

Studies in Aryltin Chemistry. 8.* Structures of Tetraethylammonium Dibromotriphenyl- and Dibromotris(*p*-methylthiophenyl)stannate(IV)

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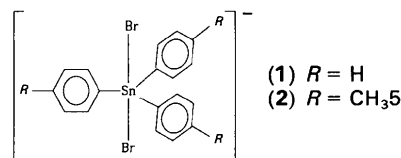
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Abstract. (1) $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Sn}(\text{C}_6\text{H}_5)_3\text{Br}_2]$, $M_r = 640.1$, monoclinic, $P2_1/c$, $a = 10.594$ (3), $b = 13.838$ (3), $c = 20.077$ (13) Å, $\beta = 113.55$ (3)°, $V = 2698.1$ (25) Å³, $Z = 4$, $D_x = 1.576$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 11.3$ mm⁻¹, $F(000) = 1272$, $T = 295$ K, $R = 0.038$ for 3637 [$I > 3\sigma(I)$] reflections. (2) $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Sn}(\text{p-CH}_3\text{SC}_6\text{H}_4)_3\text{Br}_2]$, $M_r = 778.3$, triclinic, $P1$, $a = 9.208$ (3), $b = 13.138$ (4), $c = 13.562$ (5) Å, $\alpha = 89.90$ (3), $\beta = 82.77$ (3), $\gamma = 85.31$ (2)°, $V = 1622.1$ (11) Å³, $Z = 2$, $D_x = 1.594$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 11.3$ mm⁻¹, $F(000) = 780$, $T = 295$ K, $R = 0.058$ for 5205 [$I > 3\sigma(I)$] reflections. Both compounds have slightly distorted trigonal-bipyramidal anions with axial Br atoms. For (2), the differing torsion angles (CH₃S—phenyl ring), -42.6 (7), 0.9 (7), -27.6 (8)° indicate crystal-packing effects are predominant. The cations are disordered with occupancy factors, (1) 0.75:0.25 and (2) 0.80:0.20, for the two forms.

Introduction. Substitution on all the phenyl rings of a tetraaryltin usually produces only small changes in the molecular geometry around tin although minor space group changes may occur. However, when *para*-hydrogen is replaced by the large CH₃S(O₂) group (Wharf, Simard & Lamparski, 1990) a decrease in the crystal symmetry from tetragonal to monoclinic is observed. Triaryltin compounds are of more general interest because Ph₃SnX (X = OH or OAc) are used as commercial fungicides (Evans & Karpel, 1985) and many triphenyltin structures have been reported including Ph₃SnCl (Tse, Lee & Gabe, 1986) and Ph₃SnBr (Preut & Huber, 1979). The crystal symmetry changes that may be caused by *para*-substitution have received little attention. Replacement of *p*-H in Ph₃SnCl by CH₃S gave a

trivial space group change† but the same substitution in $[\text{Et}_4\text{As}][\text{Ph}_3\text{SnBr}_2]$ (1) to form (2), gave a decrease in crystal symmetry which thus prompted the full structure determinations reported here. The bromo anions were chosen for study since a survey of the Cambridge Structural Database (1990) showed there to be many more reports of organochlorotins compared with those for the bromo analogues and few direct comparisons like that given above as well as Et₂SnX₂ (Alcock & Sawyer, 1977) or C₃SnX [X = Cl, Calogero, Granis, Peruzzo & Tagliavini (1979); X = Br, Calogero, Granis, Peruzzo, Tagliavini & Valle (1981)], are available. Here the structure of $[\text{Ph}_3\text{SnBr}_2]^-$ will be compared with that of the chloroanion, albeit with a different counterion (Harrison, Molloy, Phillips, Smith & Crowe, 1978).



