

## The Crystal Structure of $\text{SnCl}_4 \cdot 2\text{POCl}_3$

CARL-IVAR BRÄNDÉN

*University of Uppsala, Institute of Chemistry, Uppsala, Sweden*

The crystal structure of  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  has been determined and refined from three-dimensional X-ray data. The structure comprises discrete molecules of  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ . The tin atom is octahedrally coordinated with the two  $\text{POCl}_3$  groups lying in the *cis*-position. The oxygen atom in each  $\text{POCl}_3$  group functions as a donor atom. The two  $\text{POCl}_3$  groups in the molecule are crystallographically different but both preserve their approximately tetrahedral structure.

Tin tetrachloride forms a considerable number of addition compounds with different donor molecules but in almost all cases the mole ratio acceptor molecule:donor atom is 1:2. With the similar acceptor molecule titanium tetrachloride, however, compounds with the mole ratio 1:1 are also formed. As part of an investigation of the coordination and chemical bonds in addition compounds of phosphorus oxychloride the crystal structures of the compounds  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$ ,  $\text{TiCl}_4 \cdot 2\text{POCl}_3$  and  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  have been examined.

From a study of the infra-red spectra of these compounds Sheldon and Tyree<sup>1</sup> conclude that the oxygen atom in the  $\text{POCl}_3$  group functions as a donor atom. The compound  $(\text{TiCl}_4 \cdot \text{POCl}_3)_2$  has been shown<sup>2</sup> to be dimeric with double chlorine-bridges linking the two titanium atoms and it has also been shown<sup>3</sup> that  $\text{TiCl}_4 \cdot 2\text{POCl}_3$  is isostructural with  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ . The structure of the similar compound  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$  which was published<sup>4</sup> during the course of the present investigation affords interesting comparisons with  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ .

### PREPARATION OF CRYSTALS

The liquidus curve<sup>5</sup> for the system  $\text{SnCl}_4 - \text{POCl}_3$  demonstrates the formation of only one addition compound,  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  which melts congruently at + 56°C.

Single crystals of the hygroscopic compound were prepared in sealed capillary tubes by a zone-melting technique. Although this method has been successfully used at this Institute in a number of similar cases single crystals of this compound were obtained only with difficulty. The crystal finally used was quite small and for a reasonable exposure-time gave only a limited number of the possible X-ray reflexions.

## CRYSTAL DATA

The unit cell dimensions of the orthorhombic crystals were determined by a method described by Löfgren <sup>6</sup>. The values are:

$$\begin{aligned} a &= 14.53 \pm 0.02 \text{ \AA} \\ b &= 14.24 \pm 0.05 \text{ \AA} \\ c &= 8.02 \pm 0.01 \text{ \AA} \end{aligned}$$

The value 1.5405 Å was assumed for the wavelength of  $\text{CuK}\alpha_1$  radiation. Observed extinctions were  $k + l$  odd for  $0kl$  and  $h + l$  odd for  $h0l$  reflexions. It was assumed that the structure belongs to the centrosymmetric space-group  $Pn\bar{1}m$ .

The density calculated on the basis of a unit cell containing four molecules of  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  is  $2.27 \text{ g}\cdot\text{cm}^{-3}$ . The density of the ideal mixture formed between  $\text{SnCl}_4$  and  $\text{POCl}_3$  in the mole ratio 1:2 would be  $1.93 \text{ g}\cdot\text{cm}^{-3}$ . Because of the hygroscopic nature of the crystals their density could not be measured very easily and it was therefore assumed that the unit cell contained four molecules. This was later confirmed by the structure determination.

The single crystal was rotated around the  $b$ -axis and Weissenberg photographs were taken with  $\text{CuK}$ - and  $\text{MoK}$ -radiation. 12 zones (0–11) were recorded with  $\text{MoK}$ -radiation using the multiple-film technique with iron foils between the films. Correlation between the zones was obtained using a method described by Magnéli <sup>7</sup>. A visual estimate of 499 independent intensities was made and the data were corrected for Lorentz and polarisation effects.

