

## The Crystal and Molecular Structure of Tetraphenylarsonium Methyltetrachlorostannate(IV) Showing Marked Variation in Anion Geometry

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*The structure of  $[(C_6H_5)_4As][CH_3SnCl_4]$  has been determined by three dimensional X-ray analysis using photographic data and refined to  $R$  of 0.054 for 1168 observed reflections. The crystals are monoclinic,  $a = 13.06(2)$ ,  $b = 7.78(2)$ ,  $c = 13.01(2)$  Å,  $\beta = 91.7(2)^\circ$  with space group  $P2$  and with  $Z = 2$ . The structure contains two crystallographically independent discrete anions with twofold symmetry. The tin atoms have approximately trigonal bipyramidal coordination with the carbon atoms occupying an equatorial position. The  $Cl(ax)-Sn-Cl(ax)$  angles ( $174.6(6)^\circ$  and  $172.6(7)^\circ$ ) are similar in the two anions but the  $Cl(eq)-Sn-Cl(eq)$  angle shows a pronounced variation ( $104.9(7)$  and  $126.0(6)$ ). The geometry of the cation is as expected from earlier studies.*

### Introduction

Infrared and Raman solution studies in nitromethane on the interaction between  $MeSnCl_3$  and chloride ions have established the formation of two species, the  $MeSnCl_4^-$  and  $MeSnCl_5^{2-}$  anions [1]. Four, five and six coordinate organo-tin compounds are well known and whilst it is likely that the  $MeSnCl_4^-$  ion is five coordinate, the importance of any weak ion-solvent interaction on the geometry of the ion is difficult to assess. The vibrational spectra did not yield the symmetry of the  $MeSnCl_4^-$  ion and surprisingly only one solid compound of the correct empirical composition has been reported when the counterion is the tetraphenylarsonium cation [1, 2]. Other related compounds of the formula  $[\phi_4As][RnCl_4]$ ,  $R = Et, n-Bu, \phi$ , have been isolated [2, 3]. With the tetraphenylarsonium ion it has not proved possible to synthesise the compound containing the  $MeSnCl_5^{2-}$  group although this ion and other related halogeno species are well known with other large cations [1, 4]. As part of our program on the detailed stereochemistry of organotin anions and to support the solution studies we undertook a single crystal X-ray examination of the compound  $[(C_6H_5)_4As][MeSnCl_4]$ .

### Experimental

The compound was prepared by mixing equimolar amounts of reagent from aq. HCl (using  $\phi_4AsCl$  and  $MeSnO(OH)[5]$ ) or from ethanol (using  $\phi_4AsCl$  and  $MeSnCl_3$ ). On recrystallization from EtOH, small rather opaque white air stable crystals were obtained which were used for crystallographic examination. M.pt.  $204-205^\circ$ , lit.  $207-209^\circ C$  [2]. Found: C = 45.62; H = 3.71; Cl = 21.64. Calc. for  $[\phi_4As][MeSnCl_4]$ : C = 45.57; H = 3.52; Cl = 21.52%.

### Crystal Data

Cell dimensions and diffraction symmetry were obtained from Weissenberg and precession photographs and established the crystals as monoclinic,  $a = 13.06(2)$ ,  $b = 7.78(2)$ ,  $c = 13.01(2)$  Å,  $\beta = 91.7(2)^\circ$ ,  $V = 1321.3$  Å<sup>3</sup>. The calculated density ( $C_{25}H_{23}AsCl_4Sn$ , M.Wt. = 658.9) of  $1.65$  gm<sup>-3</sup> for  $Z = 2$  agrees satisfactorily with the value of  $1.60(3)$  gm<sup>-3</sup> obtained by flotation. The lack of systematic absences was consistent with space groups  $P2$ (No. 3),  $Pm$ (No. 6) or  $P2/m$ (No. 10) with  $P2$  being confirmed by the subsequent analysis. The linear absorption coefficient is  $\mu(Cu-K\alpha)$   $127.2$  cm<sup>-1</sup> and  $\mu(Mo-K\alpha)$   $25.3$  cm<sup>-1</sup>. A crystal of approximate dimensions  $0.25 \times 0.70 \times 0.15$  mm mounted on a glass fibre about the  $b$  axis was used to record multiple film equi-inclination Weissenberg photographs ( $h0l-h6l$ ) using nickel filtered  $Cu(K\alpha)$  radiation ( $\lambda = 1.5418$  Å). Intensities were measured using an Optronics P1000 photostan microdensitometer.\* The associated software indexed the spots, established film to film scale factors and after rejecting observations on various criteria produced a list of 2178 integrated intensity measurements. These included multiple measurements of some reflections from the top and bottom halves of the film and symmetry related reflections. After suitable averaging and the application of the absorption correction, 1168 observed

