Inorg. Chem. **2003**, *42*, 4141–4146

Inorganic Chemistry
Article

The Structure of Tri(cyclohexyl)tin Chloride between 108 and 298 K: A Compound in Which Molecular Dimensions Vary with Temperature

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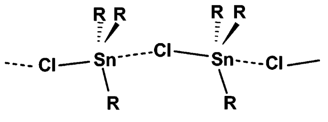
Received December 16, 2002

Care is necessary when relating physical data obtained at one temperature on compounds showing significant intermolecular interactions to X-ray data obtained at other temperatures. This is revealed by the determination of the structure of tri(cyclohexyl)tin chloride at nine different temperatures between 108 and 298 K. In the crystal, the molecules pack in chains parallel to the *c* axis with the Sn and Cl atoms close to the plane, with $y = 0.25$. At low temperature, successive molecules in the chain are related by the glide plane in space group $P2_1/c$, and there is significant intermolecular interaction. As the temperature is raised, the $Cy_3SnCl\cdots Sn$ interactions weaken and the intramolecular Sn–Cl bonds strengthen. At about 248 K, there is an order–disorder transition to space group $P2_1/m$ with the *c* axis halved, and at room temperature the structure is best described as comprising discrete molecules, as previously reported. Thus, some of the molecular dimensions, in particular the Sn–Cl bond lengths, are not constant but are functions of temperature.

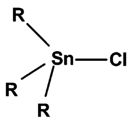
Introduction

Thousands of X-ray structures of organometallic compounds are determined each year, and many of the data are collected from crystals held at low temperatures. There are two main reasons for this practice. First, coating a crystal with oil and then freezing it is the easiest way to deal with air-sensitive compounds, and normally the crystal is completely stabilized during data collection. Second, data sets measured at low temperature give more accurate determinations of molecular structure. It is assumed that, as the crystal cools, the molecules vibrate less and move more closely together and that the internal geometry of the molecule does not significantly change.

This assumption may, however, not be valid for compounds that contain atoms that can increase their coordination by formation of secondary bonds to atoms in adjacent molecules.[1] These include atoms with incomplete valence shells and those that can be hypervalent, i.e., that can form more than four electron-pair bonds.[2] The trialkyltin chlorides R_3SnCl form one group of such compounds. Their structures have been classified into those that contain intermolecular $Sn\cdots Cl$ interactions (Type A) and those in which the molecules are discrete (Type B).[3,4]



A



B

The best-established examples of the first category are the trimethyl (**1a**)[5] and tribenzyl (**1b**)[6] derivatives. The second category comprises the trialkyl compounds with bulky groups R, e.g., $(Me_3Si)_2CH$ (**2a**),[7] $PhMe_2CCH_2$ (**2b**), and $PhMe_2SiCH_2$ (**2c**),[8] and triaryl derivatives with R = Ph (**3a**),[9–11]

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10.1021/ic026272f CCC: $25.00

