Journal of Organometallic Chemistry, 289 (1985) 271–279
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ORGANOTIN BIOCIDES

V *. THE STRUCTURE OF DICYCLOHEXYLTIN DICHLORIDE

K.C. MOLLOY **,
School of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY (Great Britain)

K. QUILL,
School of Chemical Sciences, National Institute for Higher Education, Glasnevin, Dublin 9 (Ireland)

and I.W. NOWELL
Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB (Great Britain)

(Received January 2nd, 1985)

Summary

The crystal and molecular structure of dicyclohexyltin dichloride has been solved by heavy atom methods in conjunction with least-squares data collected on a two-circle automatic diffractometer. Crystals are orthorhombic, space group *Pbcm*, cell dimensions *a* 6.671(5), *b* 9.445(6), *c* 24.203(12) Å, *U* 1525.0 Å^3 and $Z = 4$. The structure was refined using 1527 reflections to final discrepancy factors of $R = 0.047$ and $R' = 0.058$. The local geometry at tin is a severely distorted *trans*-R_2SnCl_4 octahedron. Chlorine atoms serve as bridging groups to link sub-units into a one dimensional polymer along *b*.

Introduction

Our interest in the structural chemistry of organotin compounds which either possess [1] or have the potential to exhibit [2] biocidal properties has caused us to focus attention on derivatives of phenyl- and cyclohexyl-substituted tin. Compounds of these two classes are highly active as fungicides [3] and acaricides [4,5] respectively, while showing low mammalian toxicity, and $(C_6H_5)_3SnO_2CCH_3$, $(C_6H_5)_3$-SnOH, $(C_6H_{11})_3SnOH$ and $(C_6H_{11})_3$Sn-1,2,4-triazole are all commercially exploited agrochemicals. Surprisingly, the structural chemistry of these two types of organotin,

---

* For part IV see ref. 2.

** Address for correspondence.

0022-328X/85/$03.30

and particularly the cyclohexyltins, is substantially less well evaluated than that of their methyltin counterparts [6], and the unpredictable effects that the bulky cyclohexyl groups will render on the stereochemistry of the metal make extrapolation of this latter data at best tentative.

The organotin halides are of importance both as structural models for other more complex systems, and also as the starting point for most synthetic work in the field. To complement existing reports on the complete range of tricyclohexyltin halides [7,8], we herein report our findings on the structure of dicyclohexyltin dichloride, and correlate these results with our previous inferences based upon variable temperature Mössbauer spectroscopic data [9].

Experimental

Dicyclohexyltin dichloride was prepared by a redistribution reaction between equimolar quantities of tetracyclohexyltin and stannic chloride. Crystals suitable for X-ray crystallography were obtained by slow evaporation of an ether solution. Analysis: Found, C, 40.36; H, 6.55; $C_{12}H_{22}Cl_2Sn$ calcd.: C, 40.50; H, 6.23%. M.p. 88–89°C, lit. [10] 88–89°C.

Crystal data

$C_{12}H_{22}Cl_2Sn$, $M = 355.9$, orthorhombic *Pbcm*, *a* 6.671(5), *b* 9.445(6), *c* 24.203(12) Å, *U* 1525.0 Å^3, $Z = 4$, D_c 1.55 Mg m^{-3}, μ(Mo-K_α) 18.4 mm^{-1}, *F*(000) 712.

Data collection and reduction

A crystal of approximate dimensions 0.42 × 0.35 × 0.24 mm was used for data collection. 1722 unique reflections were collected on a Stöe Stadi-2 two circle diffractometer, of which 1527 were considered observed [$I \geqslant 3\sigma(I)$] and used for subsequent analysis. Corrections were made for Lorentz and polarisation effects; no absorption corrections were included due to the low μ(Mo-K_α) coefficient.