Experimental. Evaporating an *n*-propanol (25 ml) solution of (*p*-CH₃SC₆H₄)₃SnBr (2.92 mmol) with (C₂H₅)₄NBr (3.96 mmol) followed by cooling gave (2); m.p. 420 K. Found: C, 44.6; H, 5.35; N, 1.6; calc. for C₂₉H₄₁Br₂NS₃Sn: C, 44.8; H, 5.3; N, 1.8%. Compound (1) was made earlier (Wharf, Cuenca & Onyszchuk, 1984). Evaporation of ethanol solutions gave plates [(1)] or cube shaped crystals [(2)]. Unit cell from 25 reflections, range 20° < θ < 22°. Enraf-Nonius CAD-4 diffractometer, Cu Kα radiation, graphite monochromator, ω/2θ scans, scan rate = 4° min⁻¹, 2θ_{max} = 140.0°, seven standard reflections

† Crystal data for C₂₁H₂₁ClS₃Sn at 298 K: monoclinic, $P2_1/c$, $a = 9.178$ (5), $b = 21.634$ (12), $c = 13.097$ (9) Å, $\beta = 122.28$ (5)°, $V = 2198$ Å³, $Z = 4$.

* Part 7: Wharf, Lamparski, Reeleder & Simard (1991).

checked for intensity every hour, largest fluctuation ± 2.2 (1) or 2.0% (2). Lorentz, polarization and absorption corrections performed using a Gaussian integration technique (grid $10 \times 10 \times 10$). All other structure determination details are given in Table 1.

Structure solved by direct methods and difference Fourier calculation. Refinement based on F (full-matrix least squares), with all non-H atoms having anisotropic thermal parameters (minor disorder excepted) was carried out initially without disorder at the cation position but the large anisotropic temperature factors of the ethyl groups as well as the existence of additional peaks close to the central N atom indicated that disorder was present. Introduction of the two orientations using a constrained model [$d(\text{C}-\text{C})$ and $d(\text{C}-\text{N})$] gave converged values of occupancy factors for (1) 0.755 (4):0.245 (4) and (2) 0.809 (7):0.191 (7). The occupancies were fixed at 0.75:0.25 and 0.80:0.20, respectively, for the subsequent refinement which with H atoms assigned isotropic thermal parameters and placed in ideal positions [$d(\text{C}-\text{H}) = 1.08 \text{ \AA}$; (1) $U_{\text{iso}} = 0.10 \text{ \AA}^2$ (phenyl) and 0.14 \AA^2 (ethyl); (2) $U_{\text{iso}} = 0.10 \text{ \AA}^2$ (phenyl and methylene) and 0.14 \AA^2 (methyl)] led to the results given in Table 1. Scattering curves for all non-H atoms from Cromer & Waber (1965), for H atoms from Stewart, Davidson & Simpson (1965) with anomalous-dispersion factors from Cromer & Liberman (1970). Programs used: *SHELXS86* (Sheldrick, 1986), *SHELX76* (Sheldrick, 1976), *ORTEP* (Johnson, 1965) and modified *NRC Crystallographic Programs for the IBM360 System* (1973).

Discussion. Final atomic coordinates and isotropic temperature factors are listed in Table 2 and selected bond lengths and angles in Table 3.* For (2) the anion is shown in Fig. 1, while views of the unit cells of (1) and (2) are in Figs. 2(a) and 2(b) respectively.

Both anions have the expected, almost trigonal bipyramidal structure with Br atoms in the axial positions, but the distortions from the ideal geometry are not the same and also differ from those found for $\text{Ph}_3\text{SnCl}_2^-$ (Harrison *et al.*, 1978). In addition, we note that the varied values for the dihedral angles between the phenyl rings and the equatorial plane [C(11)—C(21)—C(31)] for (1) and (2) as well as for $[\text{Ph}_3\text{SnCl}_2]^-$ are also more probably due to differing crystal-packing requirements rather than to any intramolecular effects.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters least-squares planes, torsion angles and phenyl ring and cation bond lengths and angles for (1) and (2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53905 (62 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Structure determination details