\*The SRC Microdensitometer Service at the Atlas Computer Laboratory, Harwell, England.

reflections were obtained which were used as the data set for the structure solution. Comparison of the films with some of the measured intensities confirmed the satisfactory indexing. Lorentz and polarization factors were applied and scattering factors for the neutral atoms, carbon, chlorine and arsenic taken from reference 6, and for tin from reference 7. Anomalous dispersion corrections for Sn, As and Cl were used [6].

### Structure Solution

The distribution of normalized structure factors ( $E$ 's) clearly pointed to a noncentrosymmetric space group and consideration of the three dimensional Patterson function only produced a plausible solution for the Sn and As positions in the space group P2. All the tin and arsenic atoms occupy sites with two fold symmetry (1-fold special positions) and the two atoms of whatever type (As or Sn) are crystallographically distinct. An electron density synthesis phased on the heavy atoms yielded the expected number of chlorine atoms and on repeating this procedure including the chlorine atoms in the model, all 24 carbon atoms of the phenyl rings were located. Full matrix least square refinement followed by a difference electron density synthesis gave clear indications for a carbon atom lying on the 2-fold axis and bonded to each tin atom and no evidence for any additional atoms. Least squares refinement (scale factors, atom positional and isotropic temperature factors, unit weights) reduced  $R_1$  to *ca.* 9%. An empirical weighting scheme was derived from an analysis of  $\Delta F^2$  vs.  $F_o$  for various ranges of  $F_o$  [ $w = 1/(A + BF_o)$ ,  $A = 4.82$ ,  $B = 0.286$ ]. The resulting  $\Sigma w\Delta^2$  showed an acceptable dependence on  $F_o$  and  $\sin\theta/\lambda$ . Further refinement (with calculated weights) reduced  $R_1$  to 7.5% and the introduction of anisotropic temperature factors for Sn, As and Cl atoms (162 parameters) reduced  $R_1$  to a final converged value of 5.4%. This decrease in the R factor is highly significant when Hamilton's statistical

TABLE I. Final Positional ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\times 10^2$ ) with Standard Deviations in Parentheses.

Atom <sup>a</sup>	x/a	y/b	z/c	U( $\text{\AA}^2$ )
Sn(1)	0000	0000	0000	
Sn(2)	5000	2014(4)	5000	
As(1)	5000	1584(15)	0000	
As(2)	0000	0478(14)	5000	
Cl(1)	1769(12)	-0151(22)	0764(12)	
Cl(2)	3214(13)	2214(25)	4464(13)	
Cl(3)	4479(13)	3420(22)	6551(13)	
Cl(4)	0420(15)	-1781(23)	-1306(14)	
C(1)	0000	2768(121)	0000	5.6(1.8)
C(2)	5000	-0731(185)	5000	10.7(4.2)
C(11)	3955(45)	3023(87)	0484(45)	5.9(1.6)
C(12)	3548(35)	4369(65)	-0288(34)	5.8(1.2)
C(13)	2830(31)	5390(61)	0114(32)	6.1(1.2)
C(14)	2428(26)	5314(55)	1042(27)	4.5(0.9)
C(15)	2798(29)	3996(59)	1788(32)	6.2(1.2)
C(16)	3547(37)	2745(76)	1467(39)	7.2(1.7)
C(21)	4508(28)	0022(57)	8916(26)	3.7(1.1)
C(22)	3602(28)	0184(52)	8515(26)	3.8(0.8)
C(23)	3282(32)	-1130(60)	7756(32)	5.0(1.2)
C(24)	3817(34)	-2452(67)	7522(35)	7.8(1.5)
C(25)	4975(50)	-2372(99)	7852(55)	4.1(2.4)
C(26)	5213(24)	-1297(49)	8651(24)	4.1(0.9)
C(31)	1109(40)	-1054(77)	4624(38)	3.7(1.3)
C(32)	1320(45)	-2195(89)	5261(46)	5.9(2.0)
C(33)	2160(29)	-3553(60)	5093(30)	5.9(1.2)
C(34)	2615(46)	-3302(86)	4138(44)	9.5(2.0)
C(35)	2314(28)	-2016(56)	3455(29)	4.0(1.1)
C(36)	1486(24)	-0976(52)	3647(24)	2.9(0.8)
C(41)	0397(32)	1914(60)	6053(30)	5.2(1.3)
C(42)	1495(41)	2056(76)	6390(43)	8.0(1.8)
C(43)	1841(32)	3192(63)	7057(33)	6.9(1.3)
C(44)	0998(29)	4272(54)	7550(29)	4.7(1.0)
C(45)	0119(34)	4455(64)	7181(34)	9.1(1.5)
C(46)	-0277(32)	2988(63)	6494(32)	6.5(1.3)