The silica capillary tube used had an internal diameter of 0.14 mm. As the linear absorption coefficient of the compound is  $34.5 \text{ cm}^{-1}$  for  $\text{MoK}\alpha$  no correction was made for absorption errors.

## DETERMINATION OF THE ATOMIC POSITIONS

There are three different 4-fold positions in the space group  $Pn\bar{1}m$ . In order to determine the positions of the tin atoms the Harker-functions  $P(x, y, 0)$ ,  $P(x, y, \frac{1}{2})$ ,  $P(0, 0, z)$  and  $P(\frac{1}{2}, \frac{1}{2}, z)$  were calculated on the Hägg-Laurent machine <sup>8</sup>. From these functions it was evident that tin atoms occupy the 4(g) positions with approximate parameters  $x_{\text{Sn}} = 0.159$ ,  $y_{\text{Sn}} = 0.250$  and  $z_{\text{Sn}} = 0$ .

Using all the observed  $F^2(h, k, l)$  as Fourier-coefficients the functions  $P_1(x, y, 0)$  and  $P_1(x, y, \frac{1}{2})$  were studied in order to investigate Sn–Cl vectors. No unique solution could be obtained for these vectors since  $y_{\text{Sn}} \simeq 1/4$ . (This results in an identical set of Sn–Cl vectors for positions  $x_{\text{Cl}}, y_{\text{Cl}}, 0$  and  $x_{\text{Cl}}, \frac{1}{2} - y_{\text{Cl}}, 0$ ). Approximate positions could be derived, however, for six atoms each of which had two possible  $y$ -coordinates.

A unique solution could only be obtained from a study of the Cl–Cl vectors. These are too weak to be detected in functions containing Sn-vectors. Tin does not contribute, however, to  $F^2(h, k, l)$  if  $h + l$  is odd. These reflexions were therefore used as Fourier-coefficients to calculate the new functions  $P_2(x, y, 0)$  and  $P_2(x, y, \frac{1}{2})$ . By investigating Cl–Cl vectors in these functions unique  $y$ -coordinates could be assigned to the six atomic positions derived

earlier. Two more atoms were located from the remaining vectors. These were assumed to be oxygen atoms from the shape of that part of the molecule which had been determined so far. By comparison with the similar molecule  $\text{SbCl}_5 \cdot \text{POCl}_3$ <sup>9</sup> it was assumed that the six remaining chlorine atoms in the molecule would occupy three different 8-fold positions. These were located by calculating the electron-density projections  $\rho(x,y)$ ,  $\rho(x,z)$  and  $\rho(y,z)$ . The signs of the Fourier coefficients were determined using the atomic positions already determined. This and the following structure-factor and Fourier calculations were made on the electronic computer BESK in Stockholm using programmes devised by Åsbrink *et al.*<sup>10</sup> and Westman *et al.*<sup>11</sup>

## REFINEMENT

The refinement was first carried out by three-dimensional back-shift corrections using an over-all temperature factor in the calculation of the structure factors. After two cycles of refinement using only observed reflections the discrepancy factor  $R$  remained at the high level of 0.233. Further work on this structure was then abandoned until the least-squares refinement

Table 1. Weight-analysis.

$\sin \Theta$ interval	$\overline{\omega A^2}$	number of reflexions
0.00–0.26	1.20	216
0.26–0.32	1.03	147
0.32–0.37	0.58	81
0.37–0.41	0.36	36
0.41–0.51	1.72	12
$F_o$ interval		
0–40	0.95	163
40–80	0.87	215
80–120	1.26	64
120–160	1.06	31
160–200	1.95	11
200–360	1.97	8

programme devised by Åsbrink and Brändén<sup>12</sup> for the Swedish electronic computer FACIT EDB had been completed. The main outlines of this programme have been briefly described in another paper<sup>13</sup>. The parameters refined were atomic coordinates, individual isotropic vibration parameters and 12 separate scale-factors; one for each layer-line. The weights,  $\omega$ , were calculated according to an equation suggested by Cruickshank *et al.*<sup>14</sup> as follows,

$$\omega = 1/(a + |F_c| + c|F_o|^2) \text{ with } a = 25 \text{ and } c = 0.0058.$$

Reflexions where  $|F_c| < 0.33 |F_o|$  were rejected from the refinement. Atomic scattering factors for the elements were obtained from the following references; tin from Thomas and Umeda<sup>15</sup>, oxygen from Berghuis *et al.*<sup>16</sup>, and phosphorus and chlorine from Tomii and Stam<sup>17</sup>.