	(1)	(2)
Crystal dimensions (mm)	0.05 (001, 00 $\bar{1}$) \times 0.15 (10 $\bar{2}$, 102) \times 0.42 (010, 0 $\bar{1}$ 0)	0.21 (010, 0 $\bar{1}$ 0) \times 0.24 (001, 00 $\bar{1}$) \times 0.27 (100, 100)
Scan width ($^\circ$)	1.00 + 0.15 tan θ	1.00 + 0.14 tan θ
h, k, l range	0 \rightarrow 12, 0 \rightarrow 16, -24 \rightarrow 24	11 \rightarrow 11, -16 \rightarrow 16, -16 \rightarrow 16
Number of measured reflections	5651	11935
Number of unique reflections	5117	6136
$R_{\text{int}} = \sum(I - \langle I \rangle) / \sum I$ (number of reflections used)	0.021 (288)	0.046 (5802)
Reflections with $I > 3\sigma(I)$	3637	5205
Parameters refined	304	358
Transmission-factor range	0.09–0.45	0.09–0.25
R	0.038	0.058
wR	0.042	0.072
S	1.82	3.50
w^{-1}	$\sigma^2(F) + 0.0001F^2$	$\sigma^2(F) + 0.0001F^2$
$(\Delta/\sigma)_{\text{max}}$	0.35	0.34
$(\Delta/\sigma)_{\text{ave}}$	0.03	0.02
$(\Delta\rho)_{\text{max}}$ (e \AA^{-3})	0.30	0.55
Largest peaks in final ΔF map (e \AA^{-3})	Seven between 0.66–0.42; 1.04–1.44 \AA from Sn or Br	Six between 1.90–0.85; 1.13–1.20 \AA from Sn or Br

In (1), cations and anions pack in alternating columns [Fig. 2(a)] but (2) has the cations sandwiched between phenyl rings on neighbouring anions [Fig. 2(b)]. The CH_3S groups attached to these phenyl rings are almost coplanar with them, but the two other CH_3S groups in each anion have torsion angles of -42.6 and -27.6° with respect to the phenyl rings to which they are attached. Since Schaeffer & Baleja (1986) have shown the barrier to rotation of the CH_3S group in thioanisole about the $\text{S}-\text{C}_{\text{sp}^2}$ bond is quite small, it is probable that the coplanarity of the $\text{CH}_3\text{SC}_6\text{H}_5$ group mentioned above may be due to the sandwiching of this phenyl ring between cations in the crystal lattice rather than to any electronic effects. However, all three $\text{S}-\text{C}_{\text{sp}^2}$ bonds are still shorter than expected for $d(\text{C}-\text{S})$, 1.80–1.82 \AA (Wharf & Simard, 1987).

A comparison of tin—chlorine and tin—bromine bond lengths for various exact or closely analogous pairs is given in Fig. 3. While the points have errors of $\sim 0.01 \text{ \AA}$, the trend is clearly for the line to have zero intercept, indeed if points f , g , i and k , with residuals $> 0.03 \text{ \AA}$ are deleted, the relation is $d(\text{SnBr}) = 1.084 (\pm 0.035)d(\text{SnCl}) - 0.047 (\pm 0.084)$ ($r = 0.994$). Brown (1980) has extensively promoted the concept of partial bond order or bond valence (s) as an aid to analyzing crystal structures, particularly those of minerals and related compounds, following previous work by Pauling (1929, 1947) and Donnay & Allmann (1970). Two expressions are in common use to relate bond lengths (r) and bond valence (s)

$$s = (r/r_0)^{-N} \quad (\text{I})$$

and

$$s = \exp[(r - r_0)/B], \quad (\text{II})$$

where r_0 , N and B are empirically determined parameters for each MX system using the maximum

Table 2. Atomic coordinates ($\times 10^5$ for Sn and Br and $\times 10^4$ for other atoms) and thermal parameters ($\text{\AA} \times 10^3$)
$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