Table 1. Crystal Data for Cy_3SnCl (**1c**) at Various Temperatures

temp / K	298	273	248	223	198	173	148	123	108
formula	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$	$C_{18}H_{33}ClSn$
mol wt	403.58	403.58	403.58	403.58	403.58	403.58	403.58	403.58	403.58
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a / Å	10.5453(4)	10.5668(4)	10.6230(4)	10.6523(3)	10.6669(3)	10.7651(3)	10.7814(3)	10.7818(3)	10.7797(4)
b / Å	17.1991(7)	17.1827(5)	17.0754(6)	17.0131(4)	16.9776(4)	16.9704(4)	16.9696(5)	16.9636(4)	16.9558(5)
c / Å	5.7130(2)	5.6769(2)	5.6281(2)	11.1760(3)	11.1303(3)	11.0152(3)	10.9668(3)	10.9411(3)	10.9191(4)
β / deg	107.392(2)	107.852(2)	108.487(2)	108.945(1)	109.259(1)	110.941(1)	111.475(1)	111.671(1)	111.747(1)
V / Å^3	988.79(6)	981.10(6)	968.21(6)	1915.70(9)	1902.88(9)	1879.43(9)	1867.15(9)	1859.67(8)	1853.73(11)
Z	2	2	2	4	4	4	4	4	4
μ / cm^{-1}	1.42	1.43	1.45	1.47	1.48	1.49	1.50	1.51	1.51
D_{calc} /g·cm^{-3}	1.36	1.37	1.38	1.40	1.41	1.43	1.44	1.44	1.45
reflns measured	8850	8829	8913	17329	17184	16982	16322	16421	13895
reflns unique	2388	2403	2382	4547	4514	4474	4444	4420	4374
R_{int}	0.049	0.045	0.050	0.059	0.052	0.051	0.052	0.050	0.055
reflns with $I > 2\sigma(I)$	1488	1846	1788	3131	3230	3199	2910	3017	2859
R1 (for $I > 2\sigma(I)$)	0.055	0.051	0.051	0.041	0.040	0.033	0.031	0.029	0.033
wR2 (for all data)	0.164	0.145	0.137	0.091	0.091	0.071	0.068	0.061	0.075

C_6H_4X (X = m-Me (**3b**),[12] p-^{t}Bu (**3c**)[13] or m-OMe (**3d**)[14]) or 3,5-$C_6H_3Me_2$ (**3e**).[12]

Tri(cyclohexyl)tin choride Cy_3SnCl (**1c**) was considered to be a borderline case. The room-temperature structure was published in 1979.[15] The molecules in the crystal were found to stack in the same way as those in the trimethyl and tribenzyl compounds, but the intermolecular Sn···Cl distance (3.31 Å) was thought to be too long to be associated with tin hypervalency. The structure was therefore described as consisting of "discrete tetrahedral molecules".[15] Data in the CCDC include a comment about "inconsistencies in published and calculated bond lengths". There were large anisotropic thermal parameters, which were attributed to conformational disorder, and the published bond lengths and angles appear to have been taken from the last but one least-squares refinement cycle. The quadrupole splitting in the Mössbauer spectrum ($\Delta = 3.49$ mm s^{-1}) was greater than the usually accepted upper limit ($\Delta = 2.8-3.0$ mm s^{-1}) for four-coordination,[16,17] and the discrepancy was attributed to distortions of the bond angles at tin from the tetrahedral value.[15]

This prompted us to reexamine the structure of **1c**. Because the structure at 173 K was found to be significantly different from the structure reported at room temperature,[15] we went on to make a detailed study of how the molecular parameters change with temperature. We describe the results below and consider the possible general implications of our investigation.

Experimental Section

Tri(cyclohexyl)tin chloride forms fine needles elongated along the c axis. To grow a crystal for the detailed study described in this paper, we tried a variety of solvents and crystallization conditions, but most of the crystals were too thin or fragile. We finally obtained a satisfactory batch by slow crystallization from hexane at −20 °C. Data were collected from a piece ca. 0.1 mm long cut from a needle of cross section 0.1 × 0.1 mm^2. By use of monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), reflections were measured out to $\theta = 28°$ on a Nonius Kappa CCD diffractometer. With the crystal in a cold nitrogen gas stream, data sets were obtained at a range of temperatures from 298 to 108 K using a similar collection strategy and timing. Corrections for absorption were made semiempirically.[18] Structure solutions and refinements were by SHELX-97,[19] as incorporated in the package WINGX,[20] and the results are shown in Table 1. The molecular structure from data collected at 173 K is shown in Figure 1. The molecules have no crystallographically imposed symmetry, but the SnC_3Cl fragment has an approximate three-fold axis along the Sn−Cl bond. The packing diagram in projection down c is shown in Figure 2, and the molecules in a single chain are shown in Figure 3. The ORTEP drawings show 50% ellipsoids.[21]

At 298 K, the space group is clearly $P2_1/m$ with $Z = 2$. At 223 K, it is clearly $P2_1/c$ with $Z = 4$, and the length of the c axis is twice that at room temperature. Between these temperatures there is an order−disorder transition at about 248 K. The extra Bragg peaks corresponding to the larger cell are absent at 250 K and present at 240 K. They appear weakly at 248 K, and an extra data set was collected at this temperature on the basis of the larger cell. However, attempts to refine the structure as $P2_1/c$ simply converged to the averaged disordered structure of $P2_1/m$. Plots of the cell dimensions as a function of temperature (Figure 4) give no indication of a sudden transition.