Table 2. Final atomic parameters and their e.s.d.'s.

Atom	$x$	$\sigma(x)\text{\AA}$	$y$	$\sigma(y)\text{\AA}$	$z$	$\sigma(z)\text{\AA}$	$B\text{\AA}^2$	$\sigma(B)\text{\AA}^2$
Sn(1)	0.1557	0.004	0.2450	0.004	0	—	3.38	0.06
Cl(2)	0.0301	0.023	0.1462	0.024	0	—	6.33	0.50
Cl(3)	0.0880	0.019	0.3959	0.020	0	—	5.87	0.40
Cl(4)	0.1800	0.014	0.2384	0.013	0.2868	0.014	4.78	0.25
O(5)	0.2509	0.036	0.1160	0.042	0	—	4.21	0.87
O(6)	0.2959	0.042	0.3125	0.046	0	—	4.65	0.90
P(7)	0.3437	0.019	0.0860	0.019	0	—	5.05	0.36
P(8)	0.3552	0.016	0.3976	0.018	0	—	4.31	0.33
Cl(9)	0.3492	0.023	-0.0491	0.025	0	—	7.84	0.54
Cl(10)	0.4150	0.015	0.1256	0.015	0.1943	0.015	6.58	0.32
Cl(11)	0.4880	0.024	0.3618	0.026	0	—	7.88	0.55
Cl(12)	0.3480	0.020	0.4710	0.023	0.1961	0.022	7.44	0.44

After seven cycles of refinement  $R$  had fallen to 0.117 for the observed reflections and the shifts in all parameters were less than one tenth of the estimated standard deviations. At a number of stages in the refinement difference-syntheses were calculated on FACIT using a programme devised by Liminga *et al.*<sup>18</sup> and some atoms were given shifts according to the results of this synthesis in the early stages of the refinement procedure. The least-squares programme computes a weight-analysis for each cycle of refinement, where the mean value of  $\omega(|F_o| - |F_c|)^2$  is calculated both as a function of  $\sin \theta$  and  $F_o$ . The weight-analysis for the last cycle of refinement is given in Table 1. The final parameters are given in Table 2 together with their estimated standard deviations calculated from the inverse least-squares matrix. The observed and calculated structure factors are compared in Table 3.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of one adduct molecule is shown in Fig. 1 and the bond lengths and bond angles are given in Table 4 together with their standard deviations. Table 5 lists distances between chlorine atoms located in symmetrically related molecules calculated on the basis of the atomic coordinates given in Table 2.

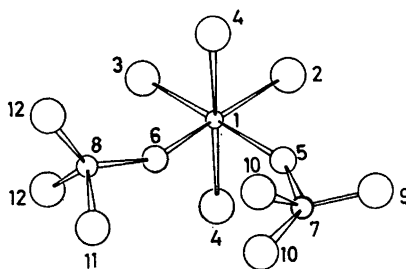
Fig. 1. The molecule of  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ .

Table 3. Observed and calculated structure factors.