(1)	x	y	z	$U_{eq}(\text{\AA}^2)$
Sn	21626 (4)	78924 (3)	1738 (2)	58
Br(1)	10322 (7)	91962 (5)	-9732 (3)	74
Br(2)	32984 (8)	67342 (6)	13821 (4)	94
N	1550 (4)	1698 (3)	7468 (2)	66
C(11)	3329 (5)	9068 (4)	813 (3)	63
C(12)	4431 (5)	9441 (4)	688 (3)	67
C(13)	5196 (6)	10179 (5)	110 (4)	89
C(14)	4891 (7)	10572 (5)	1635 (4)	100
C(15)	3792 (8)	10238 (5)	1758 (4)	121
C(16)	3000 (7)	9483 (5)	1338 (4)	99
C(21)	136 (5)	7579 (4)	110 (3)	58
C(22)	-815 (5)	8313 (4)	4 (3)	71
C(23)	-2129 (6)	8117 (5)	-33 (3)	93
C(24)	-2513 (6)	7177 (5)	18 (4)	102
C(25)	-1572 (7)	6447 (5)	120 (4)	102
C(26)	-250 (6)	6642 (4)	175 (3)	76
C(31)	2984 (5)	7006 (3)	-452 (3)	57
C(32)	3224 (7)	6051 (5)	-309 (4)	95
C(33)	3674 (7)	5468 (5)	-726 (4)	120
C(34)	3911 (7)	5842 (5)	-1293 (4)	106
C(35)	3680 (6)	6801 (5)	-1453 (4)	92
C(36)	3199 (5)	7381 (4)	-1028 (4)	81
C(41)	132 (7)	2091 (6)	7352 (4)	79
C(42)	-264 (9)	1905 (6)	7996 (5)	102
C(43)	2648 (7)	2010 (6)	8193 (4)	78
C(44)	2833 (9)	3072 (7)	8303 (5)	126
C(45)	1863 (8)	2044 (6)	6841 (4)	84
C(46)	3347 (8)	1811 (6)	6929 (5)	100
C(47)	1559 (8)	593 (5)	7507 (5)	87
C(48)	564 (10)	135 (8)	6779 (6)	139
C(41')	1307 (14)	1571 (13)	8127 (11)	106
C(42')	-329 (14)	1563 (13)	7934 (13)	97
C(43')	1231 (15)	2779 (13)	7213 (12)	135
C(44')	2014 (14)	3506 (13)	7802 (11)	109
C(45')	3088 (14)	1504 (13)	7641 (11)	109
C(46')	3225 (14)	1391 (13)	6893 (12)	104
C(47')	639 (15)	1098 (14)	6772 (12)	137
C(48')	572 (15)	33 (14)	7039 (12)	116
(2)				
Sn	37954 (5)	59927 (3)	71740 (3)	47
Br(1)	53063 (9)	60504 (6)	88224 (6)	63
Br(2)	25267 (10)	59325 (6)	54624 (6)	65
S(1)	9053 (2)	8856 (2)	5159 (2)	68
S(2)	2937 (3)	1044 (1)	8059 (2)	70
S(3)	-1893 (2)	9143 (2)	9170 (2)	90
N	1831 (6)	7146 (4)	1986 (4)	53
C(11)	5523 (7)	6816 (5)	6421 (5)	48
C(12)	6973 (8)	6449 (5)	6322 (5)	55
C(13)	8073 (8)	7042 (5)	5922 (5)	58
C(14)	7716 (8)	8040 (5)	5650 (5)	50
C(15)	6240 (8)	8412 (5)	5729 (5)	59
C(16)	5163 (8)	7795 (5)	6091 (5)	57
C(17)	10483 (10)	8609 (6)	5927 (7)	77
C(21)	3617 (7)	4391 (4)	7401 (5)	46
C(22)	3825 (9)	3690 (5)	6614 (5)	57
C(23)	3629 (9)	2664 (5)	6791 (5)	58
C(24)	3218 (7)	2321 (5)	7752 (5)	49
C(25)	3007 (7)	3019 (5)	8536 (5)	52
C(26)	3220 (7)	4042 (5)	8358 (5)	51
C(27)	3331 (14)	384 (6)	6888 (8)	101
C(31)	1977 (7)	6956 (5)	7892 (5)	48
C(32)	539 (8)	6677 (5)	7906 (5)	55
C(33)	-661 (8)	7303 (5)	8309 (5)	58
C(34)	-444 (9)	8257 (5)	8680 (5)	57
C(35)	973 (9)	8543 (5)	8685 (5)	60
C(36)	2172 (8)	7891 (5)	8304 (5)	54
C(37)	-3390 (10)	8852 (7)	8544 (9)	98
C(41)	1348 (11)	8177 (7)	2483 (8)	69