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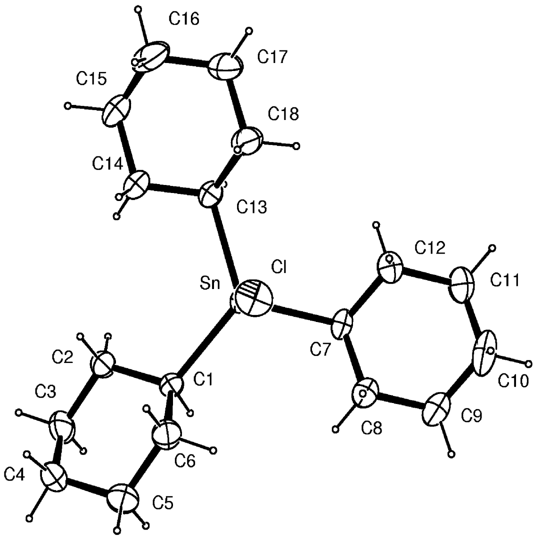

Figure 1. Molecular structure of Cy$_3$SnCl (**1c**) at 173 K.

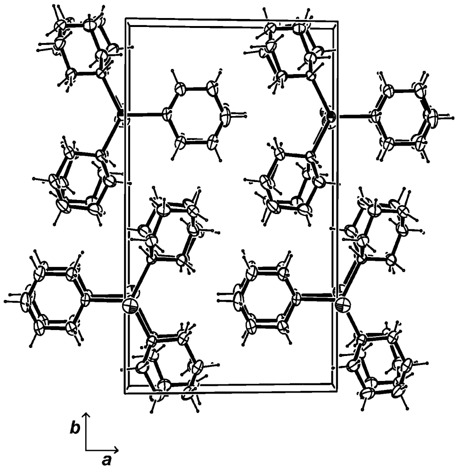

Figure 2. Packing diagram for **1c** at 173 K, viewed along *c*.

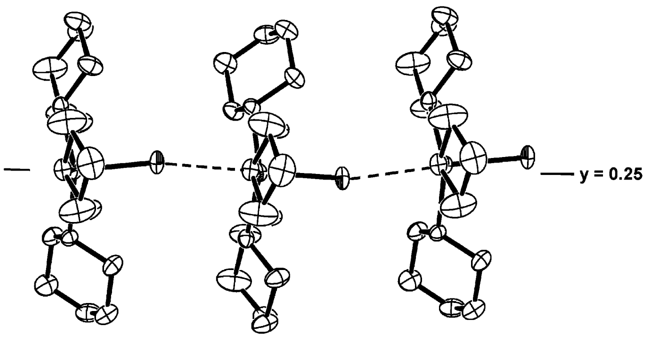

Figure 3. A single chain in **1c** at 173 K. Adjacent molecules are related by the *c* glide plane at $y = 0.25$.