$h$	$l$	$ F_o $	$ F_c $	$h$	$l$	$ F_o $	$ F_c $	$h$	$l$	$ F_o $	$ F_c $
$k = 0$				1	7	105	88	1	5	55	64
				2	2	139	131	1	7	51	45
0	2	255	266	2	3	74	82	2	3	65	63
0	4	334	371	2	4	118	120	2	4	61	49
0	6	170	191	2	6	53	49	3	1	194	218
0	8	69	67	2	8	37	41	3	2	117	108
0	10	57	53	3	1	123	109	3	3	156	160
1	3	172	162	3	2	127	148	3	4	30	26
1	7	61	49	3	4	34	32	3	5	82	96
2	4	64	56	3	5	69	69	3	7	98	80
3	1	52	37	4	0	183	181	4	1	49	51
3	3	124	133	4	2	72	66	4	2	63	62
3	5	32	33	4	4	74	69	4	3	23	29
3	7	100	57	4	6	31	27	4	4	44	37
4	0	227	287	5	0	135	128	4	5	33	38
4	2	31	32	5	1	88	95	4	6	35	23
4	4	136	111	5	2	28	14	5	0	83	92
4	6	70	76	5	3	147	128	5	1	34	11
4	8	42	28	5	4	30	37	5	3	53	47
5	1	49	40	5	5	54	50	5	7	41	25
5	3	29	37	5	7	68	65	6	0	125	116
6	0	213	252	6	2	69	76	6	1	38	28
6	2	150	134	6	3	84	87	6	2	80	76
6	4	153	149	7	1	81	65	6	3	30	26
6	6	71	71	7	2	36	38	6	4	106	90
6	8	47	45	7	3	111	111	6	6	47	41
7	1	26	5	7	7	50	49	6	8	35	31
7	5	38	19	8	0	142	138	7	1	150	162
7	7	34	12	8	2	55	55	7	2	35	37
8	2	77	82	8	4	79	76	7	3	101	93
8	4	29	2	8	6	44	47	7	4	32	13
9	1	52	47	9	1	83	78	7	5	92	98
9	3	87	78	9	2	36	36	7	7	42	44
10	0	103	108	9	3	71	65	8	0	52	64
10	2	106	110	9	5	42	51	8	1	85	82
10	4	72	77	10	0	41	55	8	2	27	37
10	6	54	55	10	3	44	55	8	5	42	51
10	10	44	16	10	4	38	40	9	1	103	101
11	3	32	32	11	1	69	72	9	2	57	58
12	0	106	111	11	3	43	57	9	3	87	89
12	2	41	31	12	2	39	53	9	5	47	51
12	4	57	57	14	2	50	52	9	7	45	45
12	6	41	35	14	4	39	32	10	1	53	51
13	3	32	36	15	1	51	53	10	2	65	74
15	1	30	29	15	5	46	42	10	4	36	34
15	3	37	31					10	5	37	34
16	0	57	50					10	6	40	29
16	2	42	49					11	1	40	42
16	4	49	34					11	5	36	39
								12	0	37	39
								12	4	38	30
								13	1	54	71
								13	3	43	43
								13	5	48	52
								16	2	36	38
				$k = 2$							
				0	2	66	92				
				0	4	145	116				
				0	6	59	46				
				0	8	41	38				
				1	2	58	55				
				1	3	108	91				
				$k = 1$							
1	3	227	205								
1	5	97	102								

