 1018 to 1047  $\text{cm}^{-1}$  and by comparative protonation studies,<sup>19</sup> all show isomer shifts ranging from 0.38 to 0.42 mm/sec. For P–O-donor ligands the  $\nu_{\text{E-O}}$  of the ligands range from 1150  $\text{cm}^{-1}$  for strong donors to 1308  $\text{cm}^{-1}$  for weak donors. The isomer shifts are spread likewise from 0.24 mm/sec for the strong and hydrolysis-resistant complex  $\text{SnCl}_4 \cdot 2(n\text{-C}_4\text{H}_9)_3\text{PO}$  to 0.51 mm/sec for the weak, low-melting  $\text{POCl}_3$  adduct.

The occurrence of stable 1:1 and 2:1 complexes for the ligands tri-*n*-butylphosphine oxide and triphenylphosphine oxide, depending on the method of preparation, is surprising. Only the 2:1 compound formed by  $(\text{C}_6\text{H}_5)_3\text{PO}$  has been reported previously.<sup>15</sup> The melting points and the large differences in the observed isomer shifts indicate true stable compounds with 1:1 stoichiometry rather than mixtures of  $\text{SnCl}_4$  and the 2:1 adducts. The high isomer shifts of 0.53 and 0.41 mm/sec, respectively, suggest pentacoordination as found for example in the  $\text{SnCl}_5^-$  ion,<sup>20</sup> rather than hexacoordination with a bidentate phosphine oxide as a bridging ligand, as has been found recently for the adduct  $\text{SeOCl}_2 \cdot (\text{C}_6\text{H}_5)_3\text{PO}$ .<sup>21</sup> The quadrupole splitting is unresolved for  $\text{SnCl}_4 \cdot (\text{C}_6\text{H}_5)_3\text{PO}$  and extremely small, 0.52 mm/sec, for  $\text{SnCl}_4 \cdot (n\text{-C}_4\text{H}_9)_3\text{PO}$ , which is rather surprising for pentacoordinated structures; however small  $\Delta$  values are also reported for the  $\text{SnCl}_5^-$  ion. The observed large negative shifts of the PO stretching frequencies indicate a strong interaction between acceptor and donor. More details on the structure and chemistry of these 1:1 adducts will be reported shortly.

A relatively small isomer shift is also found for  $\text{SnCl}_4 \cdot \text{C}_4\text{H}_9\text{O}_2$ , where oxygen is present in an ether-type configuration rather than in a keto-type arrangement. The presence of a noticeable Mössbauer effect

at room temperature for this compound may indicate a polymeric structure<sup>22,23</sup> with dioxane as a bridging ligand and hexacoordination for tin as suggested previously for this compound.<sup>24</sup>

**Quadrupole Splitting.**—For tin-119m with a spin of  $3/2$  the quadrupole splitting has been found to follow the equation

$$\Delta E_Q = \frac{1}{2} e^2 q Q \left( 1 + \frac{\eta^2}{3} \right)^{1/2}$$

where  $eq$  is the electric field gradient in the  $z$  direction,  $Q$  is the quadrupole moment of the  $^{119\text{m}}\text{Sn}$  nucleus, and  $\eta$  is the asymmetry parameter which is usually zero when the molecule possesses axial symmetry. The extent of the splitting will therefore be proportional to  $q$ , since  $e$  and  $Q$  are constant, and will reflect an imbalance of electrons primarily in the bonding orbitals. For hexacoordinated tin of the general type  $\text{SnX}_4\text{L}_2^{\text{I}}$  or  $\text{SnX}_4\text{L}^{\text{II}}$ , where  $\text{L}^{\text{I}}$  is a monodentate and  $\text{L}^{\text{II}}$  a bidentate ligand, Greenwood's rule<sup>8</sup> would have predicted the absence of a resolvable splitting since all ligand atoms surrounding tin are potentially capable of  $p\pi$ - $d\pi$  interactions. A quadrupole splitting of 0.45 mm/sec may be considered as a limit for resolution.

Greenwood's concept, placing great emphasis on the presence of appreciable  $\pi$  interactions, has been questioned quite recently. Parish and Platt<sup>25</sup> showed that for tetrahedrally coordinated tin, the quadrupole splitting is induced by  $\sigma$ -bonding effects and responds to electronegativity differences of the ligand. Hill, *et al.*,<sup>26</sup> came to the same conclusions. Fitzsimmons, *et al.*,<sup>27</sup> found for hexacoordinated tin compounds with two tin-carbon bonds the quadrupole splitting depends on the geometrical configuration. *trans* isomers of  $\text{SnA}_4\text{B}_2$  were found to exhibit about twice as large splittings as the *cis* isomers. Quadrupole splittings for hexacoordinated  $\text{SnCl}_4$  adducts were reported previously.<sup>4,5</sup>

The present study shows that, in all but six cases, quadrupole splittings of 0.50–1.6 mm/sec are observed. Two of the six adducts,  $\text{SnCl}_4 \cdot 2\text{C}_6\text{H}_5\text{NO}$  and  $\text{SnCl}_4 \cdot 2(\text{CH}_3\text{O})_2\text{SO}$ , show unusually large line widths of 1.53 and 1.40 mm/sec, respectively, indicating an unresolved splitting.