<sup>a</sup>The carbon atoms of the phenyl rings are labelled C(ij) where i (1-4) refers to the ring and j (1-6) refers to the carbon atoms of one ring numbered cyclically.

TABLE II. Anisotropic Temperature Factors<sup>a</sup> ( $\times 10^2$ ) of the Heavy Atoms with Standard Deviations in Parentheses.

Atom	U11	U22	U33	U12	U13	U23
Sn(1)	4.4(4)	4.5(7)	6.5(4)	- <sup>b</sup>	0.2(3)	- <sup>b</sup>
Sn(2)	4.8(5)	4.6(7)	6.4(5)	-	0.3(4)	-
As(1)	4.2(6)	4.3(8)	4.3(5)	-	0.1(4)	-
As(2)	4.7(6)	4.1(8)	4.8(5)	-	0.5(4)	-
Cl(1)	4.7(6)	7.7(1.0)	7.5(7)	-0.1(6)	-0.6(4)	0.2(6)
Cl(2)	5.7(7)	9.6(1.1)	9.0(9)	-0.9(6)	-1.5(6)	-0.2(7)
Cl(3)	7.6(7)	13.2(1.3)	9.6(8)	1.4(6)	-0.0(6)	-4.0(7)
Cl(4)	8.2(8)	12.8(1.3)	15.2(1.3)	3.3(7)	-0.7(8)	-8.7(1.0)

<sup>a</sup>In the form  $T = \exp [-2\pi^2(U11h^2a^{*2} + \dots + 2U12hka^*b^* \cos\gamma^* + \dots)]$ . <sup>b</sup>U12 and U23 constrained by symmetry to be zero for Sn and As atoms.

test is applied [8]. No hydrogen atoms were included in the structure factor calculations and a final difference electron density map showed no features  $>0.5$  or  $<-0.3$   $e\text{\AA}^{-3}$  except close to As or Sn. A number of these are in plausible positions to be hydrogen atoms on the phenyl ring.

At this point refinement was terminated and in Tables I and II we report the final positional and thermal parameters together with their standard deviations derived from the least squares matrix. A table of structure factors is available from the editor or the authors upon request.

All calculations except for some sorting and averaging procedures were carried out on the ICL 1906A computer Harwell, England, using the X-ray system of crystallographic programs [9].

### Description of Structure and Discussion

The structure consists of discrete  $[MeSnCl_4]^-$  anions and  $[\phi_4As]^+$  cations, and the manner in which these ions pack together is shown in Figure 1. Selected bond lengths and angles are presented in Table III.

The two crystallographically distinct tin atoms are located on two-fold axes and each is five coordinate. The anions have approximate  $C_{2v}$  point group symmetry and the coordination about tin can best be described as a trigonal bipyramidal arrangement, with the carbon atom occupying an equatorial position. The  $Cl(ax)-Sn-Cl(ax)$  bond angle is bent  $\sim 5^\circ$  from the idealized linear arrangement and away from the

carbon atom in both anions, whereas the  $Cl(eq)-Sn-Cl(eq)$  angle are very different and differs by  $\sim 21^\circ$  between the two ions (see Table III and Figure 2). In gross terms the structure fits in with the chemistry of the  $[Me_2SnCl_3]^-$  [10, 11] and  $[Me_3SnCl_2]^-$  [12] ions both of which are based on trigonal bipyramidal coordination of tin with the methyl group in equatorial positions.