$h$	$l$	$ F_o $	$ F_c $	$h$	$l$	$ F_o $	$ F_c $	$h$	$l$	$ F_o $	$ F_c $
$k = 3$				$k = 4$				$k = 5$			
0	3	87	110	0	2	56	70	0	2	87	102
0	5	26	26	0	4	50	39	0	7	30	31
1	2	132	161	1	2	32	26	1	3	96	88
1	3	138	137	1	3	58	60	1	4	26	28
1	4	39	47	1	4	34	28	1	5	26	27
1	7	69	54	1	5	51	51	1	5	26	27
2	4	161	140	1	7	35	36				
2	6	75	81	2	3	52	62				
2	8	37	33	2	4	77	87				
3	0	73	64	2	6	41	40				
3	1	58	44	3	0	102	74				
3	2	21	28	3	1	124	133				
3	3	21	19	3	2	46	49				
4	0	215	220	3	3	215	201				
4	1	19	1	3	4	32	32				
4	2	109	90	3	5	61	50				
4	3	65	62	3	7	95	86				
4	4	140	128	4	0	136	139				
4	6	56	57	4	1	16	24				
4	8	41	38	4	2	111	97				
5	0	118	134	4	4	74	79				
5	1	141	127	4	6	42	42				
5	2	24	26	5	0	68	79				
5	3	132	135	5	3	107	105				
5	4	49	47	5	4	33	24				
5	5	50	51	5	6	29	12				
5	7	54	55	5	7	43	37				
6	0	67	60	6	0	218	235				
6	1	26	23	6	4	94	95				
6	2	77	80	6	6	58	54				
6	4	56	42	7	1	123	121				
7	0	73	45	7	3	160	155				
7	1	56	57	7	5	65	57				
7	2	50	48	7	7	50	58				
7	3	73	74	8	0	51	46				
7	7	36	39	8	4	34	30				
8	0	148	161	9	1	62	62				
8	2	147	129	9	3	77	88				
8	4	111	113	9	7	40	42				
8	6	59	68	10	0	65	83				
8	8	41	43	10	2	34	44				
9	1	32	40	10	4	50	44				
9	5	43	40	10	6	36	36				
10	0	61	72	11	1	34	25				
11	1	46	45	13	1	70	67				
11	3	55	55	13	3	43	45				
12	0	48	48	13	5	45	48				
12	2	65	76								
12	4	35	40								
12	6	36	36								
14	0	54	53								
14	2	43	37								
14	4	36	34								



$h$	$ F_o $	$ F_c $	$h$	$l$	$ F_o $	$ F_c $	$h$	$l$	$ F_o $	$ F_c $
$k = 11$			3	2	26	22	7	1	29	38
			4	0	77	70	7	3	37	41
0	3	36	4	1	32	27	8	0	67	66
1	2	19	4	2	40	36	8	2	54	53
1	3	60	4	4	51	47	8	4	40	47
2	2	35	5	1	48	50	9	1	27	29
2	3	28	5	3	58	57	11	3	27	29
2	4	61	6	2	33	23				

The coordination of the tin atom is approximately octahedral, the ligands being four chlorine atoms and two oxygen atoms, one from each  $\text{POCl}_3$ -group. The coordination around each phosphorus atom is approximately tetrahedral. The bond angles  $\text{Sn}-\text{O}-\text{P}$  are  $144^\circ$  and  $151^\circ$ . Lindqvist<sup>19</sup> has recently discussed the factors which determine the magnitude of the bond angle subtended at the oxygen atom in adducts of this type. This angle should depend mainly on the distribution of the  $s$ -electrons of the oxygen atom, but the experimental evidence suggests that steric factors also must be important.

The  $\text{POCl}_3$ -groups are bonded to the tin-atom in the *cis*-position, the same configuration as in the similar molecule  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ <sup>4</sup>. A preliminary investigation of  $\text{TiCl}_4 \cdot 2\text{POCl}_3$ <sup>3</sup> has shown that the *cis*-configuration is also present in this compound. On the other hand Hulme *et al.*<sup>20</sup> have shown that the *trans*-configuration occurs in  $\text{GeCl}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  (pyridine) and probably also in the corresponding  $\text{SiCl}_4$ - and  $\text{TiCl}_4$ -adducts.

Although the structures of  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  and  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$  are closely similar, they differ in one important respect. Assuming that the structure of  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$  belongs to the centro-symmetric space-group  $C2/c$ , the two

Table 4. Bond distances and bond angles in  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  and their e.s.d.'s.