Structure determination and refinement

Structure analysis was initially conducted in the non-centrosymmetric space

TABLE 1

FRACTIONAL POSITIONAL PARAMETERS (×10^5 for Sn, otherwise ×10^4) WITH e.s.d.'s IN PARENTHESES

Atom	*x*	*y*	*z*
Sn	7507(6)	14109(4)	25000
Cl(1)	2404(2)	3676(2)	2500
Cl(2)	−2522(2)	2391(2)	2500
C(11)	1388(7)	651(5)	3319(2)
C(12)	193(13)	1483(8)	3753(3)
C(13)	631(2)	911(4)	4336(3)
C(14)	2889(13)	874(10)	4458(3)
C(15)	3991(9)	73(1)	4033(3)
C(16)	3618(8)	595(7)	3447(2)

TABLE 2

BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d.'s IN PARENTHESES [a]

Bond distances			
Sn–Cl(1)	2.407(2)	C(14)–(15)	1.473(11)
Sn–Cl(2)	2.371(1)	C(15)–C(16)	1.523(8)
Sn–Cl(1′)	3.332(2)	C(16)–C(11)	1.520(7)
Sn–Cl(2′)	3.976(1)		
Sn–C(11)	2.151(4)		
C(11)–C(12)	1.535(7)		
C(12)–C(13)	1.540(10)		
C(13)–C(14)	1.535(10)		
Bond angles			
Cl(1)–Sn–Cl(1′)	168.1(1)	Cl(2′)–Sn–Cl(1)	135.5(1)
Cl(1)–Sn–Cl(2)	94.3(1)	Cl(2′)–Sn–Cl(2)	130.3(1)
Cl(1)–Sn–C(11)	101.9(1)	Cl(2′)–Sn–Cl(1′)	56.5(1)
Cl(2)–Sn–Cl(1′)	73.8(1)	Cl(2′)–Sn–C(11)	67.8(1)
Cl(2)–Sn–C(11)	108.2(1)	C(11)–Sn–C(11′)	134.4(2)
Cl(1′)–Sn–C(11)	82.3(1)		
Sn–C(11)–C(12)	110.9(3)		
Sn–C(11)–C(16)	113.1(3)		
C(12)–C(11)–C(16)	112.8(5)		
C(11)–C(12)–C(13)	110.4(5)		
C(12)–C(13)–C(14)	111.7(6)		
C(13)–C(14)–C(15)	111.6(7)		
C(14)–C(15)–C(16)	113.7(6)		
C(15)–C(16)–C(11)	111.2(5)		

[a] Primed atoms are related to their unprimed counterparts (x,y,z) by: $(')-x,\ y-0.5,\ z$; $('')x,\ y,\ 0.5-z$.

group $Pca2_1$, [a 9.445(6), b 6.671(5), c 24.203(12) Å]. The structure was solved using conventional Patterson and Fourier methods to final value of $R = 0.046$ and $R' = 0.054$. The presence of an apparent mirror plane perpendicular to c through the Sn and Cl atoms (relating the two cyclohexyl groups) led us to impose exact mirror symmetry and to refine the structure in the centrosymmetric space group $Pbcm$ ($Z = 4$). Although the final R values were marginally higher ($R = 0.047$, $R' = 0.058$), this is to be expected given that imposition of exact mirror symmetry reduces the number of independent variables. Refinement in $Pbcm$ did lead to a significant improvement in the bond distances and angles associated with the cyclohexyl group and hence we feel the centrosymmetric space group to be the more appropriate. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were localised in ideal positions and given a common isotropic temperature factor which finally refined to U 0.131(9) Å^2. Scattering factors were calculated using an analytical expression [11] and the weighting scheme employed was $w = 1.0000/[\sigma^2(F_0) + 0.007(F_0)^2]$.

Final positional parameters for the non-hydrogen atoms are given in Table 1, bond distances and angles in Table 2. The asymmetric unit with atomic labelling is shown in Fig. 1. Tables of hydrogen atom positions, thermal parameters and structure factors are available upon request from the authors (I.W.N.).

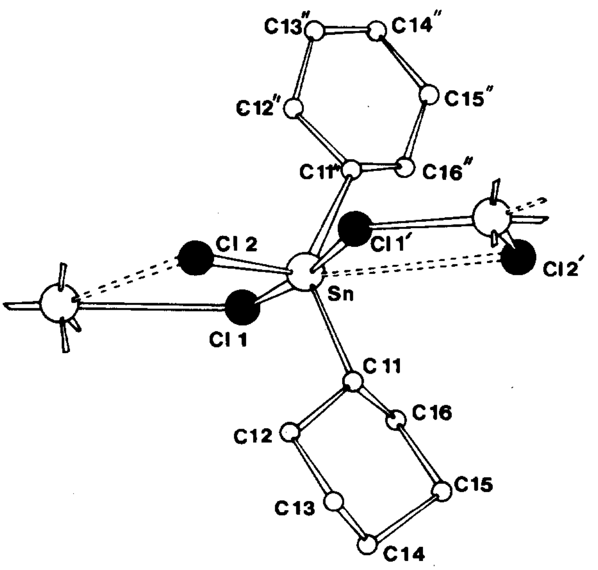

Fig. 1. Part of the polymeric structure of $(C_6H_{11})_2SnCl_2$, showing atomic labelling. Hydrogen atoms have been omitted for clarity. Primed and double-primed atoms are related to their unprimed counterparts by the symmetry operations $-x$, $y-0.5$, z and x, y, $0.5-z$ respectively.