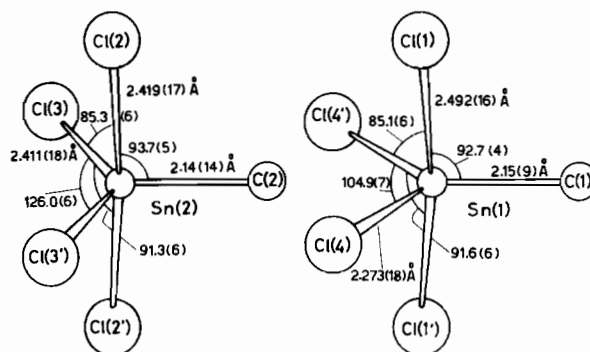


Fig. 2. Bond lengths and angles in the  $[MeSnCl_4]^-$  anions.

Inspection of Table I and II shows large standard deviations (e.s.d.) in the positional parameters of C(1) and C(2), and hence in the corresponding Sn-C bonds, and a large U (and e.s.d. of U) for C(2). The origin of this effect is not clear and various points seem worth discussing. The e.s.d.'s of the y coordinate is larger than in the two other directions (although C(1) and C(2) remain anomalous) which is probably due to the method of collecting data. Inclusion of higher layer lines was not possible and consideration was given to including  $hk0$  and  $0kl$  zones of data recorded using a precession camera ( $Mo(K\alpha)$  radiation). This would have added 51 new reflections, 7 for  $k = 7$  and 44 reflections obscured by the Weissenberg camera back stop, ( $k = 0-6$ ) but made the inclusion of anomalous dispersion impossible (due to two sorts of radiation) and on balance was not thought valuable. The Sn-C vector was visible in the 3-D Patterson map and appeared normal in shape and height and there is no evidence to suggest a static disordered structure in which a larger unit cell ought to be chosen. The cell has shown some pseudo-symmetry both in cell dimensions ( $a \approx c$  and  $\beta \approx 90^\circ$ ) and in the intensities but inspection of the diffraction photographs clearly establishes that we are dealing with a monoclinic crystal. The  $h0l$  zone shows an approximate (non space group) absence for  $h + l = 2n + 1$  and the projection (Figure 1) shows a view with considerable pseudo symmetry (compare with space group  $P4_2/n$  (No. 86) with the tetragonal  $c = 2b$ ). Refinement allowing C(1) and C(2) to have anisotropic motion was not helpful due to large e.s.d.'s on the parameters. The location of C(1) and C(2) on the two

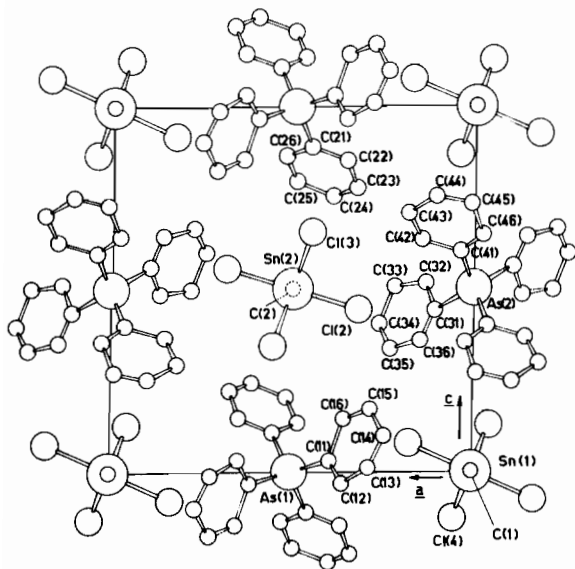


Fig. 1. Projection of the unit cell (from  $y = -0.4$  to  $y = 0.6$ ) viewed from the positive  $b$  direction looking towards the origin.

TABLE III. Bond Lengths (Å) and Angles (deg.) with Standard Deviations in Parenthesis.