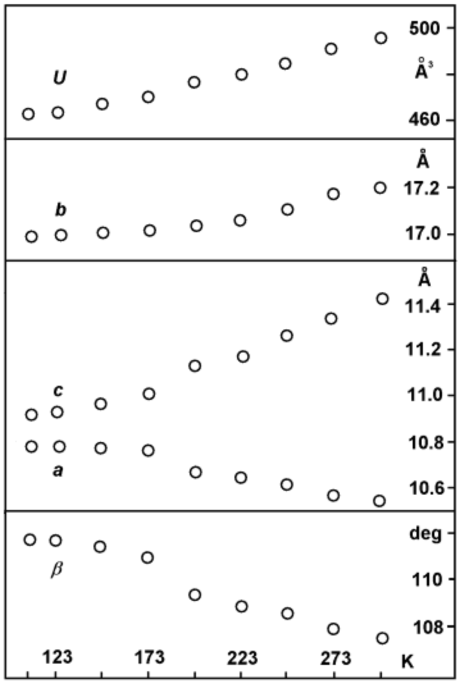

Figure 4. Variation of molecular volume *U* and cell dimensions *a*, *b*, *c*, and β of **1c** with temperature. The values of *c* are those for space group $P2_1/c$ and, for temperatures above 223 K, the values plotted are twice those measured in space group $P2_1/m$. Above 223 K, $U = 0.5V$ (Table 1); below 248 K, $U = 0.25V$.

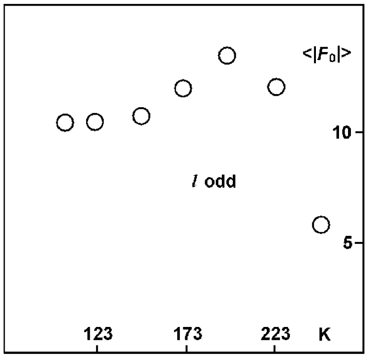

Figure 5. Variation of mean structure factor $\langle|F_0|\rangle$ with temperature for *l* odd.

For the $P2_1/m$ structure determinations, the unit cell was chosen to correspond to that of the $P2_1/c$ structure, i.e., one with the same directions for the *a* and *c* axes. This cell can be derived from that in the previously published structure by the transformation (1 0 1/0 1 0 / −1 0 0). In both space groups, the molecules are arranged in chains along the *c* axis (Figure 2). In the $P2_1/c$ structure, the lattice is arranged in an ordered fashion, with adjacent molecules within a particular chain being related by the *c* glide plane, as shown in Figure 3, with the tin atom close to the plane at $y = 0.25$. As a result, the mean value of the structure factor $\langle|F_0|\rangle$ is smaller when *l* is odd than when *l* is even. As the temperature is raised, the value of $\langle|F_0|\rangle$ for *l* even decreases in the usual way but the value for *l* odd (Figure 5) first increases slightly, as displacement of tin from the glide plane increases, and then falls sharply as the structure becomes disordered and the space group changes to $P2_1/m$. A mirror plane at $y = 0.25$ then appears to bisect the molecule, and the structure is determined as the average of the two molecular orientations related by the *c* glide in $P2_1/c$.

A trace from a 13.78 mg sample, heated at 20 K min^{-1}, was obtained by use of a Perkin-Elmer Diamond differential scanning calorimeter and appeared to show a step at 218 K, a minor peak at 238 K ($\Delta H = 0.24$ kJ mol^{-1}), and a major peak at 255 K ($\Delta H = 0.89$ kJ mol^{-1}) associated with the onset of disorder detected by crystallography. The minor peak may be associated with changes in ring conformation, for instance, but we cannot at present be more specific.

Table 2. Bond Lengths (Å) and Angles (deg) for Cy_3SnCl (**1c**) at Various Temperatures

temp / K	298	273	248	223	198	173	148	123	108
Sn−Cl	2.415(3)	2.416(3)	2.426(2)	2.4412(11)	2.4440(11)	2.4558(7)	2.4609(7)	2.4654(6)	2.4657(7)
Sn⋯Cl	3.298(3)	3.261(3)	3.202(2)	3.1884(11)	3.1638(11)	3.0777(8)	3.0398(7)	3.0201(6)	3.0077(7)
av Sn−C	2.151(10)	2.160(8)	2.159(6)	2.169(4)	2.166(4)	2.166(3)	2.172(3)	2.171(2)	2.169(3)
av C−Sn−C	116.9(5)	117.2(4)	117.4(2)	117.57(16)	117.63(16)	117.97(11)	118.10(10)	118.17(9)	118.20(10)
av C−Sn−Cl	100.3(3)	99.7(2)	99.5(2)	99.10(12)	98.90(11)	98.27(8)	97.93(7)	97.77(7)	97.73(7)