Discussion

The structure of dicyclohexyltin dichloride consists of sub-units intermediate in geometry between *cis*-R_2SnCl_3 and *trans*-R_2SnCl_4 linked by chlorine bridges into a one-dimensional polymer. The complexities of this arrangement will be considered in two parts: the intramolecular geometry about tin and the spacial distribution of monomers from which the polymer is constructed. The local geometry about tin can be best understood in terms of a two-step reaction between a tetrahedral R_2SnCl_2 and two chlorine atoms (Fig. 2). The first step involves intermolecular approach of Cl(1′) towards the C(11),C(11″),Cl(2)-triangular face of the tetrahedron, to produce a *cis*-R_2SnCl_3 trigonal bipyramidal (tbp) geometry at tin with Cl(1) and Cl(1′) in the axial positions. The significant results in terms of bond angles about tin are the closing of those angles between Cl(1) and each of C(11), C(11″) and Cl(2) from 109° 28′ towards the ideal tbp value of 90° [101.9(1), 101.9(1) and 94.3(1)°, respectively]. The corresponding angles involving Cl(1′) are all less than 90° [82.3(1), 82.3(1), 73.8(1)°], and the magnitude of the Cl(1′): → Sn interaction, while relatively weak [3.332(2) Å], is clearly significant. Indeed, in comparison with Sn–Cl bond lengths in other diorganotin dichloride structures [12–15, Table 3], the intra- and inter-molecular Sn–Cl(1′) bonds [2.407(2), 3.332(2) Å] are the longest and shortest respectively of their types yet reported. Only in solid $(CH_3)_3SnCl$ are the two analogous bonds more similar in length [2.430(2), 3.269(2) Å] [16]. Further comparison for this primary mode for coordination expansion at tin in $(C_6H_{11})_2SnCl_2$ can be made with $(C_6H_{11})_3SnCl$, in which the stereochemical arrangement of tin and chlorine atoms along *c* is suggestive of lattice association [7]. The two Sn–Cl bond lengths here [2.407(5), 3.30 Å] are almost identical with those in the title compound. In each of these organotin chlorides, the arrangement of bond lengths (and angles, vide supra)

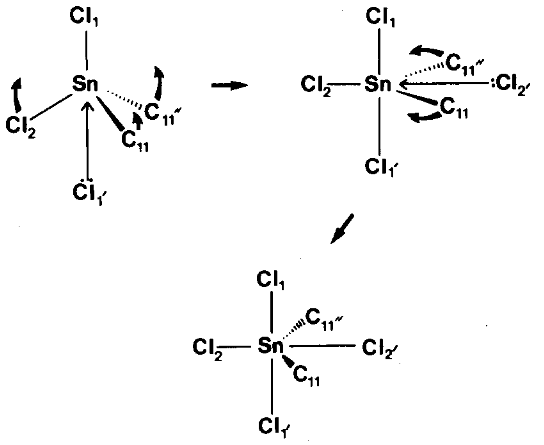

Fig. 2. The formation of the coordination sphere about tin, depicted schematically in terms of the sequential approach of chlorine atoms to an initially tetrahedral $(C_6H_{11})_2SnCl_2$ molecule.

is totally consistent with a re-distribution of the chlorine bonding electrons between two, rather than one, bonds to tin and the intramolecular Sn–Cl bond is always longer than in tetrahedral $(C_6H_5)_3SnCl$ (2.32 Å; [17]).