For two of the remaining compounds which have no splittings,  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$  and  $\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{SO}$ , the molecular structures have been determined by X-ray diffraction, as well as  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  which shows a large splitting. All three adducts are *cis* isomers. The tin-oxygen and tin-chlorine bond distances together with similar reported parameters and the oxygen-tin-oxygen angles are listed in Table II.

(22) See R. Herber and H. A. Stöckler in "Applications of the Mössbauer Effect in Chemistry and Solid State Physics," International Atomic Energy Agency, Vienna, 1966.

(23) H. A. Stöckler, H. Sano, and R. H. Herber, *J. Chem. Phys.*, **47**, 1567 (1967).

(24) S. T. Zenchelsky and P. R. Segatto, *J. Am. Chem. Soc.*, **80**, 4796 (1958).

(25) R. V. Parish and R. H. Platt, *Chem. Commun.*, 1118 (1968).

(26) J. C. Hill, R. S. Drago, and R. H. Herber, *J. Am. Chem. Soc.*, **91**, 1644 (1969).

(27) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *J. Chem. Soc.*, **A**, 143 (1969).

(17) W. J. Lehmann, *J. Mol. Spectry.*, **7**, 261 (1961).

(18) J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, **29**, 2191 (1967).

(19) S. K. Hall and E. A. Robinson, *Can. J. Chem.*, **42**, 1113 (1964).

(20) K. M. Harmon, L. Hesse, L. P. Klemann, C. W. Kochler, S. V. McKinley, and A. E. Young, *Inorg. Chem.*, **8**, 1054 (1969).

(21) Y. Hermodsson, *Arkiv Kemi*, **30**, 15 (1969).

TABLE II

Compound	$r(\text{Sn}-\text{O}), \text{\AA}$	$r(\text{Sn}-\text{Cl}), \text{\AA}$	O-Sn-O, deg
$\text{SnCl}_4 \cdot 2\text{POCl}_3^{10}$	$2.30 \pm 0.04$	$2.31 \pm 0.02$	$78.3 \pm 1.6$
	$2.25 \pm 0.05$	$2.36 \pm 0.02$	
$\text{SnCl}_4 \cdot 2\text{SeOCl}_2^{11}$	$2.121 \pm 0.016$	$2.33 \pm 0.02$	$81.9 \pm 0.6$
		$2.360 \pm 0.007$	
$\text{SnCl}_4 \cdot 2(\text{CH}_3)_2\text{SO}^{12,a}$	$2.17$	$2.409 \pm 0.006$	$87.3$
		$2.10$	
$\text{SnCl}_4^{27}$		$2.44$	
$\text{SnCl}_6^{2-29}$		$2.36$	
$(\text{C}_2\text{H}_5)_3\text{Sn}-\text{O}-\text{Ar}^b$	$2.08 \pm 0.06$	$2.42$	
$(\text{C}_6\text{H}_{11})_3\text{Sn}-\text{O}-\text{COCH}_3^c$	$2.12 \pm 0.03$	$2.47$	
$(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}-\text{O}-\text{COCH}_3^d$	$2.14 \pm 0.02$	$2.31 \pm 0.01$	
		$2.41 \pm 2.43$	

<sup>a</sup> Confidence limits were not given for this structure determination. <sup>b</sup> P. J. Wheatley, *J. Chem. Soc.*, 5027 (1961). <sup>c</sup> N. W. Alcock and R. E. Timms, *ibid.*, A, 1876 (1968). <sup>d</sup> N. W. Alcock and R. E. Timms, *ibid.*, A, 1873 (1968).