Results and Discussion

The Unit Cell. As expected, the molecular volume decreases from 494 Å^3 at 298 K to 463 Å^3 at 108 K (Figure 4), but this change results from a combination of several factors:

(a) The *b* and *c* axes (if we take the length of *c* for two cells in $P2_1/m$) decrease with decreasing temperature, with the larger decrease along the chain direction *c*;

(b) The *a* axis increases with decreasing temperature;

(c) The angle β increases from 107.4° at 298 K to 111.7° at 108 K;

(d) Although there are no abrupt changes in cell parameters, the plots against temperature deviate significantly from completely smooth curves. The principal reorganization of the molecular packing occurs between 170 and 200 K, about 50 K lower than the order−disorder transition revealed by the change in diffraction pattern.

The Accuracy of the Structure Determination. As the temperature decreases from 298 to 108 K, the weighted *R* factor wR2 (for all data) decreases markedly from 0.164 to 0.075, the conventional residual R1 (for $I > 2(I)$) decreases from 0.055 to 0.033, the esd on the Sn−Cl bond decreases from 0.003 to 0.0007 Å, and that for the Sn−C bond from 0.010 to 0.003 Å. Most of the increase in accuracy is achieved by 173 K, with only small gains at lower temperatures.

The Intra- and Intermolecular Dimensions. Selected bond lengths and angles are given in Table 2, and some of the data are shown graphically in Figure 6. The most striking effect upon cooling the crystal is in the intermolecular Sn⋯Cl distance, which decreases from 3.298(3) Å at 298 K to 3.0077(7) Å at 108 K. Hence, although it was appropriate to deduce from the previous structure determination[15] that there was no significant intermolecular electronic interaction, a different conclusion would have been reached if the structure had been determined at low temperature. As the intermolecular Sn⋯Cl distance contracts, the intramolecular Sn−Cl bond distance increases significantly (by 15σ) from 2.415(3) to 2.4657(7) Å, and the average C−Sn−C and C−Sn−Cl angles both change by more than 8σ [116.9(5) to 118.20(10)° and 100.3(3) to 97.73(7)°, respectively]. Taken together, the changes in molecular parameters show the change from essentially tetrahedral toward trigonal bipyramidal coordination at tin.

Comparison with Similar Structures. Structural data for **1c** are given in Table 3 together with those of the other trialkyltin chlorides, **1a**[5] and **1b**,[6] with Type A structures. In all three compounds, the C−Sn−C angles are wider and the C−Sn−Cl angles are narrower than the tetrahedral value. This general feature is found also in Type B structures, as illustrated by electron diffraction data for gaseous Me_3SnCl (Table 3)[22] and X-ray data for the compounds R_3SnCl with R = $(Me_3Si)_2CH$ (**2a**, range for C−Sn−C and average C−Sn−Cl angles 112.5(3)−116.8(3) and 103.9(3)°, respectively),[7] $PhMe_2CCH_2$ (**2b**, average 117.2(5) and 99.7(2)°), $PhMe_2SiCH_2$ (**2c**, average 113.3(6) and 105.3(6)°),[8] and Ph (**3a**, range 109.46(13)−118.45(13) and average 105.03(10)°).[10] The Sn⋯Cl distances in Table 3 are all shorter than the sum of the van der Waals radii (3.85 Å [23]), and the distance in Cy_3SnCl is the shortest reported thus far for compounds with Type A structures. Data in Tables 2 and 3 show that the longer the Sn−Cl distance, the shorter the Sn⋯Cl distance and the wider the C−Sn−C angle. For **1c**, the Sn−C bond lengths remain the same within the experimental uncertainty as the Sn−Cl bonds change. The change in configuration can be expressed in ionic terms by saying that, on cooling, the bridging chloride becomes attracted to two tin centers rather than one, or it can be described as a transfer of electron density from lone pairs on chlorine into σ^* orbitals of the intramolecular tin−chlorine bonds.