Table 2 (cont.)

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(42)	2447 (15)	8484 (10)	3234 (9)	98
C(43)	3412 (9)	7139 (7)	1468 (7)	55
C(44)	3678 (12)	8024 (7)	762 (7)	67
C(45)	808 (11)	7042 (9)	1205 (8)	71
C(46)	1063 (14)	6078 (9)	604 (8)	86
C(47)	1826 (10)	6283 (7)	2698 (7)	59
C(48)	296 (13)	6091 (10)	3265 (9)	87
C(41')	2978 (33)	7274 (23)	2800 (23)	48
C(42')	2390 (48)	8221 (32)	3451 (33)	80
C(43')	1817 (47)	7983 (34)	1321 (33)	81
C(44')	3255 (60)	8276 (36)	673 (35)	84
C(45')	2464 (37)	6146 (26)	1471 (26)	57
C(46')	1363 (42)	5738 (29)	763 (29)	66
C(47')	320 (38)	7125 (27)	2594 (26)	59
C(48')	326 (34)	6224 (23)	3332 (23)	49

Table 3. Selected bond distances (\AA) and angles ($^\circ$)

Compound (1)			
Anion			
Sn—C(11)	2.134 (5)	Sn—Br(1)	2.7908 (7)
Sn—C(21)	1.143 (6)	Sn—Br(2)	2.7512 (9)
Sn—C(31)	2.171 (5)		
C(11)—Sn—C(21)	121.0 (2)	Br(2)—Sn—C(21)	90.6 (1)
C(11)—Sn—C(31)	120.6 (2)	Br(2)—Sn—C(31)	92.6 (1)
C(21)—Sn—C(31)	118.3 (2)	Sn—C(11)—C(12)	120.1 (4)
Br(1)—Sn—Br(2)	175.21 (3)	Sn—C(11)—C(16)	121.4 (4)
Br(1)—Sn—C(11)	87.6 (2)	Sn—C(21)—C(22)	120.7 (4)
Br(1)—Sn—C(21)	89.6 (1)	Sn—C(21)—C(26)	120.8 (4)
Br(1)—Sn—C(31)	91.5 (1)	Sn—C(31)—C(32)	120.9 (4)
Br(2)—Sn—C(11)	88.3 (2)	Sn—C(31)—C(36)	121.0 (4)
Cation: N—C and C—C bond lengths, and C—N—C and N—C—C angles range from 1.502 (9) to 1.531 (9) [mean 1.519 (9)], 1.49 (1) to 1.56 (1) [mean 1.530 (1)], 104.4 (5) to 112.1 (5) [mean 109.5 (5)], and 111.8 (7) to 115.4 (7) [mean 113.4 (7)] (major form) and from 1.46 (2) to 1.58 (2) [mean 1.54 (2)], 1.52 (3) to 1.62 (3) [mean 1.57 (3)], 103.6 (11) to 118.2 (11) [mean 109.4 (11)], and 106.5 (14) to 113.3 (14) [mean 109.3 (14)] (minor form) respectively.			
Compound (2)			
Anion			
Sn—Br(1)	2.7820 (9)	S(1)—C(14)	1.765 (7)
Sn—Br(2)	2.7309 (9)	S(1)—C(17)	1.788 (9)
Sn—C(11)	2.148 (7)	S(2)—C(24)	1.760 (6)
Sn—C(21)	2.143 (6)	S(2)—C(27)	1.79 (1)
Sn—C(31)	2.145 (6)	S(3)—C(34)	1.761 (8)
		S(3)—C(37)	1.77 (1)
C(11)—Sn—C(21)	131.6 (2)	Sn—C(21)—C(26)	119.1 (5)
C(11)—Sn—C(31)	113.8 (2)	Sn—C(31)—C(32)	120.4 (5)
C(21)—Sn—C(31)	114.5 (2)	Sn—C(31)—C(36)	121.6 (5)
Br(1)—Sn—Br(2)	175.37 (3)	S(1)—C(14)—C(13)	122.6 (5)
Br(1)—Sn—C(11)	86.0 (2)	S(1)—C(14)—C(15)	118.1 (5)
Br(1)—Sn—C(21)	89.4 (2)	C(14)—S(1)—C(17)	103.1 (4)
Br(1)—Sn—C(31)	92.1 (2)	S(2)—C(24)—C(23)	124.5 (5)
Br(2)—Sn—C(11)	90.1 (2)	S(2)—C(24)—C(25)	116.4 (5)
Br(2)—Sn—C(21)	91.4 (2)	C(24)—S(2)—C(27)	103.6 (5)
Br(2)—Sn—C(31)	91.7 (2)	S(3)—C(34)—C(33)	123.3 (6)
Sn—C(11)—C(12)	122.8 (5)	S(3)—C(34)—C(35)	116.9 (6)
Sn—C(11)—C(16)	118.2 (5)	C(34)—S(3)—C(37)	104.2 (4)
Sn—C(21)—C(22)	122.1 (5)		
Cation: N—C and C—C bond lengths, and C—N—C and N—C—C angles range from 1.49 (1) to 1.53 (1) [mean 1.52 (1)], 1.49 (2) to 1.60 (2) [mean 1.54 (2)], 105.1 (6) to 113.3 (6) [mean 109.5 (6)], and 112.0 (8) to 115.6 (8) [mean 114.3 (8)] (major form) and from 1.42 (4) to 1.64 (3) [mean 1.53 (4)], 1.55 (5) to 1.60 (5) [mean 1.57 (5)], 101 (2) to 116 (2) [mean: 109 (2)], and 107 (2) to 121 (2) [mean 112 (2)] (minor form) respectively.			