The second intermolecular tin–chlorine interaction, step two of the reaction shown in Fig. 2, is markedly weaker and more subjective in its significance. Cl(2′) approaches tin in the plane of the metal and the three halogen atoms, from below the equatorial plane of the tbp and between the two carbon atoms C(11) and C(11″). The final intermolecular Sn–Cl(2′) distance is long [3.976(1) Å] and in excess of the

TABLE 3

COMPARATIVE STRUCTURAL [a] DATA FOR ORGANOTIN CHLORIDES

Compound	Sn–Cl (Å)	Sn···Cl (Å)	C–Sn–C (°)	Structure [b] type	Ref.
$(C_6H_{11})_2SnCl_2$	2.407(2)	3.332(2)	134.4(2)	3c	this work
	2.371(1)	3.976(1)			
$(CH_3)_2SnCl_2$	2.40(4)	3.54(5)	123.5(4.5)	3d	12
$(C_2H_5)_2SnCl_2$	2.385(3)	3.483(4)	134.0(6)	3d	13
	2.384(3)	3.440(4)			
$(ClCH_2)_2SnCl_2$	2.37(2)	3.71	135.0(6)	3c	14
$(C_6H_5)_2SnCl_2$	2.336 [c]	3.77	125.5 [c]	3a [d]	14, 15
	2.355 [c]				
$(CH_3)_3SnCl$	2.351(7) [e]		114.9(1.6)	tetrahedral	23
	2.430(2)	3.269(2)	117.1 [f]	tbp	16
$(C_6H_5)_3SnCl$	2.32		112.3	tetrahedral	17
$(C_6H_{11})_3SnCl$	2.407(5)	3.30	115.0(6),		
			119.0(5)	tbp	7

[a] X-ray diffraction unless stated otherwise. [b] See Fig. 3 for representations of 3a–d. [c] Mean value for two molecules in the asymmetric unit. [d] See also ref. 19. [e] Gas phase electron diffraction data. [f] Mean value of the three independent C–Sn–C angles.

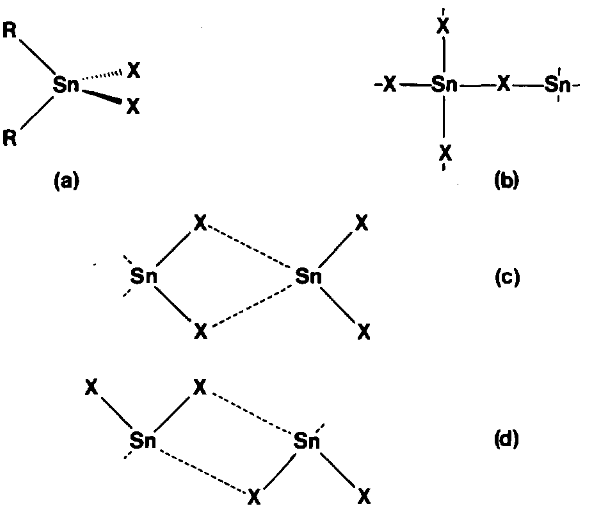

Fig. 3. Structural variations in diorganotin dihalide chemistry: (a) tetrahedral monomer, (b) 2-d polymer, (c) 1-d polymer with bridging/chelating chlorine atoms, and (d) 1-d polymer with purely bridging chlorine atoms. For each of structures (b)–(d), the R groups lying above and below the polymer plane have been omitted for clarity.

Van der Waals radii sum of 3.85 Å [18] generally taken as the limit of meaningful electronic interactions between these atom types. The proximity of Cl(2′) to tin does however, manifest itself in angular distortions about that atom which do imply a real, albeit very weak interaction. The most relevant of these angular changes occurs at C(11)–Sn–C(11″) which is opened to 134.4(2)°, and C(11)–Sn–Cl(2), C(11″)–Sn–Cl(2) which close to 108.2(1)°, all three of which would be 120° in a regular tbp geometry and all of which have altered in a manner consistent with the formation of a distorted six-coordinate, octahedral *trans*-R_2SnCl_4 geometry at tin in which the idealized angles would be 180 and 90° for the each of the two angular types. It is notable that in $(C_2H_5)_2SnI_2$ the intermolecular Sn–I interaction at 4.284(5) Å is also in excess of the sum of the tin and iodine Van der Waals radii (4.08 Å [18]), but still results in a C–Sn–C of 130.2(11)° [13]. Accordingly, we prefer to describe the structure of $(C_6H_{11})_2SnCl_2$ in terms of distortions of an octahedral rather than tbp geometry, a distinction which has chemical and not merely semantic significance.