All three compounds show the tin atom in a more or less distorted octahedral environment. The Sn-O bond distances are found to be unequal for the  $\text{POCl}_3$  and  $(\text{CH}_3)_2\text{SO}$  adducts. All O-Sn-O angles differ from the expected  $90^\circ$ ; the largest deviation is  $78.3 \pm 1.6^\circ$  found for  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ , and the smallest deviation is found for the  $(\text{CH}_3)_2\text{SO}$  adduct. The tin-oxygen bond distances in the  $(\text{CH}_3)_2\text{SO}$  and  $\text{SeOCl}_2$  cases closely approach the sum of the covalent radii for octahedrally coordinated tin; however the  $\text{POCl}_3$  compound shows bond distances longer by about  $0.15 \text{\AA}$ , indicating only a weak interaction. This is reflected also in the relatively small negative shift of the P-O stretching frequency and the high isomer shift of  $0.51 \text{ mm/sec}$ . It is also noteworthy that the tin-chlorine distances of the  $\text{POCl}_3$  adduct are closer to the value of  $2.31 \text{\AA}$  reported for  $\text{SnCl}_4^{28}$  than to the value of  $2.41\text{--}2.43 \text{\AA}$  reported for the  $\text{SnCl}_6^{2-}$  ion,<sup>29</sup> indicating large s character for these bonds. Interesting in this connection is the fact that  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$  has a highly distorted structure as reflected in the bond angle of  $81.9 \pm 0.6^\circ$ . This distortion, apparently not due to a weak donor-acceptor bond, has been explained by the tendency of the selenium atom to act in turn as an acceptor. In general, the reported structures reveal the great complexity of the donor-acceptor interaction and there is good reason to believe the remaining adducts show similar distortions. It is possible that these distortions around tin are large enough to give rise to a nonzero asymmetry parameter,  $\eta$ .

From this discussion of structural parameters, it appears safe to say that a primary reason for a field gradient and subsequently a quadrupole splitting is the weak acceptor-donor bond due to weak interaction, leading to an imbalance of electrons in the tin orbitals. This is supported by the following observations.

(1) All adducts in our series which do show single-line spectra also show large negative stretching frequency shifts.

(2) Philip, *et al.*,<sup>5</sup> have found that replacement of  $\text{SnCl}_4$  by the weaker acceptor  $\text{SnBr}_4$  results in an increase in splitting.

(3) No quadrupole splittings have as yet been found for stannic chloride complexes with N donors. Nitrogen donors are generally regarded as stronger bases than chemically similar oxygen compounds. This view, placing the main emphasis on the  $\sigma$  interaction, does not exclude the possible existence of a  $p\pi\text{--}d\pi$  interaction of tin with chlorine and oxygen; only such an interaction when present has apparently no bearing on the quadrupole splitting.

The negative stretching frequency shift is of course only a very crude measure of the donor-acceptor strength, and a quantitative relationship between  $\Delta\nu_{\text{E-O}}$  and  $\Delta$ , the quadrupole splitting, should not be expected. Unfortunately only very limited thermochemical measurements have been reported for these adducts.<sup>14</sup>

A second reason for the occurrence of quadrupole splitting becomes apparent in a trend, found for the alkyl sulfoxide complexes. Subsequent replacement of  $\text{CH}_3$  by  $\text{C}_2\text{H}_5^-$ ,  $n\text{-C}_3\text{H}_7^-$ , and  $\text{C}_4\text{H}_9^-$  produces first a line widening and then very small quadrupole splitting in spite of the fact that all sulfoxides are strongly interacting donors. The E-O stretching frequency is shifted by about  $100 \text{ cm}^{-1}$  and in nearly all compounds split into a doublet. The only plausible explanation for quadrupole splitting must be seen in steric hindrance caused by the bulky ligand group. The absence of such a splitting for  $\text{SnCl}_4 \cdot 2(\text{CH}_2)_4\text{SO}$  seems to support this point of view.

All sulfone adducts show fairly large quadrupole splittings; the  $\Delta$  values are all in the same range, and no dependence on the R-group size can be noticed for this group of adducts. This fact and the vibrational spectra indicate that the 1:1 adducts formed in this group are truly hexacoordinated complexes of tin. It cannot of course be determined whether the  $\text{R}_2\text{SO}_2$  acts as a bidentate chelating or bridging group, leading eventually to rings or chain-type polymers. None of the adducts studied appears to have a room-temperature effect. The weak acceptor-donor interaction is evidenced by the low-melting or decomposition points. The isomer shifts are almost always higher for the sulfones than for the corresponding sulfoxides. The occurrence of two different forms of  $\text{SnCl}_4 \cdot (n\text{-C}_3\text{H}_7)_2\text{SO}_2$  formed in two different preparations seems to indicate

(28) R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, **30**, 339 (1959).

(29) G. Engel, *Z. Krist.*, **90**, 341 (1935).

the existence of *cis* and *trans* isomers, adopting the ideas presented by Fitzsimmons, *et al.*<sup>27</sup> It is not quite clear under what experimental conditions the different isomers are formed.