number of cation M environments available. Equation (II) has a particular advantage over (I) because B , unlike N , varies very little from one MX pair to another, meaning that one value of B [0.37 (5)] could be used for most of the MX systems, leaving only r_0 to be determined for each given atom pair (Brown & Altmatt, 1985).

An alternative approach (Wharf, Cuenca & Onyszchuk, 1984) is to specify two model systems with defined bond valences and known bond lengths to determine N or B for each MX atom pair. For the

comparison made here, we have chosen $\text{Sn}X_4$ ($\text{Sn}-X$, $s = 1.00$) and $\text{Ph}_3\text{Sn}X_2^-$ (axial $\text{Sn}-X$, $s = 0.50$) with $r_{\text{Sn}X}$ values ($X = \text{Cl}$) of 2.28 and 2.54 Å or ($X = \text{Br}$) 2.44 and 2.77 Å respectively. Substituting these data in (I) or (II) respectively gives $N = 5.44$ and $B = 0.45$ with $r_0 = 2.28$ Å for the SnCl system and $N = 5.46$ and $B = 0.48$ with $r_0 = 2.44$ Å for the SnBr system. Since N or B are essentially the same for the SnCl and SnBr atom pairs, assuming these parameters are the same for both systems gives the relations,

$$r_{\text{SnBr}} = Ar_{\text{SnCl}} [A = r_{0(\text{SnBr})}/r_{0(\text{SnCl})} = 1.07] \quad (\text{III})$$

and

$$r_{\text{SnBr}} = r_{\text{SnCl}} + C [C = r_{0(\text{SnBr})} - r_{0(\text{SnCl})} = 0.16 \text{ \AA}] \quad (\text{IV})$$

from (I) and (II) respectively. Since (III) is clearly more consistent with the data presented in Fig. 3 and