The second structural feature of interest is the stereochemical relationship of bonds which give rise to polymer formation. The various known senarios on this theme in diorganotin dihalide chemistry are depicted in Fig. 3, while the nature of the polymer architecture for $(C_6H_{11})_2SnCl_2$ can be seen in the simplified diagram of cell contents in Fig. 4. In addition to a tetrahedral monomer such as $(C_6H_5)_2SnCl_2$ [19], three types of polymer are known which embody a *trans*-R_2SnX_4 geometry at tin. In the unique case of $(CH_3)_2SnF_2$ (Fig. 3b), all the Sn–F bonds are equivalent, the polymer is two-dimensional, and the Sn–F–Sn residue is linear [20], a situation that we have termed a "Class 1" type polymer in as much as the bridging is as rigid as possible [9]. Two other arrangements are known, which incorporate two distinct types of Sn–X bond, and where the spacial arrangement of the Sn–X–Sn unit is zig-zag or "Class 2" (less rigid) type: the halogens which form the longer, bridging

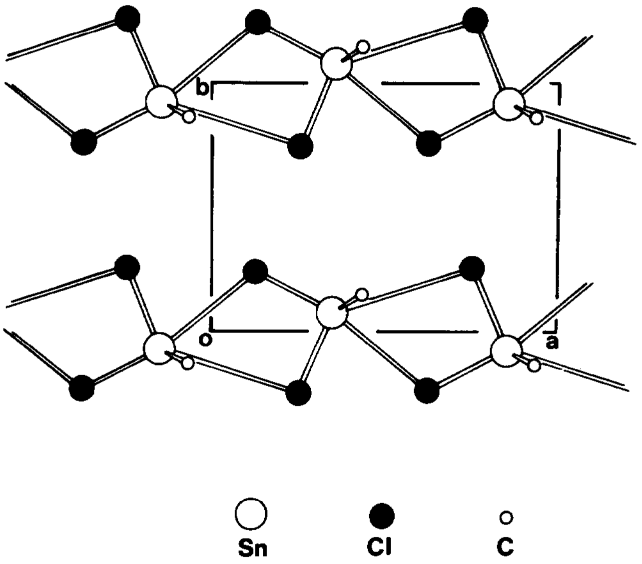

Fig. 4. Unit cell viewed along *c*, showing the nature of polymer propogation. Only the α-carbon of the C_6H_{11} ring above the polymer plane has been included for clarity.

bonds to tin can be from the same molecule (Fig. 3c; e.g. $(C_2H_5)_2SnI_2$ [13]) or different molecules (Fig. 3d; e.g. $(CH_3)_2SnCl_2$ [12]). The title compound adopts a 3(c) type structure with the Cl(1′)–Sn(1′)–Cl(2′) unit both bridging and chelating Sn(1), although the mode of chelation is markedly anisobidentate. While it would not have been possible to predict which of the two types of Class 2 polymer would be formed by dicyclohexyltin dichloride, we have previously indicated a preference for this Class of polymer rather than that of Class 1, based upon variable temperature Mössbauer spectroscopic studies [9].

Compounds such as $(C_6H_{11})_2SnCl_2$ are often used as models for correlating spectroscopic properties and structure. In the case of organotin chemistry in which Mössbauer spectroscopy plays a prominent role, two parameters – the quadrupole splitting (*QS*) and the temperature coefficient of the recoil free fraction ($a = -\mathrm{d}\ln f/\mathrm{d}T$) – are often cited and it is of interest to review the significance of these parameters within the context of the present structure.

The *QS* is a function of the electric field gradient at tin, and a model exists [21] which correlates this value with C–Sn–C in six-coordinate diorganotin compounds using a point charge approach:

$$|QS| = 4\{R\}[1 - 3\sin^2\theta\cos^2\theta]^{1/2}$$

where $\{R\}$ = partial quadrupole splitting for R (-1.03 for C_6H_{11} [22]) and C–Sn–C $= 2\theta$. On this basis, for an experimentally observed *QS* value of 3.40 mm s^{-1} [9], the calculated C–Sn–C is 139°, in good agreement will the observed value of 134.4(2)°, particularly in the light of the assumptions made in the model, namely that contributions to the *QS* are negligible for ligands other than *R*.