Distance(Å) e.s.d.(Å)			Angle(°) e.s.d.(°)		
$\text{Sn}(1)-\text{Cl}(2)$	2.31	0.02	$\text{Cl}(2)-\text{Sn}(1)-\text{Cl}(3)$	103.0	0.8
$\text{Sn}(1)-\text{Cl}(3)$	2.36	0.02	$\text{Cl}(2)-\text{Sn}(1)-\text{Cl}(4)$	95.5	0.7
$\text{Sn}(1)-\text{Cl}(4)$	2.33	0.02	$\text{Cl}(2)-\text{Sn}(1)-\text{O}(5)$	89.3	1.2
$\text{Sn}(1)-\text{O}(5)$	2.30	0.04	$\text{Cl}(3)-\text{Sn}(1)-\text{Cl}(4)$	95.7	0.7
$\text{Sn}(1)-\text{O}(6)$	2.25	0.05	$\text{Cl}(3)-\text{Sn}(1)-\text{O}(6)$	89.4	1.2
$\text{P}(7)-\text{O}(5)$	1.41	0.05	$\text{Cl}(4)-\text{Sn}(1)-\text{O}(5)$	82.9	1.1
$\text{P}(8)-\text{O}(6)$	1.49	0.05	$\text{Cl}(4)-\text{Sn}(1)-\text{O}(6)$	83.1	1.1
$\text{P}(7)-\text{Cl}(9)$	1.93	0.03	$\text{O}(5)-\text{Sn}(1)-\text{O}(6)$	78.3	1.6
$\text{P}(7)-\text{Cl}(10)$	1.95	0.03	$\text{Cl}(4)-\text{Sn}(1)-\text{Cl}(4)$	161.9	1.1
$\text{P}(8)-\text{Cl}(11)$	2.00	0.03	$\text{Sn}(1)-\text{O}(5)-\text{P}(7)$	144.5	2.7
$\text{P}(8)-\text{Cl}(12)$	1.89	0.03	$\text{Sn}(1)-\text{O}(6)-\text{P}(8)$	150.7	2.7
			$\text{O}(5)-\text{P}(7)-\text{Cl}(9)$	110.0	2.1
			$\text{O}(5)-\text{P}(7)-\text{Cl}(10)$	114.7	2.0
			$\text{Cl}(9)-\text{P}(7)-\text{Cl}(10)$	105.4	1.2
			$\text{Cl}(10)-\text{P}(7)-\text{Cl}(10)$	105.7	1.3
			$\text{O}(6)-\text{P}(8)-\text{Cl}(11)$	110.6	2.1
			$\text{O}(6)-\text{P}(8)-\text{Cl}(12)$	114.7	2.0
			$\text{Cl}(11)-\text{P}(8)-\text{Cl}(12)$	101.2	1.2
			$\text{Cl}(12)-\text{P}(8)-\text{Cl}(12)$	112.5	1.3



Table 5. Packing distances in  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ .

		Distance (Å)
Cl(2) — Cl(12)	$(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$	3.97
Cl(2) — Cl(12)	$(\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})$	3.91
Cl(3) — Cl(3)	$(-x, 1 - y, -z)$	3.91
Cl(3) — Cl(10)	$(x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$	3.52
Cl(11) — Cl(11)	$(1 - x, 1 - y, -z)$	3.95
Cl(11) — Cl(4)	$(x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z)$	3.57
Cl(11) — Cl(12)	$(1 - x, 1 - y, z)$	3.72
Cl(9) — Cl(4)	$(\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2})$	3.50
Cl(9) — Cl(10)	$(1 - x, -y, z)$	3.92
Cl(9) — Cl(12)	$(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$	3.77
Cl(4) — Cl(4)	$(x, y, 1 - z)$	3.42
Cl(4) — Cl(12)	$(\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$	3.83

$\text{SeOCl}_2$ -groups are crystallographically identical. In  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  on the other hand, although the two  $\text{POCl}_3$ -groups of the molecule are very similar they are crystallographically independent. Consequently corresponding chlorine atoms in the two  $\text{POCl}_3$  groups form very different van der Waals bonds with neighbouring molecules. In their investigation of the infrared spectra of these compounds Sheldon and Tyree<sup>1</sup> detected a splitting of the phosphoryl bond stretching frequency in  $\text{SnCl}_4 \cdot 2\text{POCl}_3$ . This splitting has been confirmed and discussed by Kinell *et al.*<sup>21</sup> who point out that the explanation of this splitting as being due to the existence of two different  $\text{POCl}_3$ -groups in the molecule must be rejected for several reasons. Thus, for example, this splitting has also been found in some pure phosphoryl compounds.