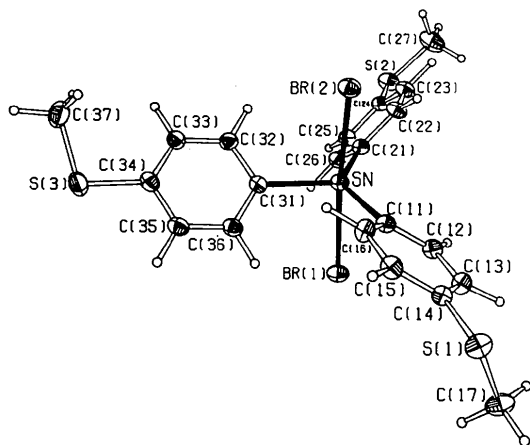


Fig. 1. The anion of $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{p}\text{-CH}_3\text{SC}_6\text{H}_4)_3\text{SnBr}_2]$.

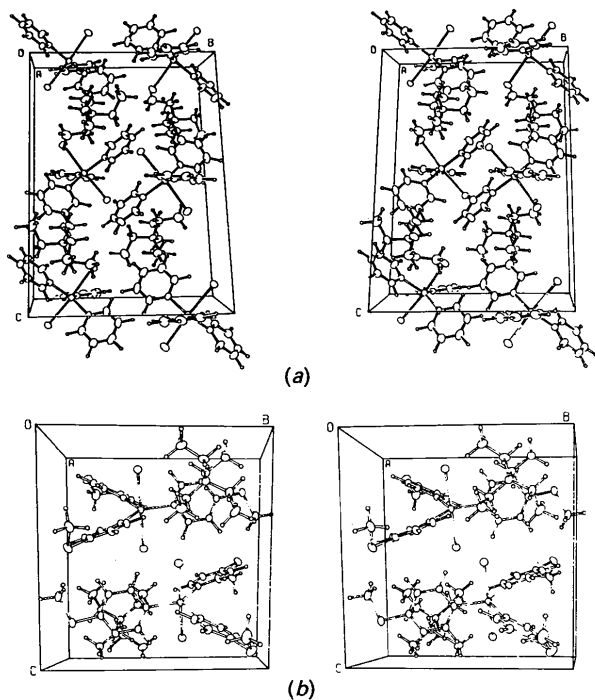


Fig. 2. Stereoview of the unit cell for (a) $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{C}_6\text{H}_5)_3\text{SnBr}_2]$, and (b) $[(\text{C}_2\text{H}_5)_4\text{N}][(\text{p}\text{-CH}_3\text{SC}_6\text{H}_4)_3\text{SnBr}_2]$.