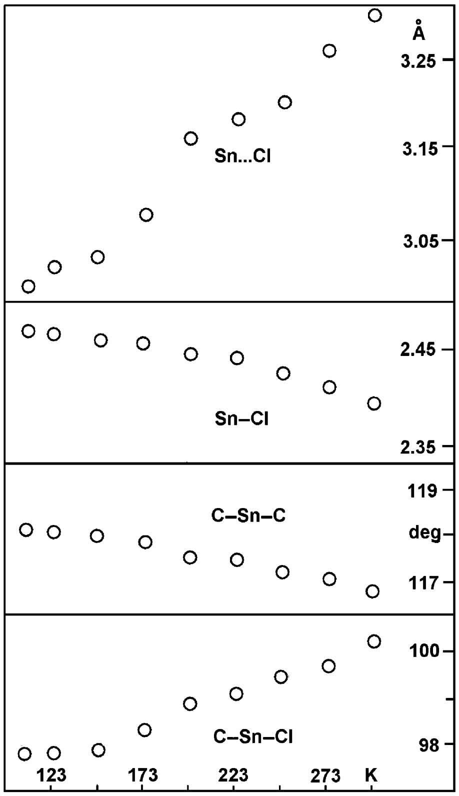

Figure 6. Variation of inter- and intramolecular tin−chlorine distances (Å) and C−Sn−C and C−Sn−Cl angles (deg) in **1c** with temperature.

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Table 3. Selected Mean Bond Lengths (Å) and Angles (deg) for Trialkyltin Chlorides

	Cy_3SnCl (**1c**)	Me_3SnCl (s) (**1a**)[d]	Me_3SnCl (g)[f]	Bz_3SnCl (**1b**)[g]
temp / K	173	138	365	298
Sn−C	2.166(3)[a]	2.119(8)[a]	2.108(6)	2.136(3)
Sn−Cl	2.4558(7)	2.430(2)	2.354(8)	2.387(2)
Sn···Cl′	3.0777(8)	3.269(2)		3.531(2)
C−Sn−C	117.97(11)[b]	117.1(3)[e]	114.8(16)	115.46(8)
C−Sn−Cl	98.27(8)[c]	99.9(2)[a]	103.2(6)	102.5(1)
Cl−Sn−Cl	177.95(2)	176.85(6)		180
Sn−Cl···Sn	169.25(3)	150.30(9)		180

[a] Esd's are for individual measurements; none differs significantly from the mean. [b] C(7)−Sn−C(1) 115.37(11), C(7)−Sn−C(13) 116.49(11), C(1)−Sn−C(13) 122.03(11)°. [c] C(7)−Sn−Cl 96.68(11), C(1)−Sn−Cl 100.05(8), C(13)−Sn−Cl 97.98(8)°. [d] Reference 5. [e] Values range from 115.2(3) to 119.8(3)°. [f] Gas-phase electron diffraction (ref 22). [g] Reference 6. The Sn−Cl···Sn−Cl skeleton lies on a three-fold axis.

The high-temperature structure determined for **1c** resembles the structure determined for Bz_3SnCl (**1b**) at 298 K, with the Cl−Sn···Cl−Sn skeleton almost linear (Cl−Sn−Cl and Sn−Cl···Sn angles 178−179°). The low-temperature structure resembles that of Me_3SnCl (**1a**) determined at 138 K, with a puckered Cl−Sn···Cl−Sn skeleton having narrower Sn−Cl···Sn than Cl−Sn−Cl angles. A previous variable-temperature Mössbauer study of phenyl- and cyclohexyltin compounds[24] suggests that a transition from zigzag (Sn−Cl···Sn and Cl−Sn−Cl $<180°$) to rodlike chains (Sn−Cl···Sn linear) is associated with a stiffening of the lattice as the intermolecular interaction increases. The detailed results for **1c** show that as the temperature is raised the chains become more zigzag, then apparently less so. The maximum puckering of the axis (Sn−Cl···Sn = 166°) is reflected in the discontinuities in the plots of a, c, and β shown in Figure 4. The observed linearity at high temperature is, however, an artifact arising from the disorder across the mirror plane. Near-linear Sn−Cl···Sn axes, as determined by X-ray crystallography, are not therefore always associated with rigidity. When all three compounds **1a**−**1c** are viewed along the Cl−Sn···Cl−Sn axis, the alkyl groups are eclipsed.