The bond angles about the tin atom in  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$  and in  $\text{SnCl}_4 \cdot 2\text{POCl}_3$  are strikingly similar. The deviation from ideal octahedral coordination in adduct molecules has recently been discussed<sup>22</sup> in terms of two steric effects namely the van der Waals radii of the ligand atoms and their distances from the central atom.

Since the standard deviations of the bond distances are rather large owing to the limited number of observed reflexions a detailed discussion of the bond lengths is not possible. Some marked effects may be pointed out, however. The Sn—Cl bond lengths are 2.31–2.36 Å and are significantly shorter than the bond lengths of 2.39–2.45 Å found in  $\text{SnCl}_6^{2-}$ . This difference has been discussed by Lindqvist<sup>23</sup> for similar compounds. The Sn—O bond length of 2.27 Å is significantly larger than the corresponding bond length of 2.12 Å in  $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ .

The  $\text{POCl}_3$  groups in the adduct are not appreciably different from free  $\text{POCl}_3$ . The same results have been found in all other similar adducts studied.

The author wishes to thank Professor Hägg for all the facilities placed at his disposal and Professor Lindqvist for his stimulating interest in this work. Thanks are also due to Drs Y. Hermodsson, A. Hansson and M. Zackrisson for valuable discussions. This work has been sponsored by a grant from *Air Force Office of Scientific Research*, OAR, through the European Office, Aerospace Research, United States Air Force under Contract No. AF 61(052)–43. This grant is gratefully acknowledged. Facilities for use of the electronic computers BESK and FACIT were given by the Swedish Board for Computing Machinery.

## REFERENCES

1. Sheldon, J. C. and Tyree, S. Y. *J. Am. Chem. Soc.* **80** (1958) 4775.
2. Brändén, C.-I. and Lindqvist, I. *Acta Chem. Scand.* **14** (1960) 726.
3. Brändén, C.-I. *Acta Chem. Scand.* **16** (1962) 1806.
4. Hermodsson, Y. *Acta Cryst.* **13** (1960) 656.
5. Agerman, M., Andersson, L.-H., Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **12** (1958) 477.
6. Löfgren, T. *Acta Cryst.* **14** (1961) 85.
7. Magnéli, A. *Acta Chem. Scand.* **2** (1948) 501.
8. Hägg, G. and Laurent, T. *J. Sci. Instr.* **23** (1946) 155.
9. Lindqvist, I. and Brändén, C.-I. *Acta Cryst.* **12** (1959) 642.
10. Åsbrink, S., Blomqvist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
11. Westman, S., Blomqvist, G. and Åsbrink, S. *Arkiv Kemi* **14** (1959) 535.
12. Åsbrink, S. and Brändén, C.-I. *To be published.*
13. Brändén, C.-I. and Lindqvist, I. *Acta Chem. Scand.* **17** (1963) 353.
14. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem*, Pergamon Press, Oxford 1961, p. 32.
15. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
16. Berghuis, J., Haanappel, I. J. M., Potters, M., Loopstra, B. O., Mac Gillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
17. Tomii, Y. and Stam, C. H. *Acta Cryst.* **11** (1958) 126.
18. Liminga, R. and Olovsson, I. *To be published.*
19. Lindqvist, I. *Inorganic adduct molecules of oxo-compounds*, Springer Verlag. *To be published.*
20. Hulme, R., Liegh, G. J. and Beattie, I. R. *J. Chem. Soc.* **1960** 366.
21. Kinell, P.-O., Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **13** (1959) 1159.
22. Brändén, C.-I., Hansson, A., Hermodsson, Y. and Lindqvist, I. *Z. Krist.* **117** (1962) 462.
23. Lindqvist, I. *Nova Acta Regiae Soc. Sci. Upsaliensis* (IV) **17** (1960) No. 11.

Received September 24, 1962.