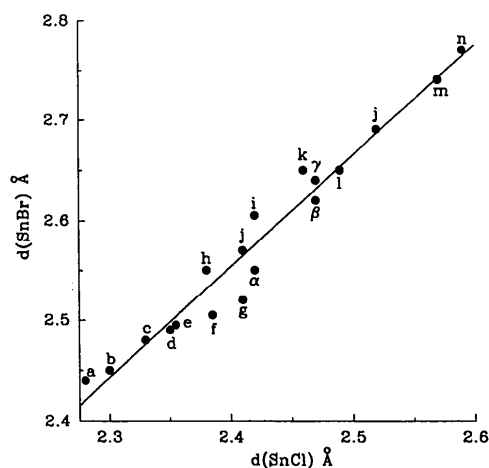


Fig. 3. A comparison of bond lengths, $d(\text{Sn}-\text{Br})$ with $d(\text{Sn}-\text{Cl})$; data are electron diffraction (ED) gas-phase or averaged X-ray diffraction solid-state values. (a) $\text{Sn}X_4$ (ED) ($X = \text{Cl}$; Fujü & Kimura, 1970) ($X = \text{Br}$; Lister & Sutton, 1941a), (b) $\text{MeSn}X_3$ (ED) ($X = \text{Cl}$; Beagley, McAloon & Freeman, 1974) ($X = \text{Br}$; Skinner & Sutton, 1944), (c) $\text{Me}_2\text{Sn}X_2$ (ED) ($X = \text{Cl}$; Fujü & Kimura, 1971) ($X = \text{Br}$; Skinner & Sutton, 1944), (d) $\text{Me}_3\text{Sn}X$ (ED) ($X = \text{Cl}$; Beagley, McAloon & Freeman, 1974) ($X = \text{Br}$; Skinner & Sutton, 1944), (e) $\text{Ph}_3\text{Sn}X$ ($X = \text{Cl}$; Tse, Lee & Gabe, 1986) ($X = \text{Br}$; Preut & Huber, 1979), (f) $\text{Et}_2\text{Sn}X_2$ (Alcock & Sawyer, 1977), (g) $\text{Cy}_3\text{Sn}X$ ($X = \text{Cl}$; Calogero *et al.*, 1979) ($X = \text{Br}$; Calogero *et al.*, 1981), (h) $\text{Sn}X_4 \cdot 2\text{hmpa}$ (Aslanov, Ionov, Attiya, Permin & Petrosyan, 1977), (i) $\text{Sn}X_2^-$ (Sowa, Druk & Kutoglu, 1981) ($X = \text{Br}$; Paseshnitchenko, Aslanov, Jathsenko & Medvedev, 1985), (j) EtSnCl_2^- , $n\text{-BuSnBr}_2^-$ (Paseshnitchenko *et al.*, 1985); (k) $\text{MeSn}X_3 \cdot 2\text{hmpa}$, equatorial bonds (Aslanov *et al.*, 1977), (l) $\text{Ph}_3\text{SnCl} \cdot \text{Ph}_2\text{P}(\text{O})\text{C}_2\text{H}_5\text{P}(\text{O})\text{Ph}_2$ (Pelizzi & Pelizzi, 1980), (3- $\text{C}_4\text{H}_9\text{S}$) $_3\text{SnBr} \cdot \text{Ph}_3\text{Po}$ (Allen, Derbyshire, Nowell & Brooks, 1984), (m) $\text{Me}_2\text{Sn}X_2 \cdot 2\text{hmpa}$ (Aslanov *et al.*, 1977), (n) $\text{Ph}_3\text{Sn}X_2$ ($X = \text{Cl}$; Harrison *et al.*, 1978) ($X = \text{Br}$; this work); (α) $\text{Sn}X_2$ (ED) (Lister & Sutton, 1941b), (β) $\text{Sn}X_3^-$ (Müller, Mronga, Schumacher & Dehnicke, 1982), (γ) $\text{Sn}X_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ ($X = \text{Cl}$; Hough & Nicholson, 1976) ($X = \text{Br}$; Andrews, Donaldson, Hough & Nicholson, 1977). The line is $d(\text{Sn}-\text{Br}) = 1.107 (\pm 0.057) d(\text{Sn}-\text{Cl}) - 0.104 (\pm 0.139)$ ($r = 0.979$).

the trend for the line to have zero intercept, we suggest that equation (I), from which (III) is derived, is the more appropriate expression for determining bond valence values from bond length data.

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N(8)-Coordinating Allopurinol: Structure of Bis(allopurinol)triqua(sulfato)copper(II) Hydrate

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Abstract. $[\text{Cu}(\text{SO}_4)(\text{C}_5\text{H}_4\text{N}_4\text{O})_2(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$, $M_r = 503.89$, triclinic, $P\bar{1}$, $a = 8.286$ (2), $b = 9.836$ (5), $c = 10.860$ (3) Å, $\alpha = 96.68$ (4), $\beta = 91.95$ (2), $\gamma = 94.41$ (3)°, $V = 875.7$ (10) Å³, $Z = 2$, $D_x = 1.911$, $D_m = 1.92$ g cm⁻³, $\mu = 14.36$ cm⁻¹, $F(000) = 514$, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $T = 296$ K. The

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