A fairly large splitting is also observed for the Cl<sub>2</sub>-(C<sub>6</sub>H<sub>5</sub>)PO adduct. Again a *trans* isomer is indicated. The same seems to apply for the 1:1 adduct with dioxane, even though no real comparison is possible for this compound. The postulation of *trans* isomers for the above-mentioned complexes will have to be confirmed either by determination of dipole moments or by vibrational spectroscopy according to Beattie and Rule.<sup>30</sup>

Another interesting facet is shown in the last group of compounds. All complexes formed with bidentate donor groups exhibit quadrupole splittings even though the interaction is apparently quite strong as indicated by the negative stretching frequency shifts. The reason for the occurrence of splitting can again be seen in the distortion around tin caused by the rigid donor group. In this connection it is found that the C-N vibration is shifted to higher frequency upon complex formation. This has been observed and discussed previously.<sup>31</sup>

The stereoisomers methyl fumarate and methyl maleate show very similar Mössbauer data; however the *trans* isomer has been found to exhibit a weak but noticeable room-temperature effect, indicating possibly a polymeric structure.<sup>22</sup>

(30) I. R. Beattie and L. Rule, *J. Chem. Soc.*, 3267 (1964).

(31) W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *ibid.*, 2182 (1960).

In conclusion, it can be said that Mössbauer spectroscopy presents a convenient tool for the investigation of donor-acceptor complexes of the described type. Information concerning the donor-acceptor interaction can be obtained from isomer shift and quadrupole splitting data. In addition, intermolecular association and the occurrence of *trans* isomers in a class of compounds where *cis* isomers appear to dominate can be detected quite nicely. The occurrence of quadrupole splittings appears to be the rule for tin(IV) chloride complexes with O-donor ligands rather than the exception. The consequence is that Greenwood's concept loses its experimental basis for hexacoordinated compounds as well as previously reported for tetracoordinated compounds.<sup>24</sup> The electric field gradient on the tin nucleus giving rise to the quadrupole splitting can be caused by weak donor-acceptor interaction as well as by steric hindrance due to bulky ligand groups whereby a clear distinction between both effects is often not possible. The present work also points to the limitations to Mössbauer spectroscopy for the study of tin compounds. For a meaningful understanding of Mössbauer parameters in terms of structure and bonding, support from other physical methods such as vibrational spectroscopy and X-ray diffraction is needed.

**Acknowledgment.**—Financial support by the National Research Council of Canada is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

## Fluorophosphine Ligands. VI. Difluorophosphine Oxide, Sulfide, and Selenide

BY L. F. CENTOFANTI<sup>1a</sup> AND R. W. PARRY<sup>1b</sup>

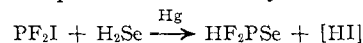
Received July 7, 1969

The interaction of PF<sub>2</sub>I and H<sub>2</sub>X has been examined and explained in terms of nucleophilic attack by H<sub>2</sub>X on PF<sub>2</sub>I. The structure of PF<sub>2</sub>HSe, prepared from H<sub>2</sub>Se and PF<sub>2</sub>I, has been established by means of the <sup>31</sup>P, <sup>19</sup>F, and <sup>1</sup>H nmr spectra. When PF<sub>2</sub>HSe is maintained in glass at room temperature for several weeks, SiF<sub>4</sub> and a red solid are obtained. PF<sub>2</sub>HSe could not be produced from H<sub>2</sub>Te and PF<sub>2</sub>I in a reaction comparable to that used for preparing PF<sub>2</sub>HSe. Reduction occurred during attempts to prepare PF<sub>2</sub>HTe. Association observed in PF<sub>2</sub>HO and PF<sub>2</sub>HS is explained in terms of a P-X-P interaction and is related to compound decomposition. PF<sub>2</sub>HSe shows little association and is moderately stable.

The recently synthesized compounds PF<sub>2</sub>HO<sup>2,3</sup> and PF<sub>2</sub>HS<sup>2</sup> exhibit association in the liquid phase. It has been suggested<sup>3</sup> that the decomposition observed for PF<sub>2</sub>HO can be correlated with the large amount of association observed in its liquid phase. This proposal

is examined further here through the preparation and characterization of PF<sub>2</sub>HSe and the evaluation of both the degree of association and the extent of decomposition for the group of molecules of formula PF<sub>2</sub>HX (X = O, S, Se).

**1. Preparation and Characterization of PF<sub>2</sub>HSe.**—PF<sub>2</sub>HSe was prepared by the reaction between H<sub>2</sub>Se and PF<sub>2</sub>I in the presence of mercury



(1) (a) Department of Chemistry, Emory University, Atlanta, Ga. 30322.  
(b) Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

(2) T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **6**, 2204 (1967).

(3) L. Centofanti and R. W. Parry, *ibid.*, **7**, 1005 (1968).