Plots of Sn···Cl against Sn−Cl distances for a wide range of compounds have been used to model the S_N2 reaction path for nucelophilic attack at tetrahedral tin with inversion of configuration,[25] and similar plots have been used to correlate intra- and intermolecular distances in a wide range of halides and organometal halides of groups 14−17.[26−30] For **1c**, a plot of $a = r_{(\mathrm{Sn-Cl})} - r_0$ against $b = r_{(\mathrm{Sn}}\cdots\mathrm{Cl}) - r_0$, where r_0 is the Sn−Cl distance in gaseous Me_3SnCl, reflects the discontinuities evident in Figure 4, but the points lie close to the curve $10^{-a/c} + 10^{-b/c} = 1$ with $c = 1.2$ Å, found previously[25] to fit data from 43 compounds containing five-coordinate tin and 12 containing four-coordinate tin.

Molecules of several triaryltin chlorides bearing bulky substituents in the organic group (**3b**−**3e**) adopt Type A structures with linear ···Sn−Cl···Sn−Cl··· chains along threefold axes but the long Sn···Cl distances (4.37−5.43 Å) indicate that in these compounds there are no intermolecular bonds.[12,14] In contrast to that observed for the trialkyltin chlorides discussed in this paper, there is no correlation between Sn−Cl and Sn···Cl distances or C−Sn−C angles, and the packing is determined largely by interactions between the bulky aryl groups. The structure of the monoclinic form of Ph_3SnCl (**3a**) has been determined at both 298 and 110 K, but there are no significant differences between corresponding intramolecular dimensions at the two temperatures.[10] The intermolecular Sn···Cl distance increases only slightly from 5.644(2) Å at 110 K to 5.847(2) Å at 298 K. That the secondary bonds in diphenyldichlorostannane are weaker than those in dialkyldichlorostannanes has been noted previously.[31]

Conclusions

The structure of Cy_3SnCl below 248 K is similar to those of Me_3SnCl at 138 K and Bz_3SnCl at 298 K. There is no need to seek to account for "anomalous" Mössbauer data because the problems discussed previously arose from attempts to reconcile X-ray data obtained at 298 K with Mössbauer measurements at 77 K.[15,32] As we have shown, the crystal structures at 298 and 77 K are significantly different.

We recognize the danger of arguing from the particular to the general, but find it intriguing to ask whether changes in structure of the type we describe are likely to be common. If they are to be observed, there must be potential intermolecular interactions that are not inhibited by packing (as might be the case in compounds containing bulky organic groups), and accurate structural data must be available over a sufficiently wide temperature range. We have found only one other example in the literature. Neutron diffraction data for $[LiCD_3]_4$ at 290 K indicate that the inter- and intratetramer Li−C distances are 2.491(14) and 2.209(14) Å, respectively, but at 1.5 K the intertetramer Li−C bonds (2.356(6) Å) have strengthened at the expense of the intratetramer bonds (2.256(6) Å). In this case, there is no change in space group.[33] Crystal structures have usually been determined over a range of temperature to examine phase changes rather than smooth transitions from low- to high-temperature structures. We

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suspect, however, that other examples of such structural transformations can be found among compounds where there are potential intermolecular interactions.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council for financial support, the Royal Society for a grant to A.A. under the Developing World Study Visit scheme, Paul Gabbott of Perkin-Elmer Instruments Ltd. for DSC data, and Professor N. C. Billingham for helpful discussions.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structural analyses of **1c** at various temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026272F