The temperature coefficient of the recoil-free fraction, *a*, is a measure of the rigidity of the lattice as experienced by the Mössbauer active atom, tin. In short, *a*

TABLE 4

VARIABLE TEMPERATURE MÖSSBAUER SPECTROSCOPIC DATA FOR SELECTED CYCLOHEXYLTIN HALIDES [a]

Compound	$10^2\ a\ (K^{-1})$
$(C_6H_{11})_3SnI$ [b]	1.60
$(C_6H_{11})_3SnBr$ [b]	1.64
$(C_6H_{11})_3SnCl$	1.40
$(C_6H_{11})_2SnCl_2$	1.13
$(C_6H_{11})_3SnF$	0.91

[a] Data taken from ref. 9 unless stated otherwise. [b] Ref. 8.

diminishes as the lattice stiffens, usually with the onset of polymerisation in one or more directions. Data for representative cyclohexyltin compounds are given in Table 4. By comparison, the tin is held in the lattice with rigidity similar to the associated (Class 1) halides $(C_6H_{11})_3SnX$ (X = Cl, F), and more tightly so than the non-interacting lattices of the corresponding bromide and iodide [7,8]. However, the bridging bonds in tricyclohexyltin fluoride and chloride are relatively long, so it seems reasonable to assume that if $(C_6H_{11})_2SnCl_2$ were also a polymer of Class 1 type [cf. $(CH_3)_2SnF_2$] it would show a substantially lower value for a than either triorganotin halide, even if one or both of the bridging bonds is weak. On this basis, we have previously suggested the likely structure for the title compound to be a polymer of Class 2 type (zig-zag), a proposal which is now substantiated by the present work.

Acknowledgements

We thank the National Board for Science and Technology (Ireland) for financial support (to K.C.M.) and the S.E.R.C. (U.K.) for equipments grants (to I.W.N.).

References

1 K.C. Molloy, T.G. Purcell, K. Quill and I.W. Nowell, J. Organomet. Chem., 267 (1984) 237.
2 For Part IV of this series: K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann and J.J. Zuckerman, submitted for publication.
3 A.K. Sijpesteijn, J.G.A. Luijten and G.J.M. van der Kerk, in D.C. Torgeson (Ed.), 'Fungicides, An Advanced Treatise', Academic Press, New York, 2 (1969) 331.
4 C.J. Evans, Tin and its Uses, 86 (1970) 7.
5 C.J. Evans, Tin and its Uses, 110 (1976) 6.
6 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.
7 S. Calogero, P. Ganis, V. Peruzzo and G. Tagliavini, J. Organomet. Chem., 179 (1979) 145.
8 S. Calogero, P. Ganis, V. Peruzzo, G. Tagliavini and G. Valle, J. Organomet. Chem., 220 (1981) 11.
9 K.C. Molloy and K. Quill, J. Chem. Soc., Dalton Trans., in press.
10 H.G. Langer, Tetrahedron Lett., (1967) 43.
11 International Tables for X-ray Crystallography, Vol. IV, 1974, Table 2.2B, Kynoch Press, Birmingham (Great Britain).
12 A.G. Davies, H.J. Milledge, D.C. Puxley and P.J. Smith, J. Chem. Soc. A, (1970) 2862.
13 N.W. Alcock and J.F. Sawyer, J. Chem. Soc., Dalton Trans., (1977) 1090.
14 N.G. Bokii, Yu.T. Struchkov and A.K. Prokofiev, J. Struct. Chem., 13 (1972) 619.
15 P.T. Greene and R.F. Bryan, J. Chem. Soc. A, (1971) 2549.
16 J.L. Lefferts, K.C. Molloy, M.B. Hossain, D. van der Helm and J.J. Zuckerman, J. Organomet. Chem., 240 (1982) 349.

17 N.G. Bokii, G.N. Zakharova and Yu.T. Struchkov, J. Struct. Chem., 11 (1970) 828.

18 A. Bondi, J. Phys. Chem., 68 (1964) 441.

19 There is disagreement between authors as to whether this molecule is a four-coordinate monomer [15] or a tetramer involving two, central, six-coordinate and two, terminal, four-coordinate tin atoms [14]. However, in neither description is the tin part of an extended polymer chain.

20 E.O. Schlemper and W.C. Hamilton, Inorg. Chem., 5 (1966) 995.

21 T.K. Sham and G.M. Bancroft, Inorg. Chem., 14 (1975) 2281.

22 M.G. Clark, A.G. Maddock and R.H. Platt, J. Chem. Soc., Dalton Trans., (1972) 210.

23 R.F. Zahrobsky, J. Solid State Chem., 8 (1973) 101.