	(i)	(ii)		
(a) <i>Anion</i>	Sn(1)–Cl(1)	2.492(16)	Sn(2)–Cl(2)	2.419(17)
	Sn(1)–Cl(4)	2.273(18)	Sn(2)–Cl(3)	2.411(18)
	Sn(1)–C(1)	2.15(9)	Sn(2)–C(2)	2.14(14)
	Cl(1)–Sn(1)–Cl(1')	174.6(6)	Cl(2)–Sn(2)–Cl(2')	172.6(7)
	Cl(4)–Sn(1)–Cl(4')	104.9(7)	Cl(3)–Sn(2)–Cl(3')	126.0(6)
	Cl(1)–Sn(1)–Cl(4)	91.6(6)	Cl(2)–Sn(2)–Cl(3)	85.3(6)
	Cl(1)–Sn(1)–Cl(4')	85.1(6)	Cl(2)–Sn(2)–Cl(3')	91.3(6)
	Cl(1)–Sn(1)–C(1)	92.7(4)	Cl(2)–Sn(2)–C(2)	93.7(5)
	Cl(4)–Sn(1)–C(1)	127.6(5)	Cl(3)–Sn(2)–C(2)	117.0(4)
(b) <i>Cation</i>	As(1)–C(11)	1.89(6)	As(2)–C(31)	1.95(6)
	As(1)–C(21)	1.95(4)	As(2)–C(41)	1.83(4)
	C(11)–C(12)	1.54(8)	C(31)–C(32)	1.24(8)
	C(12)–C(13)	1.35(6)	C(32)–C(33)	1.54(8)
	C(13)–C(14)	1.33(6)	C(33)–C(34)	1.41(7)
	C(14)–C(15)	1.48(6)	C(34)–C(35)	1.39(7)
	C(15)–C(16)	1.45(7)	C(35)–C(36)	1.38(5)
	C(16)–C(11)	1.42(8)	C(36)–C(31)	1.38(6)
	C(21)–C(22)	1.29(5)	C(41)–C(42)	1.49(7)
	C(22)–C(23)	1.47(6)	C(42)–C(43)	1.31(7)
	C(23)–C(24)	1.28(7)	C(43)–C(44)	1.54(6)
	C(24)–C(25)	1.56(8)	C(44)–C(45)	1.24(6)
	C(25)–C(26)	1.36(8)	C(45)–C(46)	1.53(7)
	C(26)–C(21)	1.43(5)	C(46)–C(41)	1.35(6)

All internal angles of the phenyl ring are in the range 110(4)° to 128(4)°

C(11)–As(1)–C(11')	107(3)	C(31)–As(2)–C(31')	105(3)
C(21)–As(1)–C(21')	103(2)	C(41)–As(2)–C(41')	105(2)
C(11)–As(1)–C(21)	112(2)	C(31)–As(2)–C(41)	111(2)
C(11)–As(1)–C(21')	111(2)	C(31)–As(2)–C(41')	112(2)

[Primed atoms (') are related to unprimed atoms by a two fold axis]

(c) *Equation of planes passing through phenyl rings*

C(11)–C(16)  $9.116x + 4.840y + 4.345z = 5.240$   
(mean deviation from plane 0.02 Å, max. deviations 0.04 Å)

C(21)–C(26)  $-4.397x - 4.567y + 9.704z = 6.634$   
(mean deviation from plane 0.06 Å, max. deviation 0.12 Å)

C(31)–C(36)  $8.648x + 4.906y + 5.010z = 2.705$   
(mean deviation from plane 0.03 Å, max. deviation 0.07 Å)

C(41)–C(46)  $-2.495x - 5.040y + 9.663z = 4.783$   
(mean deviation from plane 0.06 Å, max. deviation 0.12 Å)

x, y, z are fractional coordinates in direct space.

fold axes may be significant but we have little choice but to accept that the Sn–C distance is not well defined in this structure.

In general terms the bond lengths are those expected from earlier studies. In one anion the equatorial and axial Sn–Cl bonds are the same length, whereas the other anion shows longer (by 0.22 Å) axial bonds. A number of solid state structures are known containing, within the same unit

cell, two geometrical isomers of a species, including NiBr<sub>2</sub> [P(CH<sub>2</sub>Ph)(Ph)<sub>2</sub>]<sub>2</sub> [13], [Me<sub>2</sub>SiNH]<sub>4</sub> [14], and [Co(en)<sub>3</sub>] [Ni(CN)<sub>5</sub>] 1.5H<sub>2</sub>O [15]. This latter example contains square pyramidal and trigonal bipyramidal anions, and while the present structure is not of this type, the marked variation in Cl(eq)–Sn–Cl(eq) angle does emphasise again the importance of packing forces influencing molecular geometry in the solid state. The origin of the

difference in anion geometry is presumably the cation to anion contact distances but the effect is subtle. The minimum non hydrogen intermolecular contacts are 3.37(6) Å (Cl(1)–C(16)) and 3.42(6) Å (Cl(2)–C(42)) all other distances being >3.5 Å.

The tetraphenyl arsonium cation has  $C_2$  crystallographic symmetry but approximately  $S_4$  point group symmetry. The bond lengths and angles are in agreement with earlier studies on this ion [16] and values are presented in Table III together with the equation of the least square planes through the rings.

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